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CHEMISTRY DIVISION ANNUAL REPORT
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PREFACE

This report represents the first in several years to summarize the research carried out throughout the Chemistry Division at Argonne. The period covered is the fiscal year July 1, 1970, to June 30, 1971.

The Chemistry Division is not equivalent in breadth to a university chemistry department, and the diversity of topics, while wide indeed, reflect the interests of the atomic-energy establishment. Major chapters on nuclear chemistry, radiation chemistry, and heavy-element chemistry reflect the research of a number of independent investigators; selections on low-temperature calorimetry or specific topics in physical chemistry summarize the efforts of one or two senior investigators and a limited number of collaborators, often including students and temporary associates.

More than one-hundred scientists have contributed to the research summarized here, and the several hundred references and publications noted will offer a convenient entry to the literature in most of the topics covered.

In addition to summarizing the research carried out in the immediate past, the text may well serve as a guide to the capability of the Division in dealing with chemistry problems that can be anticipated in the near future.

An attempt has been made to identify the scientists responsible for each program, and readers are encouraged to communicate directly with them for current reprints and to keep in touch directly where sharing common interests.

TABLE OF CONTENTS

ABSTRACT	1
I. HEAVY-ELEMENT CHEMISTRY	1
A. THE PRODUCTION OF TRANSPLUTONIUM AND TRANSACTINIDE ELEMENTS	1
B. NUCLEAR PROPERTIES AND REACTIONS OF HEAVY ELEMENTS	2
1. Nuclear Reactions	2
2. Nuclear Constants	2
3. Nuclear Isomers	3
C. HEAVY-ELEMENT ISOTOPES AND DECAY SCHEMES	3
1. New Isotopes	3
2. Decay Schemes for Alpha, Beta, and Electron-capture Decay in Heavy-element Nuclides	4
D. ATOMIC-BEAM MEASUREMENTS	5
1. g_J Value for the Atomic Ground State of Fermium	5
E. SINGLE-NUCLEON TRANSFER STUDIES IN THE HEAVY-ELEMENT NUCLIDES	6
1. Experimental Studies	6
2. Single-particle States—Theoretical	8
F. NEUTRON-PROTON AND TWO-QUASIPARTICLE STATES OF ACTINIDE NUCLEI	8
G. CHEMISTRY OF THE ACTINIDE ELEMENTS	9
1. Neptunium Chemistry	10
2. Uranium(V) in Aqueous Solutions	10
3. Search for a Volatile Fluoride of Einsteinium	10
H. SECONDARY REACTIONS INDUCED BY GeV PROTONS—AN EARLY ATTEMPT TO PRODUCE SUPERHEAVY ELEMENTS	10
PUBLICATIONS	13
II. GEO- AND COSMOCHEMISTRY	15
A. ACTINIDE NUCLIDES OF GEOCHEMICAL AND COSMOCHEMICAL IMPORTANCE	15
B. ABUNDANCES AND DISTRIBUTION OF TRACE ELEMENTS	15
C. MINERALOGY OF METEORITES AND LUNAR ROCKS	16
1. Lunar Samples	16
2. Meteorites	17
D. ORIGIN OF ORGANIC MATTER IN THE EARLY SOLAR SYSTEM	17
E. USE OF THERMOLUMINESCENCE FOR DATING OCEAN SEDIMENTS	17
F. ARCHEOLOGICAL PROBLEMS	18
G. PRECISION MEASUREMENT OF HALF-LIVES OF ^{235}U AND ^{238}U	18
H. REMOTE CHEMICAL ANALYSIS BY ALPHA-PARTICLE INTERACTION WITH MATTER	19
PUBLICATIONS	19

III. NUCLEAR CHEMISTRY	21
A. RADIOCHEMICAL AND PHYSICAL STUDIES OF NUCLEAR FISSION	21
1. Spontaneous Fission of ^{244}Cm , ^{248}Cm , and ^{256}Fm	21
2. The Distribution of Angular Momentum in Fission	25
3. K X-ray Emission and the Distribution of Nuclear Charge and Mass in Fission	26
B. HIGH-ENERGY NUCLEAR CHEMISTRY	29
1. Secondary Nuclear Reactions of 11.5-GeV Protons on Uranium: A Search for the Production of Transcurium Actinide Elements	29
2. Semiconductor Detector Studies of the Interaction of 11.5-GeV Protons with Uranium	30
3. Excitation Function for the $^{209}\text{Bi}(p,2p5n)^{203}\text{Pb}$ Reaction from 0.15 to 11.5 GeV	32
4. The Response of Surface-barrier Detectors to Heavy Ions and Fission Fragments	33
5. Simple Nuclear Reactions at High Energies	34
6. Nuclear-chemistry Research Program at the National Accelerator Laboratory (NAL)	35
C. A STUDY OF SPONTANEOUSLY FISSIONING ISOMERS	36
D. ON THE EXISTENCE OF THE CHEMICALLY BOUND NEUTRON	37
E. MISCELLANEOUS RADIOACTIVITY STUDIES	38
1. Absolute Counting of Low-energy β Emitters	38
2. Organic Scintillator Studies	39
a. The Yield of Tritium in Fission	39
3. Application of Statistics to Nuclear Measurements	39
F. ISOTOPE SEPARATOR APPLICATIONS	39
G. ISOTOPIC NEUTRON SOURCES	39
PUBLICATIONS	41
IV. α, β, AND γ SPECTROSCOPY	43
A. MAGNETIC ALPHA SPECTROMETRY	43
1. 39-hour $^{254}\text{m}\text{Es}$	43
2. 20-hour ^{253}Fm	44
3. 20-day ^{253}Es	44
4. 314-day ^{249}Bk and 345-year ^{249}Cf	44
B. BETA- AND GAMMA-RAY SPECTROSCOPY	44
1. Nuclear Energy Levels	45
2. Atomic Properties in Radioactive Decay	45
a. Orbital Electron Emission Accompanying Beta Decay	45
b. Orbital Electron Emission Accompanying Internal Conversion	46
c. Experimental Atomic-electron Binding Energies in Fermium and Californium	47
d. Outer-shell Internal Conversion of the 14.4-keV Transition in ^{57}Fe : Chemical Effects and Line-shape Differences	49
e. Discovery of K-L _I Forbidden X-ray Transition	50
PUBLICATIONS	50
V. MOLECULAR BEAM STUDIES	52
A. REACTION DYNAMICS USING ACCELERATED BEAMS PRODUCED BY SPUTTERING	52
1. Reaction Dynamics of Silver, Halogen Collisions and Study of Bond Energies in Silver Compounds	52
2. The Lithium-Deuterium Reaction	53
3. Some Other Planned Studies	53

B. AERODYNAMIC CHEMICAL ACCELERATOR	54
1. Polar Ionization of Thallium Halides by Accelerated Xenon and Krypton Atoms	54
2. Electron-bombardment Ionizer for Accelerated Molecular Beams	57
C. STUDIES OF CHEMICAL SPUTTERING OF SURFACES OF POTENTIAL USE IN THERMONUCLEAR REACTORS	57
PUBLICATIONS	59
VI. RADIATION CHEMISTRY AND PHOTOCHEMISTRY	60
A. RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS	60
1. Status of Picosecond-pulse Radiolysis	60
2. Photodissociation of an ϵ_{aq} Complex in H_2 -saturated Solutions	61
3. Tritiated Water	61
4. Role of Excited-water Molecules in Aqueous Radiation Chemistry	62
5. Oxygen Atoms	62
6. Nature of the Species Released on the Dissolution of Irradiated NaCl	63
7. Aqueous Oxygen Solutions	63
8. Sulfonaphthalein Dyes	64
9. Aqueous Methane Solutions	64
10. Development of Techniques	64
B. ORGANIC RADIATION CHEMISTRY—REACTIONS IN LIQUID CARBON DIOXIDE	64
C. PULSE RADIOLYSIS OF GASEOUS SYSTEMS	65
1. New Irradiation Cell	65
2. Thermalization and Reactions of Electrons	65
3. Ion Recombination and Formation of Excited States	66
4. Pulse Radiolysis of Ammonia	66
5. Rate Constants for OH Radical Reactions	66
6. Improvements in Time Resolution	66
7. Reactions of CN Radicals	66
D. ION CYCLOTRON RESONANCE STUDIES OF IONIC REACTIONS IN GASEOUS SYSTEMS	66
1. The Ion Chemistry of Cyclopentane	67
2. Electrophilic Substitution in Aromatic Rings	67
3. Tritium Decay Studies	68
E. PHOTOCHEMISTRY OF AROMATIC COMPOUNDS	69
1. Photochemical 1,2 and 1,4 Cycloadditions of Benzene to Olefins	69
2. The Photooxidation of Aqueous Benzene	70
F. VIBRATIONAL AND ELECTRONIC ENERGY RELAXATION IN THE XYLENES	70
G. ELECTRON PARAMAGNETIC RESONANCE AND RADIATION EFFECTS IN QUARTZ	70
PUBLICATIONS	71
VII. ACCELERATOR IMPROVEMENT	74
A. ELECTRON ACCELERATOR	74
B. SUPERCONDUCTING HELIX RF CAVITY	74
PUBLICATION	74

VIII. ISOTOPE STUDIES (WITH PARTICULAR EMPHASIS ON BIOLOGICALLY INTERESTING SYSTEMS)	75
A. ESR OF CHLOROPHYLL AND THE NATURE OF THE PHOTOSYNTHETIC REACTION CENTER	75
B. HIGH-RESOLUTION PROTON-MAGNETIC-RESONANCE STUDIES WITH ^1H - ^2H ISOTOPE HYBRID ALGAL PROTEINS	76
C. ON-LINE ^1H FOURIER-TRANSFORM SPECTROSCOPY AT UNNATURAL ABUNDANCES	77
D. PREPARATION OF ISOTOPICALLY ALTERED COMPOUNDS	78
E. MOLECULAR STRUCTURE OF CHLOROPLAST XANTHOPHYLLS	78
F. THE STRUCTURE OF PERIDININ, THE CHARACTERISTIC DINOFLAGELLATE CAROTENOID	80
PUBLICATIONS	81
IX. HIGH-TEMPERATURE CHEMISTRY	83
A. APPARATUS DEVELOPMENT	83
B. LANTHANIDE AND ACTINIDE OXIDE STUDIES	84
C. SOME THEORETICAL CONSIDERATIONS	84
PUBLICATIONS	85
X. LOW-TEMPERATURE CALORIMETRY	86
A. CALORIMETRIC STUDY OF IODINE PENTAFLUORIDE: HEAT CAPACITY BETWEEN 5 AND 350° K, ENTHALPY OF FUSION AND VAPORIZATION, STANDARD ENTROPY OF THE VAPOR, AND OTHER THERMODYNAMIC PROPERTIES	86
B. THORIUM MONOSULFIDE: HEAT CAPACITY AND THERMODYNAMIC PROPERTIES FROM 1 TO 350° K	87
C. ENTHALPY OF FORMATION OF DISODIUM ACETYLIDE AND OF MONOSODIUM ACETYLIDE AT 298.15° K, HEAT CAPACITY OF DISODIUM ACETYLIDE FROM 5 TO 350° K, AND SOME DERIVED THERMODYNAMIC PROPERTIES	88
D. XENON TETRAFLUORIDE: HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS FROM 5 TO 350° K	90
E. A ^3He DILUTION REFRIGERATOR FOR HEAT-CAPACITY STUDIES	90
F. FUTURE HEAT-CAPACITY STUDIES	91
PUBLICATIONS	92
XI. PHYSICAL CHEMISTRY	93
A. LOW-TEMPERATURE PHYSICAL CHEMISTRY	93
1. Quantum Fluids. Properties of Liquid Helium	93
2. The Low-temperature Scale (2–20 mK)	94
B. STRUCTURE AND MOLECULAR INTERACTIONS IN THE LIQUID STATE AND IN SOLUTIONS OF ELECTROLYTES	94
C. VIBRATION AND DIFFUSION OF HYDROGEN ATOMS IN METAL HYDRIDES BY NEUTRON-SCATTERING MEASUREMENTS	95

PUBLICATIONS	97
XII. INORGANIC CHEMISTRY	98
A. PREPARATION, PROPERTIES, AND UTILIZATION OF REACTIVE INORGANIC FLUORIDES	98
1. Halogen Fluoride and Hydrogen Fluoride Solution Chemistry	99
2. Vapor Density of Hydrogen Fluoride	99
3. Fluorination of Organics with XeF_2	100
4. Preparative Chemistry of Reactive Fluorides	100
5. Chemistry of Nickel Fluorides	101
B. HYPOFLUOROUS ACID	101
C. PERBROMATE CHEMISTRY	102
D. AQUEOUS XENON CHEMISTRY	102
E. RADON CHEMISTRY	103
F. INORGANIC CHEMISTRY OF URANIUM	104
1. UO_3 Crystal Modifications	104
2. $\text{UO}_3\text{-H}_2\text{O}$ System	105
3. $\text{UO}_3\text{-Cr}_2\text{O}_3$ System	105
4. $\text{UO}_3\text{-RE}_2\text{O}_3$ Systems	105
G. DYNAMIC CHEMICAL BEHAVIOR OF INORGANIC SYSTEMS	105
1. Cobalt Complexes	106
2. Np Compounds	106
PUBLICATIONS	107
XIII. SEPARATIONS CHEMISTRY	110
A. LIQUID-LIQUID EXTRACTION STUDIES OF ACTINIDES AND LANTHANIDES	110
B. LIQUID-LIQUID COLUMN CHROMATOGRAPHY	111
PUBLICATIONS	112
XIV. STRUCTURAL CHEMISTRY	113
A. EXPERIMENTAL FACILITIES	113
1. Neutron Crystallography	113
2. Neutron Magnetic Diffraction	113
3. X-ray Crystallography and Techniques for Investigating Heavy-element Salts	114
B. HYDROGEN BONDING IN CRYSTALLINE STRUCTURES	114
1. $(\text{CH}_3)_4\text{NClHCl}$	114
2. $\text{CsNO}_3 \cdot \text{HNO}_3$	114
C. CARBIDES	114
1. Neutron-structure Determination of NaC_2H , Cubic CaC_2 , and Cubic KCN	114
2. Magnetic-spin Structures of $\alpha\text{-Tb}_2\text{C}_3$ and $\alpha\text{-Ho}_2\text{C}_3$	115
D. MAGNETIC-SPIN STRUCTURE OF ERBIUM	115
E. OTHER STUDIES ON RARE-EARTH COMPOUNDS	115
1. Ce_2S_3	115
2. $\text{K}_3\text{Pr}_2(\text{NO}_3)_9$	116

F. THE STRUCTURE OF URANYL COMPOUNDS	116
G. COMPLEXES OF NaF WITH UF ₆	117
H. CRYSTALLOGRAPHIC STUDIES ON NOBLE-GAS COMPOUNDS	117
1. (NO) ₂ XeF ₆	117
2. XeF ₆	118
3. NO ₂ XeF ₇	118
4. (CsCl) ₂ XeO ₃	118
I. COHERENT NEUTRON SCATTERING AMPLITUDES OF Br and ¹²⁷ I	118
J. OTHER HEAVY METAL STRUCTURAL STUDIES	118
PUBLICATIONS	119
XV. MOLECULAR SPECTROSCOPY	121
A. STRUCTURAL STUDIES AND MOLECULAR POTENTIAL FUNCTIONS OF HALIDES AND OXIDE HALIDES	121
1. Noble-gas Fluorides and Oxide Fluorides	121
2. Pentafluorides	121
3. Some Pseudo-octahedral Oxide Fluorides	121
B. SPECTROSCOPIC INVESTIGATIONS OF INORGANIC AND COORDINATION COMPOUNDS UNDER VARYING PRESSURES	122
C. RAMAN SPECTRA OF TECHNETIUM HEPTOXIDE	123
D. REACTION OF RHENIUM AND TECHNETIUM METALS WITH LITHIUM PERCHLORATE	123
PUBLICATIONS	123
XVI. ATOMIC SPECTROSCOPY	126
A. EMISSION SPECTROSCOPY	126
1. Lanthanide and Actinide Studies	126
2. Some Special Problems in the Spectrum of Barium of Astrophysical Interest	126
B. ABSORPTION SPECTROSCOPY OF THE ACTINIDE ELEMENTS	127
1. Plutonium Trichloride	127
2. Gadolinium Spectra	127
3. Pr ³⁺ Spectra	127
4. The Spectra of Bk ³⁺ and Bk ⁴⁺ . A Guidepost to Electronic Structure in the Transcurium Elements	128
C. CHEMISTRY AND SPECTROSCOPY OF HIGH-TEMPERATURE SYSTEMS	128
1. Refractory Metals and Gaseous Metal Hydrides	128
2. Rare-earth Halides	130
3. Sulfur in Molten-salt Systems	130
D. CIRCULAR DICHROISM SPECTRA	130
PUBLICATIONS	131
XVII. THEORETICAL CHEMISTRY	132
A. THE A PRIORI EVALUATION OF VAN DER WAALS FORCES	133

B. A PRIORI CALCULATIONS ON THE CHEMICAL REACTIONS $\text{Li} + \text{H}_2 \rightleftharpoons \text{LiH} + \text{H}$, $\text{Li} + \text{T}_2 \rightleftharpoons \text{LiT} + \text{T}$ AND $\text{Li} + \text{D}_2 \rightleftharpoons \text{LiD} + \text{D}$	134
C. THERMODYNAMIC AND TRANSPORT PROPERTIES OF ALKALI DIMER GASES	134
D. THE RELATIONSHIP BETWEEN EPISTEMOLOGY, MATHEMATICAL LOGIC, AND PHYSICS	135
PUBLICATIONS	136
XVIII. CENTRAL REAL-TIME COMPUTER FACILITIES	139
XIX. ANALYTICAL CHEMISTRY	141
A. MASS-SPECTROMETRY TECHNIQUES	141
1. Precision Mass Measurements	141
2. Spark-source Mass Spectrometer	141
B. ENVIRONMENTAL STUDIES	141
1. Isotopic Abundances of Atmospheric Carbon Monoxide	142
a. World-average Engine CO	142
b. Atmospheric CO	142
2. Sulfur Isotope Study of Environmental Water and Air	144
3. Lake Michigan Environmental Studies	145
4. Trace Elements in the Lake Michigan Environment	145
C. MASS SPECTROMETRY APPLIED TO DRUG TRAFFIC CONTROL	145
D. MISCELLANEOUS APPLICATIONS OF TIME-OF-FLIGHT MASS SPECTROMETRY	145
PUBLICATIONS	146
AUTHOR INDEX	147
SUBJECT INDEX	150

LIST OF FIGURES

I.1	Energy-level Diagram of ^{251}Cf	4
I.2	An Atomic-beam Magnetic-resonance Apparatus	5
I.3	Distribution of ^{254}Fm Activity as a Function of Rf Frequency	6
I.4	Triton Spectrum for the Reaction $^{244}\text{Cm}(d,t)^{243}\text{Cm}$ at $0-140^\circ$	7
I.5	Measured Excitation Energies of Single-particle States in the Odd-A Curium Isotopes	7
I.6	Single-particle Level Scheme Extracted from the Data by Means of a Pairing-force Calculation	7
I.7	Predicted Proton Single-particle Spectrum in the Mass-300 Region	8
I.8	Predicted Neutron Single-particle Spectrum in the Mass-300 Region	9
I.9	The Periodic Table with Predicted Arrangement of the Transactinide Elements	11
III.1	Mass-Yield Curve for Spontaneous Fission of ^{244}Cm Compared with That for ^{252}Cf	23
III.2	Mass-Yield Curve for Spontaneous Fission of ^{256}Fm Compared with That for ^{252}Cf	24
III.3	Mass Distributions for Spontaneous Fission of ^{248}Cm , ^{252}Cf , and ^{256}Fm	24
III.4	Mass Distributions for Spontaneous Fission of ^{252}Cf , ^{256}Fm , and ^{257}Fm and Thermal-neutron-induced Fission of ^{257}Fm	24
III.5	Comparison of the Total Average Fragment Kinetic Energy for Spontaneous Fission with That for Thermal-neutron-induced Fission	25
III.6	Calculated Root-mean-square Angular Momentum of the Compound ^{239}Pu Nucleus as a Function of Excitation Energy for the Indicated Nuclear Reactions	25
III.7	The ^{136}Cs and ^{111}Pd Isomeric Ratios $\sigma_m/(\sigma_m + \sigma_g)$ Determined as a Function of Excitation Energy for the Indicated Nuclear Reactions.	26
III.8	$^{235}\text{U}(n,f)$ Mass Distributions	27
III.9	Charge-division Results for $^{233}\text{U}(n,f)$	28
III.10	Charge-division Results for $^{235}\text{U}(n,f)$	28
III.11	Charge-division Results for $^{239}\text{Pu}(n,f)$	28
III.12	Charge-division Results for $^{252}\text{Cf}(sf)$	29
III.13	Schematic Diagram of the Experimental Arrangement	31
III.14	Block Diagram of the Electronics	31
III.15	Momentum Distributions for Selected Mass Ranges in High-energy Proton Fission of U	32
III.16	Excitation Function for the Reaction $^{209}\text{Bi}(p,2p5n)^{203}\text{Pb}$	33

III.17	Energy of Ion Incident on Detector as a Function of Pulse Height for Various Heavy Ions	34
III.18	Pulse-height Defects in LSS Units as a Function of Ion Energy in the Same Units	35
III.19	The Nuclear Potential Energy, Relative to the Ground States, vs Deformation toward Fission	36
III.20	Isomer Cross Sections as a Function of Alpha-particle Bombarding Energy for the Isomers ^{239m}Pu and ^{245m}Cm	38
III.21	Decay of Counts Observed in LiF Crystal in Chemically Bound Neutron Experiment	38
IV.1	Alpha Spectrum of Mass 254 Fraction from Neutron-irradiated ^{253}Es	44
IV.2	Experimental Momentum Plot of the Composite Nuclear Beta plus K Orbital Shakeoff Spectrum in Coincidence with K X rays	45
IV.3	Beta-ray Spectrometer Measurement of the Structure at the Base of the K-shell Internal-conversion Line of the 122-keV Transition in ^{57}Fe following the Decay of ^{57}Co	47
IV.4	Decay Scheme of 39-h $^{254}_{100}\text{Es} \rightarrow ^{254}_{100}\text{Fm}$	48
IV.5	The L_1 and L_2 Conversion Lines of the 694-keV transition	48
IV.6	Conversion Lines of O_1 , O_2 , O_3 , $O_{4,5}$, and $P_{1,3}$ Shells of the 44.988-keV Transition	49
IV.7	Outer-shell Conversion Lines of 14.4-keV Transition following the Decay of ^{57}Co from Sources Prepared in Metallic and Oxide States, on a Log Intensity Scale	49
V.1	Schematic of Cathode-accelerator/Crossed-beam Apparatus	53
V.2	Schematic of Aerodynamic Chemical Accelerator	55
V.3	Cross Section for Polar Ionization of Thallium Chloride by Accelerated Xe and Kr Atoms as a Function of Relative Kinetic Energy of the Collision Partners	55
V.4	Excitation Function for Polar Ionization of TlBr by Fast Xe and Kr Atoms	55
V.5	Variation of Cross Section for Polar Ionization of TlI by Accelerated Xe and Kr Atoms with Relative Kinetic Energy	56
V.6	Potential Curves of the Ground State and Lowest Ionic State of TlCl, TlBr, and TlI	56
V.7	Assembly of Ionizer for Fast Molecular Beams	57
V.8	Time-of-flight Velocity Distributions of $\text{H}_2 + \text{Kr}$ and of Kr with the H_2 Propellant Suppressed	58
V.9	Schematic of "Tritium Chemical Accelerator" Modified for Studies of Chemical Sputtering of Nb and Ta Surfaces	59
VI.1	Fine-structure Pulses of ANL Linac as Revealed by Cerenkov Emission	61
VI.2	Fine-structure Pulses of ANL Linac as Revealed by Hydrated Electron Absorption in Irradiated Water	61
VI.3	Uranyl Ion Emission from 0.12 M UO_2^{++} in Concentrated Sulfuric Acid Containing 1 curie/ml of Tritiated Water	62

VI.4	Decay of O_2^- at pH 9.40 in O_2 -saturated Water	63
VI.5	Relative Abundances of Prominent Ions in Cyclopentane as Functions of Cell Pressure in the Ion Cyclotron Resonance Spectrometer	67
VI.6	Variations of Abundances of Ions Observed Following β Decay in T_2 - D_2 Mixtures with Pressure of D_2	68
VI.7	Single-resonance Mass Spectra of Positive Ions in Cyclopentane after Beta Decay of Incorporated Tritium	69
VIII.1	The Proton-magnetic-resonance Spectra of 1H -flavoprotein and the Isotope Hybrid Protein 2H -flavoprotein	77
VIII.2	The Downfield Portion of the PMR Spectrum of the Reduced Form of 2H -ferredoxin	78
VIII.3	1H FT Spectra of 0.095M 2H -chlorophyll <i>a</i> in Benzene- d_6	78
VIII.4	1H FT Spectrum of 0.004M 1H -phytol in CCl_4	79
VIII.5	The Structure of Peridinin and Other Carotenoids	80
IX.1	Equipment for the Simultaneous Measurement of Mass-effusion and Mass-spectrometric Analysis of Effusate from Knudsen Cell	83
X.1	Plot of the Magnetic Heat Capacity and Magnetic Entropy of Uranium Monosulfide, Based on a Corresponding-states Calculation Involving the Heat Capacity of Thorium Monosulfide	88
X.2	Heat Capacity of Xenon Tetrafluoride at Constant Pressure	90
X.3	3He Dilution Refrigerator for Heat-capacity Measurements down to 0.03°K	91
XI.1	The Adiabatic Sound Velocity in Liquid 3He as a Function of Temperature and Pressure	93
XI.2	The Velocity of Sound in Liquid 3He as a Function of Temperature	94
XII.1	Preparation of HOF	101
XII.2	Apparatus for Testing Removal of Radon from Air	103
XII.3	Structure of Cr_2UO_6	105
XIV.1	The Linear Bichloride Ion as Found in Tetramethylammonium Bichloride	114
XIV.2	The Structure of γ - UO_3	116
XIV.3	Perspective View of $H_2U_3O_{10}$	117
XIV.4	The Archimedean Antiprism Arrangement of Fluorine Atoms about Xenon in the XeF_8^{2-} Group of $(NO)_2XeF_8$	118
XVI.1	Absorption Spectra of Bk^{3+} and Bk^{4+} in 0.4 M D_2SO_4	128
XVI.2	The Absorption Spectrum and Luminescence Spectrum of Titanium Atoms Isolated in an Argon Matrix near 4°K	129
XVII.1	Comparisons of Helium Potential Curves	133

XVII.2	Lithium Atom Has Approached H_2 Molecule Where Bond Has Already Been Stretched to 2.2 bohrs but Reaction Has Not Yet Occurred	134
XVII.3	H_2 Bond Has Now Been Stretched to 2.5 bohrs and Reaction Has Now Occurred	134
XVII.4	Rightmost Hydrogen Atom Now Moves Away to Form LiH Molecule and Free H Atom	134
XIX.1	The Isotopic Composition of Carbon and Oxygen in Carbon Monoxide in Nonurban Air	142
XIX.2	Seasonal Variations in Atmospheric Carbon Monoxide	143

LIST OF TABLES

I.1	Heavy-element Production by Irradiation of 1 kg of Uranium with 12-GeV Protons	12
I.2	Results of Fission Counting of Nonactinide Fractions	12
III.1	Fission Yields for Spontaneous Fission of ^{244}Cm	22
III.2	Fission Yields for Spontaneous Fission of ^{256}Fm	23
III.3	Comparison of 11.5-GeV and 2.9-GeV Proton Fission of Uranium	31
III.4	$^{209}\text{Bi}(p,2p5n)^{203}\text{Pb}$ Cross Sections	33
III.5	Fissioning Isomers Discovered at Argonne	37
III.6	Other Shape Isomers Studied at Argonne	37
IV.1	Electron Binding Energies to the Fermi Level of a Solid Source of Fermium Oxide	48
IV.2	Atomic-electron Binding Energies in Californium	49
VI.1	Ethylene Formation in Irradiated Aqueous 1.5 mM Cyclopentene Solutions	62
VI.2	Principal Reactions in Cyclopentane	67
VIII.1	Line Widths of In Vitro Chlorophyll ESR Signals	75
VIII.2	Observed and Calculated Line Widths of ESR Signal I in Plants	76
X.1	Calculation of the Standard Entropy S° of IF_5 Vapor at 330°K, in $\text{J}^\circ\text{K}^{-1} \text{mol}^{-1}$	87
X.2	Extrapolated Thermodynamic Properties of Na_2C_2	89
X.3	Calculation of the Standard Entropy S° of XeF_4 at 298.15°K, in Units of $\text{J}^\circ\text{K}^{-1} \text{mol}^{-1}$, from Thermal Data	90
XII.1	Raman Spectrum of Liquid Bromine Trifluoride	100
XII.2	H_O Value for BrF_3	100
XII.3	Removal of Radon from Air with Solid Fluorinating Reagents	104
XVIII.1	On-line Experiments	139

CHEMISTRY DIVISION ANNUAL REPORT
July 1970 through June 1971

ABSTRACT

This report summarizes the research carried out in the Chemistry Division at Argonne during the fiscal year 1971. Much of the research revolves around the nuclear and chemical behavior of the heavy elements. These include detailed studies of the fission process, and α , β , and γ radiation. The determination of detailed nuclear-energy levels for many nuclides may be correlated with specific nuclear models. Systematic chemical and radiochemical studies as well as emission and absorption spectroscopic measurements are reported for many of these relatively rare elements.

Radiation chemistry, including photochemistry, represents another major activity of the Division with some emphasis on the primary processes found in aqueous systems and the development of facilities and techniques for observations as shortly after irradiation as possible.

The use of ^2H and ^{13}C , coupled with a very advanced NMR system, has been most effective in studying photosynthesis and other biologically important chemical systems.

While ab initio calculations on interatomic binding energies are still limited to relatively light and simple systems, striking advances in computing capabilities and techniques have been demonstrated. Experimental programs have been guided and experimental discrepancies resolved in important chemical systems.

Molecular-beam studies, low-temperature calorimetry, and a number of other physical-chemistry research efforts are described; diverse structural studies employing spectroscopic and diffraction techniques are summarized; and measurements are reported on a number of inorganic systems, most of which have special importance in nuclear-energy programs, or have significant environmental impact, or relate to geo- or cosmo-chemical problems.

Such measurements employ an array of instrumental approaches which include some locally developed examples of essentially unique capability, especially in the field of mass spectrometry.

A central real-time computing system has been integrated into much of the research of the Division.

1. HEAVY-ELEMENT CHEMISTRY*

Among the earliest responsibilities assumed by the Chemistry Division at Argonne was the continued exploration of the elements at the heavy end of the periodic table. The steady growth in the numbers of nuclides identified in the transplutonium region has been matched by increased information about their properties and hence the ability to both interpolate and extrapolate so as to provide information about the less available entities. With time, the availability of some scarce nuclides has grown, and uncertainty about properties of the even less accessible species remains as an intellectually irresistible driving force challenging the greatest ingenuity of the experimenter, and the boldest extrapolation of the theoretician. The areas of heavy-element research being pursued at Argonne are described in the following sections.

*Chapter edited by: I. Ahmad, W. T. Carnall, R. R. Chasman, D. Cohen, H. Diamond, P. R. Fields, S. Fried, A. M. Friedman, and J. P. Unik.

A. THE PRODUCTION OF TRANSPLUTONIUM AND TRANSACTINIDE ELEMENTS (P. R. Fields, I. Ahmad, H. Diamond, R. Sjoblom, R. Barnes, D. Cohen, W. T. Carnall, E. P. Horwitz, and S. Fried)

The transplutonium elements are an important group of elements whose nuclear and atomic properties have neither been completely determined nor completely understood in terms of modern nuclear and atomic theory. The chemical properties of these elements are dominated by the behavior of the 5f electron shell; their important nuclear properties stem largely from the fact that their stable nuclear configurations yield distorted (nonspherical) nuclear shapes. Chemical and spectroscopic studies of these elements have already led to a better understanding of the interaction of the 5f electrons with each other, with other electronic configurations, and with the chemical

environment of the heavy atom. Studies of the nuclear properties of these elements have yielded considerable understanding of the nature of deformed nuclei.

Recent theoretical extrapolations indicate that an isolated region of nuclear stability may exist in the region near element 114. The possibility that relatively long-half-life superheavy elements might exist opens an exciting new area of research. These unusual elements, assuming they can be produced and isolated, would shed light on the limits of nuclear stability, on alpha decay, on spontaneous fission systematics, etc., and would provide us with elements that possess electronic structure that has never been encountered before. The basic nuclear and atomic information potentially available from a study of these elements is enormous.

Both the actinide and transactinide areas of research are worthy of large research efforts. In addition to the basic information, important practical applications for several transplutonium elements have already evolved, and other uses may develop from further research.

A coordinated effort was made last year at ANL to produce relatively large amounts of ^{256}Md and ^{256}Fm by cyclotron irradiations of ^{253}Es for an in-depth study of the spontaneous fission characteristics of ^{256}Fm . Many irradiations were carried out, and the ^{256}Md - ^{256}Fm isolated by chromatographic techniques, almost completely free from ^{253}Es and other Fm isotopes. The chemical fission yield and charge distribution determinations were carried out jointly with L. E. Glendenin, K. Flynn, and R. Clarke (cf. Chapter III); the neutron distribution in fission and fission yields prior to neutron emission were measured jointly with J. Unik and K. Wolf (cf. Chapter III.A). In addition to this large effort, ^{255}Fm was isolated from a ^{255}Es source, and ^{250}Es was prepared by helium ion bombardments of relatively large amounts of ^{249}Bk . Various other transplutonium nuclides (^{237}Am , ^{246}Am , etc.) were also prepared by helium ion irradiations at the Argonne 60-in. cyclotron. These nuclides were used for the investigation of their nuclear properties.

A large program was also initiated to search for superheavy elements as well as neutron-rich actinide nuclides in targets subjected to prolonged irradiation with high-energy protons in the Argonne ZGS and the Brookhaven AGS. The details of these experiments are given in Section G below.

B. NUCLEAR PROPERTIES AND REACTIONS OF HEAVY ELEMENTS (P. R. Fields, H. Diamond, I. Ahmad, R. F. Barnes, R. Sjoblom, F. Wagner, and W. McHarris*)

The areas of interest in heavy-element chemistry include nuclear reactions, cross sections, excitation functions and

fission, the study of synthetic methods for heavy and superheavy elements, and the actual synthesis of enough of each species to study their nuclear properties. Information on these nuclear properties is important, not only to further an understanding of the stability of nuclei, their energy levels and radioactive transitions, but also to allow identification of all the actinide and transactinide nuclei, so that one can observe and identify unusual products such as might be produced in our search for the superheavy elements.

1. Nuclear Reactions

A sophisticated gas-recoil chamber was built to collect and identify products from nuclear reactions with half-lives as short as milliseconds. The chamber is being modified to increase the speed of gas collection. This chamber will be used at Argonne and Michigan State University, primarily in our study of nuclear isomers and the role of angular momentum in the production of high-spin isomers, in the study of neutron-deficient isotopes and their decay schemes, and in the study of special delayed spontaneous-fission isomers.

We have completed our studies of the bombardment of ^{253}Es with ^4He ions, are working out the results of similar bombardments of ^{249}Bk and ^{244}Pu as well as a ^3He bombardment of ^{237}Np , and are planning studies with ^{249}Cf , ^{241}Am , and ^{233}U as targets.

We hope to devote considerable effort to the study of heavy-ion reactions, including stripping, transfer reactions, compound nucleus formation, and fission, using the Berkeley Superhilac. Our ultimate aim is to eventually transfer such studies to an Argonne heavy-ion accelerator.

2. Nuclear Constants

The following nuclear properties were measured this past year. ^{254}mEs Alpha Groups were measured in a joint experiment with J. Milsted (cf. Chapter IV).

α -particle Energy (MeV)	Intensity (%)
6.592 ± 0.004	4.0 ± 1.0
6.558 ± 0.002	4.0 ± 0.5
6.510 ± 0.002	0.21 ± 0.05
6.461 ± 0.002	0.38 ± 0.08
6.417 ± 0.002	1.1 ± 0.2
6.384 ± 0.002	78.0 ± 1.0
6.360 ± 0.002	9.0 ± 0.5
6.328 ± 0.002	1.8 ± 0.2
6.301 ± 0.002	0.22 ± 0.06
6.286 ± 0.002	0.25 ± 0.07

The fraction of ^{254}mEs decay proceeding through alpha emission was measured as $0.31 \pm 0.01\%$. The quantum

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numbers of the ground state of $^{254}\text{m}\text{Es}$ were found to be $K\pi = 2, 2^+$, differing from a previous literature assignment.

Fermium K X-ray energies were measured:

$K\alpha_1$	121.0 ± 0.1
$K\alpha_2$	115.2 ± 0.1

Electron-capture half-life values were determined:

^{237}Am	$75 \pm 5 \text{ min}$
^{238}Am	$96 \pm 5 \text{ min}$
^{239}Am	$11.9 \pm 0.1 \text{ hr}$

Alpha groups in ^{247}Cm decay were measured:

α -particle Energy (MeV)	Intensity (%)
5.265 ± 0.004	13.8 ± 0.7
5.210 ± 0.004	5.7 ± 0.5
5.145 ± 0.004	1.2 ± 0.2
4.983 ± 0.004	2.0 ± 0.2
4.941 ± 0.004	1.6 ± 0.2
4.868 ± 0.004	71.0 ± 1.0
4.818 ± 0.004	4.7 ± 0.3

Alpha decay half-life of ^{247}Cm was measured as $(1.56 \pm 0.05) \times 10^7 \text{ yr}$.

3. Nuclear Isomers

We have continued our study of odd-odd isomers. Investigating these nuclides is the only means we have for studying the two-quasi-particle states in even-even nuclides which are formed by the decay of the odd-odd parent nuclei. In addition, a study of the low-lying levels in odd-odd nuclei can provide useful information on the nature of the effective interaction between protons and neutrons in nuclear matter.

Recently, several new isomers in the heavy-element region have been discovered and studied at Argonne National Laboratory. A new isomer of ^{250}Es was produced by irradiating a ^{249}Bk target with ^4He ions in the Argonne 60-in. cyclotron [1]. The isomer of ^{250}Es was found to decay with a half-life of $2.1 \pm 0.2 \text{ h}$ and was shown to have a low nuclear spin, possibly 1-. The decay of the previously known 8.3 h isomer of ^{250}Es was also studied in greater detail. The radiations emitted by this nuclide showed that its ground state had a spin of 6+, and it decayed primarily to a $K\pi = 5^-$ state at 1395.8 keV, which de-excites to the ground state band via a $K\pi = 4^-$ and a $K\pi = 2^-$ rotational band.

A new isotope of mendelevium, ^{254}Md , was formed by irradiating ^{253}Es with ^4He ions [2]. ^{254}Md also appears to have two isomers, one with a 10-min half-life and another with a 28-min half-life. The 10-min isomer was identified

by observing the growth of ^{254}Fm formed by the electron-capture decay of the parent, ^{254}Md , and the presence of the 28-min isomer was deduced from the amount of ^{254}Fm observed in repeated chemical separations from mendelevium over a relatively long time interval.

The decay characteristics of a high-spin isomer of ^{246}Am were studied. This nuclide is formed during the irradiation of ^{244}Pu with ^4He ions. The nuclear spin of this nuclide was found to be 7, and its major decay populates a $K\pi = 8^-$ state at 1179.6 keV in ^{246}Cm , which, in turn, decays with a half-life of greater than 1 sec. This half-life is unusually long; ordinary decay times are of the order of 10^{-12} sec . This transition is highly hindered because of the large change in K required to decay to the lower-energy states that are available.

We will complete our study of ^{250}Es and ^{252}Es this fiscal year. In the near future we hope to look for isomers of ^{244}Bk , ^{246}Bk , ^{232}Np , and perhaps ^{242}Np . When our recoil chamber is completed and functioning, we will probably look for neutron-deficient isotopes such as ^{236}Am , ^{234}Am , etc.

At present we are planning to gradually shift our emphasis to isomers prepared by heavy-ion bombardments. Since heavy ions bring in large amounts of angular momentum to the compound nucleus, such reactions tend to populate a variety of high-spin isomers. Aside from their intrinsic interest, the properties of these species need to be characterized in order to delineate the products of those heavy-ion irradiations used to search for new elements. As an example, our studies of the high-spin states in ^{250}Cf offer a possible explanation of some recent heavy-ion irradiation results in the search for isotopes of 102 and 104.

C. HEAVY-ELEMENT ISOTOPES AND DECAY

SCHEMES (P. R. Fields, I. Ahmad, H. Diamond, R. Sjolom, R. F. Barnes, and W. McHarris*)

1. New Isotopes

The production and study of new isotopes is important to our general program of systematically examining and correlating the nuclear properties of the heavy elements.

We looked for the new isotopes ^{236}Am and ^{231}Pu , both at Argonne and at Michigan State University. Calculations indicated that these two isotopes could be made at MSU and possibly at Argonne. However, their half-lives were probably too short to allow detection with the chemical separations that we employed to isolate ^{236}Am , and with the recoil technique that was used for ^{231}Pu . The new recoil chamber (Sect. B.1 above) should be a valuable tool in looking for such new isotopes.

We plan to use the new recoil chamber in a search for new neutron-deficient isotopes of Np, Pu, Am, Cm, and Cf.

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The new Argonne Electron Linear Accelerator will be used to study the (γ, p) reaction as a means of producing valuable isotopes in the heavy element region, and we hope the Superhilac will be available in the near future to produce new nuclides in the actinide and transactinide region.

2. Decay Schemes for Alpha, Beta, and Electron-capture Decay in Heavy-element Nuclides

Decay-scheme studies provide important information for developing an understanding of the nuclear states in heavy-element nuclides. Such investigations uniquely determine the spins, parities, and character of the energy levels; these in turn provide us with the information to test the various nuclear theories. The observed energies of the states and their variation with deformation are very useful in

helping us to predict the properties of unknown nuclides.

In the recent past we have completed a study of energy levels in ^{251}Cf and ^{243}Pu [3,4]. The energy level diagram of ^{251}Cf constructed on the basis of our observations is shown in Fig. 1.1. We also are well on the way to completing our studies of the levels in ^{252}Cf , ^{250}Cf , ^{249}Cf (from e.c. decay of ^{249}Es), ^{250}Bk , ^{248}Bk , ^{248}Cm , ^{239}Pu , ^{238}Pu , and ^{237}Pu . In the near future we will undertake a study of the states in ^{253}Cf (from alpha-decay of ^{257}Fm), ^{250}Es , ^{246}Cf (from alpha-decay of ^{250}Fm), ^{251}Es (from e-capture in ^{251}Fm), and ^{247}Cf (from alpha-decay of ^{251}Fm). We may also have time to investigate the decay of ^{232}Np and ^{233}Np and possibly such neutron-deficient isotopes as ^{231}Pu and ^{236}Am .

We plan to concentrate on the neutron-deficient isotopes that can be studied with our new recoil chamber and on the

Fig. 1.1. Energy-level Diagram of ^{251}Cf . ANL Neg. No. 121-6727.

isotopes we can make by heavy-ion bombardment or possibly by high-energy-proton irradiations.

D. ATOMIC-BEAM MEASUREMENTS (H. Diamond, L. S. Goodman,* H. E. Stanton,* W. Childs,* M. S. Fred, and R. K. Sjöblom)

Atomic-beam magnetic-resonance measurements of transitions between Zeeman levels of neutral atoms can yield the atomic and nuclear magnetic dipole moments and the nuclear (electric) quadrupole moments. The values of these fundamental properties of atoms and nuclei can then be used to test and guide theoretical descriptions of nuclear and atomic structures.

In an atomic-beam magnetic-resonance apparatus, Fig. 1.2, the radiofrequency radiation is applied in a homogeneous magnetic field (the C field), which is preceded and followed by highly inhomogeneous magnetic deflecting fields (the A and B fields) whose gradients are in the same direction. As the atomic beam traverses the A field, all paramagnetic atoms are deflected by the strong field gradient. The beam then passes through the homogeneous C field where applied rf induces transitions between the Zeeman substates of the atoms. Finally, the strong gradient of the B field refocusses those atoms that had been deflected in the A field and then had been reversed in orientation by the rf radiation. The beam is collimated, nonmagnetic atoms blocked out, and only those atoms collected which have been suitably refocussed by the rf field. In the experiment described below, ^{254}Fm atoms refocussed at each value of the applied rf were caught on planchets and each planchet was counted for 1000 min in a low-background ion chamber.

Fig. 1.2. An Atomic-beam Magnetic-resonance Apparatus. ANL Neg. No. 121-8542.

*Physics Division, Argonne National Laboratory.

The apparatus was built (by members of the Physics Division) to respond to radioactive atoms and is operated jointly with chemists in our high-activity wing where the necessary large quantities of radioactivity can be processed.

1. g_J Value for the Atomic Ground State of Fermium [5]
(L. S. Goodman,* H. Diamond, H. E. Stanton,* and M. S. Fred)

An atomic-beam magnetic-resonance measurement of ^{254}Fm gave the atomic magnetic moment, and by inference, the electronic structure of the fermium ground state.

Fermium, the 100th element, is only obtainable in nanogram-scale amounts, and the only isotope obtainable on this scale, ^{254}Fm , decays by alpha-particle emission with a 3.24-h half-life. Thus, determining the electronic structure of fermium atoms by optical spectroscopy is not yet feasible. A beam of neutral ^{254}Fm atoms was generated and passed through the magnetic-resonance apparatus described above.

The amount of ^{254}Fm alpha activity on the planchets plotted against rf frequency at a given C-field strength (Fig. 1.3) reaches a sharp maximum at the frequency for which $h\nu$ is equal to the energy separation between adjacent Zeeman substates, and this resonant frequency can be measured with high precision. Since the even-even ^{150}Fm has zero nuclear angular momentum, the frequencies ν of the observable transitions are linear with magnetic field, i.e.,

$$\nu = g_J \mu_0 H,$$

where ν is the frequency (MHz) at the peak of the resonance, g_J is the atomic magnetic moment divided by the electronic angular momentum, $\mu_0 = 1.399677$ MHz/G is the Bohr magneton expressed in suitable units, and H is the intensity (in G) of the uniform C field. The measured g_J is 1.16052 ± 0.00014 .

The electronic structure of neutral fermium can be inferred by extrapolation from known actinide and lanthanide structures. The expected ground state is expected to be a nearly pure 3H_6 level of the $5f^127s^2$ configuration. The small amount (3%) of other levels mixing with the ground state allows the intermediate-coupling calculation of g_J to be quite good—even if the parameters used are not known precisely. The calculated $g_J = 1.1606$ agrees well with the experimental value and thus supports the assignment of the ground-state structure. Calculations of the g_J expected from alternative structures are not in good agreement with experiment.

To produce a beam of neutral atoms, fermium fluoride was heated in a zirconium carbide crucible in the presence of tungsten powder. Separate experiments suggest that zirconium carbide was the effective reducing agent. The authors believe that this was the first time that fermium

Fig. 1.3. Distribution of ^{254}Fm Activity as a Function of RF Frequency. ANL Neg. No. 209-1196.

was reduced and shown to be in the zero-valent state.

R. Sjöblom accomplished the many high-speed fermium purifications needed in this work.

E. SINGLE-NUCLEON TRANSFER STUDIES IN THE HEAVY-ELEMENT NUCLIDES (T. H. Braid,*

R. Chasman, J. P. Erskine,* and A. M. Friedman)

1. Experimental Studies (T. H. Braid, J. P. Erskine, and A. M. Friedman)

The research reported here is part of a broad and intensive investigation of the structure of the actinide nuclides by means of charged-particle-induced nuclear reactions. This research program (a continuing collaboration between members of the Physics and Chemistry Divisions) is made possible by the combined skills of nuclear chemists and nuclear physicists and by the use of an unusual combination of highly developed apparatus—the FN tandem Van de Graaff accelerator and the high-resolution magnetic spectrograph of the Physics Division and the “hot lab” and associated isotope-separator facilities of the Chemistry Division.

The purpose of this program is to develop an understanding of low-energy nuclear structure of the highly deformed nuclides in the heavy-element region. Studies of single-particle states are a particularly useful technique for gaining a detailed understanding of such structure. Although decay-scheme studies lead to the identification of some single-particle states, this approach is limited both by energetic considerations and by many quantum selection rules. The use of single-nucleon transfer reactions makes

many more nuclear states accessible to experimental investigation. To this point, our program has concentrated on those neutron single-particle states in the heavy elements which are populated in the (d,p) and the (d,t) single-neutron transfer reactions.

A recent result of this program is an extensive set of information on the single-particle states in four odd-A isotopes of curium. Many heretofore unobserved single-particle states were found and identified. The completeness of these data made possible an especially careful study of the single-particle rotational model with residual pairing forces. Another important facet of the measurements was the determination of the reaction Q values, which accurately link together the masses of seven curium isotopes. The single-particle states were observed by means of (d,p) and (d,t) reactions on targets of the even-mass curium isotopes $^{244}, ^{246}, ^{248}\text{Cm}$. This study of a series of isotopes proved to be a very useful technique, since one could recognize systematic trends by comparing the spectrum of one isotope with that of the next.

The single-nucleon transfer reactions (d,p) and (d,t) are ideal tools for the study of single-particle excitations. In the (d,p) reaction, a single neutron is transferred to one or another of the empty orbitals in the potential of the even-even core. The rotational motion of these deformed nuclei provides a substructure to the observed transition and thus provides a fingerprint or signature of a particular orbital. In other words, the intensity pattern that is observed in the excitation of the rotational bands in these transfer reactions has a unique pattern whose gross features can easily be calculated from the deformed single-particle wavefunctions. These intensity patterns for the rotational bands, together with the variation in yield as a function of observation angle, were used to identify the single-particle

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states. For example, the first clear-cut identification of the slate 1/2-[750] was made by this technique in our study.

A particularly impressive accomplishment is the ability to obtain spectra such as the one shown in Fig. 1.4, which shows the data obtained for the (d,f) reaction on the ^{244}Cm target. Even during the bombardment, the α particles coming from the radioactive decay of ^{244}Cm (half-life = 18 y) were far more abundant than were the elastically scattered deuterons or the tritons and protons produced in the reaction. Nevertheless, in spite of these unusual circumstances, the beautiful spectrum shown in Fig. 1.4 was obtained.

The peaks in this figure correspond to ^{243}Cm energy levels excited by the (d,t) reaction. Rotational bands identified in this nucleus are marked on the figure. Significant differences between the cross-section signatures of the rotational bands are readily apparent.

True single-particle level schemes were developed by removing the effects of the pairing force from the measured excitation energies. To do this, the assumed single-particle spectrum was varied until the energy-level spacings obtained from an extremely accurate pairing-force calculation agreed with experiment. When these data are combined with recent Argonne spectroscopic studies of states in ^{251}Cf , a complete picture of the 152-neutron gap, as a function of neutron number, emerges.

In Fig. 1.5, we show the single-particle spectra as measured, and in Fig. 1.6 we show the single-particle spectra extracted from the data after pairing effects have been removed.

The curium data enabled us to determine the parameters of the deformed, single-particle potential field. In calculations with a deformed, momentum-dependent, Woods-Saxon potential, the deformation parameters β_1 , β_2 , and β_3

Fig. 1.3. Measured Excitation Energies of Single-particle States in the Odd-A Curium Isotopes. ANL Neg. No. 209-1480 Rev. 1.

Fig. I.6. Single-particle Level Scheme Extracted from the Data by Means of a Pairing-force Calculation. ANL Neg. No. 209-1479.

Fig. 1.4. Triton Spectrum for the Reaction $^{244}\text{Cm}(d,1)^{243}\text{Cm}$ at $0-140^\circ$, ANL Neg. No. 109-9347 Rev. 2.

were varied to optimize the agreement between calculated and extracted single-particle energies. The most reasonable interpretation of the data fixes the deformation parameters as $\beta_2 = 0.24 \pm 0.01$, $\beta_4 = 0.00 \pm 0.01$, and $\beta_6 = 0.01 \pm 0.01$. Furthermore, we find that β_6 increases by ~ 0.01 in going from ^{247}Cm to ^{249}Cm .

We are also commencing a study of the proton single-particle states in the heavy-element region, using the reactions ($^3\text{He}, d$) and ($^4\text{He}, t$) at the cyclotron. Our eventual aim is to use results from the two sets of single-particle-state studies: (1) to test various theoretical models of nuclear structure, and (2) to predict the structure of as-yet-unobserved nuclides. For the latter, it is especially interesting to extend these studies to heavier actinide targets as they become available.

2. Single-particle States—Theoretical (R. R. Chasman)

A basic problem in the theoretical description of nuclear single-particle states is that a central potential, which properly describes the loosely bound nucleons, underbinds the most tightly bound nucleons by a considerable amount (~ 25 MeV). To overcome this difficulty, we have con-

structed a Saxon-Woods momentum-dependent potential that gives good overall agreement with nuclear single-particle spectra for both tightly and loosely bound nucleons. This potential gives a good description of spectra in the rare-earth and heavy-element regions of deformed nuclei, as well as for spherical nuclei near ^{208}Pb .

We have used this potential to analyze the single-particle states in the odd-mass Cm isotopes. This potential is also being used to estimate single-particle energy levels in the vicinity of mass 300. The spectra computed for these nuclei are shown in Figs. 1.7 and 1.8.

F. NEUTRON-PROTON AND TWO-QUASIPARTICLE STATES OF ACTINIDE NUCLEI (K. Katori,*

J. R. Erskine,* A. M. Friedman, and R. R. Chasman)

As we now have a picture of single-particle energies and wavefunctions from our neutron-transfer studies, it appears that it may be possible to interpret transfer reactions to both the two-quasiparticle states of even-even nuclei and the states of odd-odd nuclei. We have already started studying (d, p) and (d, t) reactions on ^{236}U and ^{237}Np . We hope to extend these experiments soon to targets of ^{231}Pu ,

Fig. 1.7. Predicted Proton Single-particle Spectrum in the Mass-300 Region. Proton eigenvalues are plotted as a function of spin-orbit interaction strength. ANL Neg. No. 121-7215.

*Physics Division, Argonne National Laboratory

Fig. 1.8. Predicted Neutron Single-particle Spectrum in the Mass-300 Region. Neutron eigenvalues are plotted as a function of spin-orbit interaction strength. ANL Neg. No. 121-7214.

^{239}Pu , ^{241}Pu , ^{241}Am , ^{243}Am , and ^{245}Cm .

The experiments have been planned to determine the splitting of the singlet and triplet spin states of a set of five or six neutron orbitals when these are paired with both other neutron and with proton orbitals. It is hoped that these results may lead to a better understanding of nucleon-nucleon interactions.

G. CHEMISTRY OF THE ACTINIDE ELEMENTS

(S. Fried, D. Cohen, J. Malm, K. Orlandini,
A. P. Masino,* P. Hart,* H. S. Selig,** J. Holloway,†
S. L. Ruby,†† B. D. Dunlap,‡ and M. B. Brodsky‡‡)

The study of the physical and chemical properties of the actinide elements is aimed at two goals. One goal is the attainment of a basic understanding of the position of these

elements in the periodic table, their chemical relationships to each other, and their electronic structures. In view of the recently proposed possibility of regions of stable nuclides beyond the actinides, it is especially desirable now to use our improved theoretical understanding to make accurate extrapolations concerning chemical and physical properties of elements of the extended periodic table. When these new elements are made, the ability to observe and identify them may depend strongly on the correct assessment of their probable properties.

The other goal is a practical one. The actinide elements are all radioactive, and among the various nuclides, exhibit all possible modes of decay. For example, those nuclides which emit beta and gamma radiation are useful in medical research as well as in industrial applications. The fact that spontaneous fission decay yields fast neutrons has been found useful in cancer therapy. There is no compact portable source of fast neutrons comparable with an actinide-beryllium source or a ^{252}Cf source. In addition, these fast neutrons may serve for activation analysis used in medical diagnosis, a much more convenient technique than one requiring a nuclear reactor. Those actinides decaying by

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alpha-particle emission can be and are already used in power packages in space research, and for isolated power sources in the ocean and remote arctic regions. In the long run, nuclides decaying by spontaneous fission will also become useful for power sources.

Despite intensive work on actinide chemistry, much still remains undiscovered. Understanding the details of actinide chemistry will become more and more important as the availability of actinide elements from power-reaction fuel reprocessing increases and their use becomes more widespread. Active work on the chemistry of actinides and transactinides is going on, not only in the laboratories of the USAEC, but at a rather accelerated pace in laboratories in the USSR.

1. Neptunium Chemistry (A. P. Masino, K. A. Orlandini, S. Fried, and D. Cohen)

The anion-exchange behavior of neptunium, uranium, plutonium, thorium, and several accompanying elements has been studied in aqueous tetramethyl ammonium hydroxide (TMAH) medium and in this same medium containing various complexing agents. It has been found that the neptunium in the (V) oxidation state is not retained by Dowex-1 X 8 resin from slightly basic TMAH-citrate solutions and is readily separated from uranium and thorium, which are retained by a column of this resin. Separation methods based on the properties of Np(V) in basic solution are very effective in separating Np from many other elements.

We have shown that Np(V) can be extracted by certain "anionic" solvents, notably, Aliquat 336 in xylene. For example, Np(V) is strongly extracted ($K_D = 58$) from 0.1M tetramethyl ammonium hydroxide (TMAH) solution by 1M Aliquat in xylene. The equilibrium constants (K_D) go through a maximum at about 0.1M TMAH. In contrast, the K_D 's for the extraction of Np(VI) decrease with increasing TMAH concentration. It thus becomes very easy to define conditions under which Np(V) can be readily separated.

Work on the structure and properties of Np(V) in basic solution will be continued. Preliminary studies have been made attempting to bracket the molecular weight by ultrafiltration techniques, with the goal of getting some information on the structure of the ion.

Although Np(V) is very stable in solution and PaF_5 , UF_5 , UF_6 , and NpF_6 are known, NpF_5 has not yet been characterized. Reduction of NpF_6 with I_2 in IF_3 has yielded a product which contained a Np(V) fluoride. Although an X-ray analysis of one preparation showed the pattern to be the same as UF_5 , this pattern could not be repeated with any other preparation. Mossbauer spectroscopy showed that these samples contained about 1/3 Np(V) fluoride and 2/3 Np(IV) fluoride.

Another line of attack was to prepare CsNpF_6 , a known compound, and attempt to remove CsF from this double

salt by washing with anhydrous HF. The product was shown by Mossbauer spectroscopy to contain only Np(V) , but the corresponding X-ray pattern is unknown. There is some evidence that this Np(V) compound is $\text{NpF}_5 \cdot \text{XHF}$.

We shall continue this approach and hope to isolate a reasonably pure sample of the pentafluoride.

2. Uranium(V) in Aqueous Solutions (D. Cohen)

In saturated LiCl or CaCl_2 solution, electrolytic reduction of uranyl ions yields a U(V) species. Although the stability of U(V) is poor, we have been able to observe the absorption spectrum. In 1 to 3M K_2CO_3 solutions, U(V) forms a stable species; the solution is colorless and its spectrum has been measured.

3. Search for a Volatile Fluoride of Einsteinium (S. Fried, D. Cohen, and J. G. Malm)

An examination of the periodic table would suggest that californium and einsteinium might have a valence as high as six. The known volatility of the heavy metal hexafluorides and the strong oxidizing power of some of these fluorides suggest several experiments that can check this "prediction." Up to now, attempts to demonstrate the existence of such a compound have not succeeded.

Further tracer experiments to elucidate the behavior of Es and Cf under strongly fluorinating conditions are planned (cf. Chapter XII).

H. SECONDARY REACTIONS INDUCED BY GeV PROTONS—AN EARLY ATTEMPT TO PRODUCE SUPERHEAVY ELEMENTS (E. P. Horwitz, J. Unik, P. R. Fields, I. Ahmad, K. Wolf, C. Bloomquist, S. Fried, D. Cohen, and D. Henderson)

Several recent theoretical studies have predicted that a region of relatively stable nuclei, an "island of nuclear stability," may exist for those nuclei in the region of 110–114 protons and approximately 184 neutrons. There is a large inherent uncertainty in the predicted half-lives for these "superheavy elements"; however, all calculations do indicate a good probability that nuclei in this mass region will have half-lives sufficiently long to allow detailed measurements to be made of their properties—provided that suitable methods can be found to produce and isolate these nuclei. The possibility of studying new elements which are expected to have nuclear and chemical properties different than those elements we now know has created a great deal of excitement in the scientific community. In particular, the study of the properties of these elements whose nuclei are at the very limits of nuclear stability could provide a much better insight into our knowledge of the nucleus and its electronic configuration.

Some of the predicted half-lives for isotopes of these

superheavy elements are as long as 10^8 years, and therefore there is a small probability that they could have been produced during nucleosynthesis and exist in nature today. However, virtually all of the searches conducted to date attempting to find these elements have been negative and have established very low limits for their existence in nature. These very low limits indicate that the half-lives may be shorter than 10^8 years or simply that the abundances are so low in nature as to prove impractical for future research.

On the basis of all the information available today, it now appears that the most efficient way to produce and study these superheavy elements will be by means of heavy-ion reactions. Unfortunately, it will be quite some time before the heavy-ion projectiles required to produce these elements will be available from new accelerators either proposed or now in construction. However, we have attempted to investigate the possibility of obtaining heavy ions and producing these new elements through an indirect process—secondary reactions induced by high-energy protons. The recent work of Poskanzer *et al.* [6] has demonstrated that ions as heavy as argon are produced as reaction products during the bombardment of uranium targets with 5.5-GeV protons, and a small fraction of these heavy ions have energies sufficiently high to interact with the uranium target atoms to produce heavier elements. Unfortunately, the experiment of Poskanzer *et al.* did not supply any information regarding the existence of ions heavier than argon produced in these reactions which are

required to reach this island of stability. Marinov *et al.* [7] have reported the tentative discovery of a new spontaneous fission activity which appears to be a chemical homolog of mercury and possibly element 112. This activity was produced by secondary reactions during the irradiation of a tungsten target with 24-GeV protons. These authors proposed that high-energy protons elastically scattered from tungsten atoms can impart enough energy to the tungsten atoms to allow them to interact with other tungsten atoms in the target and produce superheavy elements. The heavy ions observed in the experiments of Poskanzer *et al.* and proposed by Marinov *et al.* occur in extremely low yields. However, the small cross sections for producing these heavy ions can be compensated to some extent since very large quantities, e.g., kilograms, of target material can be irradiated due to the large range of GeV protons.

Based on this preliminary information, a program was initiated at this laboratory to investigate the potentialities of secondary reactions as a means of producing heavy elements. To date, two tungsten and two uranium targets, each irradiated with a nominal 10^{17} protons at 12 or 28 GeV, have been chemically separated and each chemical fraction analyzed for alpha-particle and spontaneous-fission activities. On the basis of their predicted electronic configurations, the superheavy elements with atomic numbers 110 through 114 are predicted to be chemical homologs of platinum through lead as shown in Fig. 1.9. The chemical isolation of the superheavy element fractions from the

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-58 La	59 Hf	60 Ta	61 W	62 Re	63 Os	64 Ir	65 Pt	66 Au	67 Hg	68 Tl	69 Pb	70 Bi	71 Po	72 At	73 Rn
87 Fr	88 Ra	89-103 Ac	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
119	120	121															

LANTHANIDE SERIES

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
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ACTINIDE SERIES

89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
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121	122	123	124	125	126	
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Fig. 1.9. The Periodic Table with Predicted Arrangement of the Transactinide Elements. ANL Neg. No. 121-7887.

TABLE I.1. Heavy-element Production by Irradiation of 1 kg of Uranium with 12-GeV Protons

Isotope	$t_{1/2}$	No. of Atoms ^a at End of Irradiation 1/10/71
²²⁷ Th	18.2 d	1.1 (14)
²²⁸ Th	1.91 y	1.4 (14)
²³⁰ Pu	2.85 y	1.4 (13)
²³² Pu	45.6 d	<5.7 (12)
²³⁸ Pu	86.4 y	2.2 (13)
²³⁹ Pu	2.44×10^3 y	5.2 (16)
²⁴⁰ Pu	6.58×10^3 y	2.1 (12)
²⁴¹ Pu	13.2 y	2.6 (10)
²⁴² Pu	3.79×10^3 y	<1.0 (9)
²⁴³ Am	458 y	
²⁴⁵ Am	7.95×10^3 y	<4.2 (8)
²⁴⁶ Cm	26.8 d	1.2 (4)
²⁴⁸ Cm	162 d	3.7 (6)
²⁴⁹ Cm	32 y	~3.8 (6)
²⁴⁹ Cm	17.6 y	6.0 (6)
²⁴⁹ Cm	9.3×10^3 y	<4.2 (8)
²⁴⁹ Cm	5.5×10^3 y	<4.2 (8)
²⁴⁷ Bk	1.4×10^3 y	<9.2 (6)
²⁴⁸ Cf	350 d	1.3 (5)
²⁵⁰ Cf	13.2 y	<3.0 (5)
²⁵² Cf	2.65 y	<3.2 (3)
²⁵⁴ Cf	60.5 d	<20
²⁵² Es	20.3 d	<2.7 (3)
²⁵⁴ Es	276 d	<1.6 (3)
²⁵⁷ Fm	80 d	<6.7 (2)
²⁵⁸ Md	54 d	<8.9 (2)

^aExponents to the base 10 are given in parentheses.

target was based on the extrapolation of only two chemical properties of their congeners, namely, the formation of insoluble sulfides and the formation of chloride complexes. Both extrapolations are very conservative, especially in view of the particular method of incorporating these properties in the actual chemical separations. Table I.1 illustrates the yields of various actinide elements that were produced by irradiating 1 kg of uranium with 12-GeV protons at the ZGS accelerator. Isotopes as heavy as ²⁴⁸Cf were observed. Most likely, carbon ions produced by the initial interaction of the high-energy protons with uranium atoms interact

TABLE I.2. Results of Fission Counting of Nonactinide Fractions

Target	Chemical Fraction	Fissions/month
Tungsten 1 5 gm AGS 30 GeV	Re, Os, Ir, Pt Hg, Bi, Po 107-110, 112, 115, 116 Pb, 114 Tl(+1), 113 Au, Tl(+3), 111, 113	<4 <1 <1 <1
Tungsten 2 25 gm AGS 28 GeV	Re, Os, Ir, Pt, Au, Hg, Tl(+3) Bi, Po, 107-113, 115, 116	<0.8
Uranium 1 1 kg ZGS 12 GeV	Re, Pt, Hg, Tl(+3), Bi, Po 107, 110, 112, 113, 115, 116 Ir, 109 Tl(+1), Pb, 113, 114 Os, 108	<1 <1 <1

with the uranium target material to produce californium isotopes. This yield of ²⁴⁸Cf corresponds to an extremely low cross section of 3×10^{-12} barns. Table I.2 summarizes the fission counting of various chemical fractions isolated from three of the irradiated targets in an attempt to observe spontaneous fission from a superheavy element which may have been produced. The transactinide or superheavy elements expected to be in each chemical fraction are indicated by their atomic numbers in this table. As can be seen, no fission activity has been observed to date with limits of generally less than one fission event per month. The fission-counting result obtained for the target labeled Tungsten 2 does not substantiate the work of Marinov *et al.* [7]. A 1-kg tungsten target is currently being irradiated with 28-GeV protons at the AGS accelerator. This target should have approximately one-hundred times more nuclear interactions than the target labeled Tungsten 2 and will therefore provide a more crucial test as to the existence or nonexistence of superheavy elements produced by means of secondary reactions.

From the extremely low limits already established for the existence of spontaneous fission activities produced by these reactions, one must conclude that the most definitive searches for superheavy elements must await the advent of very intense beams of heavy ions available from the coming generation of new heavy-ion accelerators.

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II GEO- AND COSMOCHEMISTRY*

The origin, abundances, and distributions of the elements in the solar system have been our primary interest. The knowledge gained is necessary for postulating the possible nucleosynthetic processes and the physical and chemical conditions to which solar system matter has been subjected. The materials available for our investigations are terrestrial, meteoritic, and lunar. Studies have included three general groups of elements: the actinides and possible transactinides, the heavy elements Hg → U, which are final products of nucleosynthesis, and a group of elements which may give clues to irradiation, physical, and chemical conditions existing in the solar system.

Another project to which the Division has contributed significantly is the development and application of α -scattering for the remote chemical analysis of the surfaces of the moon and other planetary objects.

In addition to studies on the genesis and distribution of particular nuclides, we include in this chapter some interesting studies on extraterrestrial materials which have led to the discovery of both new minerals and new occurrences of terrestrial minerals. A section is also included on the origin of organic matter in extraterrestrial samples.

The Argonne Chemistry Division has a primary interest in, and an exceptionally expert staff studying, the actinide elements and searching for possible transactinide nuclei (cf Chapter I). Emission spectroscopy and mass spectrometry have been utilized in these investigations. Developments in the use of the spark-source mass spectrometer (Chapter XIX, Analytical Chemistry) are closely related to the research needs of this program.

The halogens are some of the trace elements being determined. They are important chemical agents as well as contributors of rare gas isotopes from nuclear reactions induced by cosmic rays. Rare gases play key roles in chronology and in cosmic-ray studies. The elements Pb, Th, and U are important in chronology, and the latter two are sources of heat in planetary objects. Measurements of the above elements as well as Ru, Os, Ba, Te, Ag, Tl, and Bi not only provide data on elemental abundances but also, because of their widely different chemical and physical properties, provide the opportunity to study a variety of possible processes and events in the evolution of planetary and asteroidal bodies. The technique used is neutron and photon activation analysis. Concentrations range from ppm to <ppb. This method minimizes problems of contamination of the samples.

While problems of cosmic significance occupy most of the effort described in this chapter, both geological and archeological problems have aroused the interest of some of the staff and offered opportunities for significant research using the special facilities available.

A ACTINIDE NUCLIDES OF GEOCHEMICAL AND COSMOCHEMICAL IMPORTANCE** (P. R. Fields, H. Diamond, D. N. Metta, C. M. Stevens, D. Rokop, and E. P. Horwitz)

Several actinide isotopes have half-lives sufficiently long for them to exist in nature and can, therefore, be used to date geological and cosmological events. In some cases, the ratios of long-lived isotopes are also useful in studying the nucleogenesis of the solar system and in the universe. In some instances, nuclides with long half-lives, such as ^{244}Pu , may themselves be extinct, but the residues left by their radioactive decay are of great importance in deciphering the cosmological history of terrestrial and extraterrestrial materials.

Several Apollo 11 lunar samples were analyzed for actinide nuclides, and the results of these experiments have been reported [1,2]. In FY 1971, samples from the Apollo 12 flight were examined [3]. Once again it appears that the $^{235}\text{U}/^{238}\text{U}$ ratio is very close to terrestrial values, but a careful analysis of more samples will have to be made to demonstrate positively that this ratio is identical to the terrestrial value within experimental error. Several samples collected by Apollo 12 contained ^{236}U , the concentration in soil was 200 ppb (of ^{238}U), and a breccia rock contained 44 ppb. Terrestrial ^{236}U is less than 0.7 ppb relative to ^{238}U . Additional studies will be made to verify these results and to aid in developing a plausible mechanism for the presence of such an abnormally high level of ^{236}U in lunar material.

B ABUNDANCES AND DISTRIBUTION OF TRACE ELEMENTS (G. W. Reed and S. Jovanovic†)

These studies have provided many of the best-determined cosmic abundances and have been useful in developing the systematics of the solar system elemental abundances. Most of the elements studied are highly fractionated among the various classes of chondritic meteorites and, therefore, are key elements when one attempts to reconstruct the origin and evolution of meteorites. Investigations are and have been underway to determine whether the fractionation occurred in the solar nebula prior to or during the accretionary stage or subsequently during differentiation of planetary or asteroidal bodies.

Typical of the results and their interpretation is our approach to the question of *volatiles on the moon*. The

*Chapter edited by George W. Reed, Jr.

**The lunar portion of the work described in this section is funded by NASA.

†Consultant with the Chemistry Division.

presence (better still absence) and role of volatile substances on and in the moon have been of especial interest ever since astronomers reported seeing a transient reddish hue near the crater Alphonsus some years ago. This was attributed to volatiles being released from the interior of the moon.

As lunar samples have become available we have been studying this question and some of our findings may be pertinent. Three types of measurements have been made [4,5]: exterior and interior rock samples and core samples from various depths have been studied; samples have been leached with H_2O ; and samples have been subjected to heating and the volatiles trapped. A rather mixed group of elements have been measured in these experiments. They include the halogens, electropositive elements Li and U, the platinum metals Ru and Os, and the volatile element Hg. Interesting effects which appear to be surface-related have been observed in Br, Cl, Os, and Hg. In the cases of Br and Cl, significant amounts of the elements were leached with H_2O indicating the presence of water-soluble compounds. These compounds are present in the fine grained soils and in rocks, many of which are quite porous. There appears to be a parallel between the leachability of these two elements in lunar material and in terrestrial basalts. Since the latter are known to have existed in the presence of H_2O , it is tempting to speculate that H_2O has been present in spite of the fact that no direct evidence for H_2O in the moon has been found. An alternative and not necessarily different explanation is that these elements were deposited as vapors on the surfaces of grains.

The element Os appears to be more concentrated in the interior of rock than near (within 1–2 mm) the surface. Some process has apparently occurred which has caused depletion of Os. Possibly gases such as oxygen derived from the solar wind or perhaps released by photo dissociation of silicate minerals may be the agents for mobilizing the Os near the surface. If so, volatile Os compounds such as the tetroxide and halides could be present at the lunar surface.

Perhaps the most interesting element is Hg. In the laboratory we find that a significant fraction of it is volatilized from lunar matter at $130^\circ C$, which is the subsolar temperature at the surface of the moon. This Hg must be volatilized from surfaces during the lunar day and should constitute a portion of the tenuous lunar atmosphere. Furthermore, the observation that the amount of Hg present in cores, drilled into the lunar surface, increased with depth suggests that there may be higher concentrations of Hg, as well as other volatiles, at depth in the moon than might be expected by measurements of surface samples.

Experiments now being conducted on the surface of the moon to measure phenomena in the lunar atmosphere should provide complementary data to that described above. The suprathreshold ion detector, for instance, has

detected bursts of particles which could be attributed to gaseous emissions from within the moon.

Another element of great interest is Pb. We* are taking advantage of the greater freedom from contamination afforded by activation analysis relative to mass-spectrometric determinations to measure primordial Pb (^{204}Pb) via $(n,2n)^{203}Pb$ [6]. In addition, two isotopes that are primarily radiogenic in lunar samples are measured: ^{206}Pb via $(n,\alpha)^{203}Hg$ and ^{208}Pb via $(n,\gamma)^{209}Pb$. Fast-neutron irradiations are carried out in the cyclotron and also in the core of the high-flux reactor at BNL. Pb is another element whose presence on surfaces of lunar soil and rocks is detected in our experiments. Terrestrially such Pb may be associated with volcanic sublimates, and such a source could explain the lunar results.

C. MINERALOGY OF METEORITES AND LUNAR ROCKS (L. H. Fuchs)

Examination of extraterrestrial material for trace minerals has been under continuing investigation for several years. Small amounts of minerals with unusual compositions may be rare because of being produced by some unique set of pressure-temperature conditions, and thereby might provide more useful information on the origin of their parent bodies than would normally be provided by the major minerals. Due to the small size of these mineral grains, usually less than 50 microns, microtechniques using optical, X-ray and electron-microprobe methods are used for identification. Discoveries in this Laboratory of both new minerals and of the first extraterrestrial occurrences of known minerals have led to the study of the pertinent synthetic systems by several other research organizations.

1. Lunar Samples

Identifications of minerals and rock fragments in lunar samples from Apollo 12 have been made in conjunction with trace-elements studies described above. Soil and rocks were cursorily examined for rare minerals, but, with one exception, the mineral content of the samples was generally similar to that of the Apollo 11 material. During the course of this investigation, some unique rock fragments were found in a small amount of the Apollo 12 soil. These contained plagioclase-orthopyroxene mineral assemblages which had not been found in any of the crystalline rocks of Apollo 11 or 12, and only trace amounts of similar fragments had been reported in soil and breccia samples of Apollo 11. It was apparent that these fragments were more abundant in the Apollo 12 soil and constituted an important rock type. (One similar fragment, Lunar Rock #1, in the Apollo 11 soil was the oldest rock fragment dated with an age of 4.4 billion years.) After these occurrences were

*Ralph O. Allen, Jr., University of Virginia, is coinvestigator.

published by us, similar occurrences were noticed by other investigators and considerable attention was focused on this component at the Second Lunar Science Conference. This material became known as KREEP because of enrichments of potassium (K), rare-earth elements (REE), and phosphorus (P).

2 Meteorites

Studies on the Allende meteorite, a rare Type-III carbonaceous chondrite, have been continued. The outstanding finding made is the first meteoritic occurrence of the Ca-Al rich minerals wollastonite, CaSiO_3 , rhonite, $\text{Ca}_2(\text{Ca,Mg,Al,Ti})_2(\text{Si,Al})_{12}\text{O}_{40}$, and andradite garnet, $\text{Ca}_3\text{Fe}_2^{3+}\text{Si}_3\text{O}_{12}$. The presence of these minerals, together with the other associated minerals, is significant to the origin of these aggregates, which many thought to be primary condensates from a solar nebula. This hypothesis cannot, however, account for the presence of a ferro-iron garnet.

Another rare carbonaceous chondrite (a Type-II), the Murchison meteorite, has attracted considerable attention because of the discovery in it of seventeen amino acids by a NASA researcher. We have found that the meteorite contains fragments of high temperature minerals embedded in a matrix of low-temperature minerals. The matrix contains carbon or carbon compounds, water, and hydrated minerals.

D ORIGIN OF ORGANIC MATTER IN THE EARLY SOLAR SYSTEM (M. H. Studier, R. Hayatsu,* and E. Anders*)

The rare class of meteorites called carbonaceous chondrites contain appreciable quantities of organic matter. These meteorites are the oldest that have been observed and, therefore, give the earliest clues concerning the evolution of our solar system. Some scientists have attributed the organic matter in meteorites to an extraterrestrial biological source because of the similarity of the compounds found to those of biogenic origin. This postulate is not necessary, however, since we have synthesized most of the compounds found to be indigenous to meteorites by heating mixtures of carbon monoxide, hydrogen, and ammonia in the presence of an iron meteorite catalyst. On the other hand, it seems reasonable to assume that a chemical evolution of biologically important compounds preceded the evolution of life. Synthesis experiments correlated with studies of organic compounds in meteorites and ancient terrestrial deposits promise to shed some light on the path this chemical evolution has taken.

During the last year, a series of completely deuterated amino acids (glycine, alanine, aspartic acid, glutamic acid,

histidine, lysine, ornithine, and tyrosine) was prepared by heating mixtures of CO , ND_3 , and D_2 in the presence of a catalyst, followed by a hydrolysis step. A technique, developed earlier, involving formation of dinitrophenyl derivatives, paper chromatography, and mass spectrometry was used for separation and identification of the amino acids.

The organic matter in the Murchison meteorite which fell in Australia in September 1969 was isolated by vacuum distillation and by solvent extraction. Individual compounds were separated and identified by a combination of gas chromatography and mass spectrometry. The high ratio of methane to ethane and a preponderance of aromatic compounds support our theory that these compounds were formed by a catalytic process followed by reheating. The distribution was similar to that produced in some of our syntheses from $\text{CO} + \text{D}_2$.

A "porphyrin-like" compound has been isolated and will be studied further.

A sizeable fraction of the organic matter in carbonaceous chondrites consists of a high-molecular-weight aromatic polymer. To date, we have not synthesized such a polymer. In the near future we hope to investigate the conditions necessary for its formation. For example, a combination of a catalytic reaction such as the Fischer-Tropsch and a chain reaction induced by UV radiation will be tried.

The technique of radio astronomy has been used by other scientists to show the presence of a number of organic compounds in intergalactic space. Because of the high vacuum in space, it is not likely that these compounds were formed there. More probably they were formed in a condensing system such as a solar nebula followed by escape from the system into space. Synthesis experiments will be devised to produce the compounds observed in space and to predict others which might be found. On the basis of our experiments to date, we would expect that light hydrocarbons should exist in space.

E USE OF THERMOLUMINESCENCE FOR DATING OCEAN SEDIMENTS (A. M. Friedman, B. G. Oltman,** J. Kastner,** and Paul Siebold†)

The purpose of this investigation was to establish the feasibility of dating ocean sediments through the thermoluminescence of CaCO_3 shells which have stored radiation damage due to exposure to natural environmental radiation.

Similar methods have been shown to be quite successful in the dating of pottery by M. J. Aitken and D. Zimmerman at the Research Lab for Archeology, Oxford University, England [7].

To this end, the minute shells were separated from their

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bed of silica and clay, and techniques developed to establish the number of electron traps, whether their luminescence was linear with dosage (hence, with time), and whether the traps are long-lived enough to survive for a useful period. Of the three sets of traps found in CaCO_3 shells, the first two (released at 110 and 230°C) are too short-lived to be of any use for long-time dating. The third set, released around 350°C, was established as being linear with dose over the natural radiation range and having a mean lifetime of about 10^5 years at the temperature normally found at the ocean bottom. This seems to be most appropriate for the application. We were also able to artificially approximate the radiation exposure and responses found in nature.

F ARCHEOLOGICAL PROBLEMS (P. R. Fields, A. Friedman, J. Lerner, J. Milsted, and M. Dougherty*)

We have used emission spectroscopy and neutron-activation analysis in an attempt to trace copper artifacts back to their original source. The technique employed is to compare the pattern of trace impurities present in a copper artifact with the impurity patterns in copper ores. Most recently, we have been trying to adapt a spark-source mass spectrometer to this problem. This machine has the advantage of analyzing for 30 or more trace elements as compared to about 15 elements detectable by neutron activation.

Early efforts to use the mass spectrometer gave poor agreement between the neutron-activation results and the mass measurement. However, more recent work has shown that most of the deviations can be eliminated by proper treatment of the sample and by operating the spectrometer in such a manner that the lines produced on the detector plate are fairly strong. Densitometer readings are used to make the final determination of a given element. In addition, techniques have been developed whereby the copper in a sample is used as the primary standard and all impurities are related to the copper.

We will continue to perfect the technique of analysis, making use of the electronic beam chopper to improve the accuracy of the determinations. We will soon be prepared to study many of the copper artifacts and ores that we have accumulated.

G PRECISION MEASUREMENT OF HALF-LIVES OF

^{235}U and ^{238}U (A. H. Jaffey, K. F. Flynn, L. E. Glendenin, W. C. Bentley, and A. Essling)

The geologic age of a uranium-bearing rock can be measured by determining the amounts of ^{238}U and of its stable descendant (through a radioactive decay chain) ^{206}Pb . The age can also be calculated from measurement of the amounts of ^{235}U and its descendant ^{207}Pb . The most recently available standard tables give $4.51 \times 10^9 \text{ yr} \pm \sim 1\%$

for the ^{238}U half-life and $7.1 \times 10^8 \text{ yr} \pm \sim 2\%$ for the ^{235}U half-life. Hence, insofar as accuracy is limited by the amount of decay, the uranium-lead ratio is more accurately determinable from the ^{235}U chain, but the accuracy of age determination may be limited by the precision with which the decay rate itself is known, particularly for this more sensitive chain. Thus, for a sufficiently accurate measurement of the uranium-lead ratio in a 2-billion-year old rock, the ^{235}U chain would yield an age with 6% uncertainty.

With new techniques and instruments available, we attempted to improve the accuracy of the ^{235}U value by a factor of ten. We also proposed to measure the ^{238}U half-life, even though the expected improvement might not be as great.

In this experiment, the accuracy was achieved through four independent careful and accurate measurements, which involved (1) chemical analysis of the amount of uranium in several aliquoted samples, (2) deposition of uranium in very thin layers (for alpha-particle counting) on flat plates, such that deposited amounts were in accurately known ratio to the chemically analyzed samples in (1), (3) alpha-counting the samples in a counter of accurately known efficiency, and (4) energy pulse analysis and mass spectrometry to determine the fraction of alpha activity and of mass ascribable to the isotope of interest.

(1) Chemical analysis was carried out with a titration method calibrated against NBS arsenious oxide and uranium oxide. The percentage error, evaluated from the scatter in these experiments and from experience with the method, was about 0.05%.

(2) The uranium solutions were contained in small polyethylene bottles with long capillary tips. Portions were measured out and their weights accurately measured by the difference between the before and after weight of the bottle. Samples for chemical analysis and for alpha-counting were thus prepared in accurately known weight ratios. The counting samples were "molecular-plated," i.e., electroplated at high voltage from solution in an organic solvent. Over 99% was deposited for each sample, and the residual was measured by evaporation of the solvent and rough counting in a 2π alpha counter.

(3) The electroplated sample was counted in an intermediate geometry counter of accurately known dimensions. Although the sample spread was fairly smooth, the modest lack of uniformity was calibrated by counting each sample when covered with various grids. The counting efficiencies were known to about 0.01%. The number of counts measured on each sample was large enough to make counting errors less than (or at least no larger than) other errors.

(4) Energy analysis with a large solid-state detector allowed determination of the fraction of activity ascribable to ^{238}U (or ^{235}U) with an accuracy of 0.02 to 0.04%.

For each isotope, four samples were analyzed and 11 or 12 samples were alpha-counted. The results were

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$$^{235}\text{U}: T_{1/2} = (7.0381 \pm 0.0048) \times 10^8 \text{ yr} (0.07\%)$$

$$^{238}\text{U}: T_{1/2} = (4.4683 \pm 0.0029) \times 10^9 \text{ yr} (0.07\%)$$

where the errors quoted are statistical, i.e., based upon the observed data scatter. Systematic errors, if present, are felt to be no larger than the statistical errors.

The ^{238}U result is 1% lower than a number of widely accepted previous results. The ^{235}U result is consistent, within their much higher error limits (1.5 to 3.5%), with most previous measurements.

The half-life of ^{236}U is also of interest and suitable studies are underway. A preliminary analysis of measurements made on one sample yields a value of 2.342×10^7 yr with a statistical error of about 0.06%.

H. REMOTE CHEMICAL ANALYSIS BY ALPHA-PARTICLE INTERACTION WITH MATTER (J. H. Patterson, A. L. Turkevich,* and T. E. Economou**)

The number of techniques available for elemental

analysis by remote operation is rather limited. One of the most productive in early lunar probes has proved to be the alpha spectrometer.

Alpha particles are scattered by coulombic repulsion from atomic nuclei, with energy spectra that are dependent on the nuclear masses. They also produce protons with characteristic energy spectra by nuclear reactions with certain elements. A method of chemical analysis based on these energy spectra has been developed in cooperation with groups at The University of Chicago and Jet Propulsion Laboratory. The sources of the alpha particles are capsules containing curium-242, which is prepared here by neutron irradiation of americium-241 in a reactor. This method was used on three NASA Surveyor missions to analyze surface material on the moon. The method and instrument are now being adapted to the requirements of the NASA Viking missions that are expected to soft-land on Mars in 1975.

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III. NUCLEAR CHEMISTRY*

In a trivial sense there is a contradiction of terms buried in the phrase nuclear chemistry, since chemical processes, by definition, leave the nucleus essentially intact. Nuclear processes, on the other hand, are accompanied by many interesting chemical changes, and nuclear chemistry is of course concerned with these. At Argonne, the Chemistry Division deals with two broad regions of chemical phenomena under the nuclear-chemistry heading: those concerned with nuclear fission and those involving high-energy initiating bombardment. In this chapter we have also included a number of miscellaneous reports on projects which seem most closely related to the primary program discussed as nuclear chemistry.

A. RADIOCHEMICAL AND PHYSICAL STUDIES OF NUCLEAR FISSION

The ANL nuclear-chemistry research program concentrates heavily on studies of nuclear fission utilizing experimental methods both radiochemical and physical in nature. In the radiochemical method, the fission yield (number of atoms per hundred fissions) of each fission product (the new atom formed by the splitting of the fissioning atom) is determined by subsequent chemical separation of the element of interest followed by quantitative measurements of the beta and/or gamma radioactivity of its various isotopes to give the numbers of atoms as a function of fission-product mass (secondary mass after neutron emission) and atomic number (nuclear charge). Such detailed studies of fission yields contribute greatly to our knowledge of the systematics of the distribution of nuclear charge and mass in the fission process. In the physical method, the fission-product mass and kinetic-energy distributions are determined by simultaneous measurement with solid-state detectors (at the instant of fission) of the kinetic energies of the two fission-product atoms in flight (fission fragments) formed in each fission event. The fission-fragment masses (primary mass before neutron emission) are obtained from the measured kinetic energies through the basic physical laws of conservation of mass and linear momentum. In more complex "multiparameter" experiments, other quantities associated with de-excitation of the highly excited primary fragments may also be measured simultaneously, such as the numbers and energies of emitted neutrons and gamma rays (providing information on fragment nuclear-energy levels and on the deexcitation process) and energies of K X rays (giving fragment atomic-number identification and hence the distribution of nuclear charge). The usefulness of the systematics based on such fission data ranges, for example, from practical applications in evaluations of reactor operation and performance with various fissile nuclide fuels to cosmological hypotheses on the

formation of certain elements in primordial fission reactions.

From these studies of both induced and spontaneous fission over a large range of available heavy nuclides from ^{227}Th to ^{256}Fm , a systematic pattern for the distribution of fission-product mass and nuclear charge (in low-energy fission) has emerged. The mass distribution is predominantly asymmetric with the average primary mass of the heavier group of products remaining relatively fixed (near a mass of 140) while the average mass of the complementary lighter group varies directly with the mass of the fissioning nucleus. The charge distribution is observed to be such that the lighter product has a slightly higher nuclear-charge density (proton to neutron ratio) and the heavier product a correspondingly lower charge density than that of the fissioning nucleus. Relative yields (by direct formation in fission) of fission-product isomers (nuclei of the same mass and charge but differing slightly in energy level and usually by several units of nuclear spin) indicate that the primary product nuclei have high nuclear-spin values of about 8 units, evidently imparted by the fission process. The physical method of simultaneous fragment kinetic energy and K X-ray energy measurements has been applied in studies of several fissioning systems with mass and charge distribution results in good agreement with those obtained radiochemically. The following discussion gives some highlights of fission studies completed during 1971.

1. Spontaneous Fission of ^{244}Cm , ^{248}Cm , and ^{256}Fm (K. F. Flynn, R. G. Clark,** K. L. Wolf,† J. P. Unik, and L. E. Glendenin)

The distribution of mass in the spontaneous fission of ^{244}Cm has been determined by a combination of radiochemical and mass-spectrometric†† measurements of the fission-product yields (Table III.1). The observed mass-yield curve (Fig. III.1) is asymmetric (typical for low-energy fission), with light- and heavy-group peaks at average masses of 103 and 139, and with a large asymmetric yield to symmetric yield (peak-to-valley) ratio of >5700 .

In a concerted effort (in collaboration with members of the Heavy Element Group†) employing both radiochemical and physical methods, the spontaneous fission of 2.6-hr ^{256}Fm has been investigated. The intensive study of ^{256}Fm at this time was motivated by recent reports of physical studies of the mass distributions in spontaneous fission [1,2] and in thermal-neutron-induced fission [2] of ^{257}Fm indicating a marked departure from the asymmetric mass distribution typical of low-energy fission toward mass

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††Yields of the fission-produced Kr and Xe isotopes were measured mass spectrometrically in collaboration with O. K. Manuel and B. Srinivasan, University of Missouri, Rolla, Missouri.

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*Chapter edited by: L. E. Glendenin, E. P. Steinberg, and J. P. Unik.

symmetry. The ^{256}Fm sources were prepared by irradiation of ^{253}Es targets with 40-MeV ^4He ions at the ANL cyclotron to produce the 1.25-hr ^{256}Md parent which was then chemically separated and rigorously decontaminated. After an overnight period for growth of the daughter ^{256}Fm and subsequent decay by spontaneous fission, the fission products were separated from the source and prepared for counting. Fission yields were obtained for 28 fission products (Table III.2) based on initial beta activities ranging from 1 to 100 counts per min (measured in calibrated, low-background beta counting equipment). The observed mass-yield distribution (Fig. III.2) is definitely asymmetric, with average masses of 112 and 141 for the light- and heavy-group peaks as expected from extrapolation of the trends observed in lighter fissioning systems, but with a peak-to-valley ratio of only about 12. This enhancement of the probability of fission in the region of mass symmetry is clearly seen in Fig. III.2 by comparison with the mass distribution for spontaneous fission of ^{252}Cf .

The physical method based on fragment-kinetic-energy measurements was also applied to spontaneous fission of ^{256}Fm and ^{248}Cm . The resulting mass distribution for ^{256}Fm (shown in comparison with ^{248}Cm and ^{252}Cf in Fig. III.3) is asymmetric but enhanced in the yield of symmetrical fission, in agreement with the radiochemical results. Comparison of the mass distributions for spontaneous fission of ^{252}Cf , ^{256}Fm , and ^{257}Fm [1] and neutron-induced fission of ^{257}Fm [2], shown in Fig. III.4, clearly indicates the trend toward mass symmetry with increasing charge and mass of the fissioning nucleus. The abrupt transition to symmetrical fission for ^{257}Fm (n,f) is thought to be the result of the additional 5 MeV of neutron-binding energy brought into the fissioning system, raising it above the second fission barrier and thus permitting symmetric distortion of the nucleus. For fermium ($Z = 100$) this barrier is apparently just above the ground state, and for $Z = 102$ it is expected to be below the ground state.

Results obtained in the present work for the total

TABLE III.1. Fission Yields for Spontaneous Fission of ^{254}Cm

Fission Product	Fission Yield (%)	Fission Product	Fission Yield (%)
^{117}As	0.0025 ± 0.0009	^{127}Sb	0.20 ± 0.02
^{118}Br	0.116 ± 0.012	^{128}Sb	0.74 ± 0.07
^{119}Kr	0.116 ± 0.012^a	^{129}mTe	0.47 ± 0.05^d
^{120}Kr	0.166 ± 0.017^a	^{131}I	3.15 ± 0.32
^{121}Kr	0.307 ± 0.031^a	^{131}Xe	3.03 ± 0.15
^{122}Kr	0.289 ± 0.029^a	^{132}Te	4.27 ± 0.22
^{123}Rb	0.00185 ± 0.0004^c	^{132}Xe	4.27 ± 0.22^b
^{124}Sr	0.716 ± 0.036	^{133}I	7.45 ± 1.50
^{125}Sr	0.808 ± 0.081	^{133}Xe	5.78 ± 0.29^b
^{126}Sr	0.825 ± 0.083	^{134}Xe	6.94 ± 0.35^b
^{127}Zr	1.63 ± 0.16	^{135}I	5.48 ± 1.10
^{128}Zr	3.04 ± 0.30	^{135}Xe	7.50 ± 0.38^b
^{129}Mo	3.75 ± 0.20	^{136}Xe	7.59 ± 0.38^b
^{130}Ru	6.94 ± 0.70	^{136}Cs	0.13 ± 0.02^c
^{131}Ru	9.25 ± 0.93	^{137}Cs	8.14 ± 0.81
^{132}Ru	7.40 ± 0.74	^{138}Ba	7.16 ± 0.72
^{133}Ru	5.02 ± 0.50	^{140}Ba	6.04 ± 0.32
^{134}Ag	2.87 ± 0.14	^{141}Ce	5.79 ± 0.29
^{135}Pd	2.03 ± 0.20	^{142}Ce	3.90 ± 0.20
^{136}Ag	0.79 ± 0.08^d	^{144}Ce	4.04 ± 0.40
^{137}Cd	0.233 ± 0.012^d	^{141}Nd	1.44 ± 0.29
^{138}Cd	0.025 ± 0.002^d	^{143}Nd	1.54 ± 0.15
115 Total Chain	0.258 ± 0.013	^{145}Pm	1.66 ± 0.17
^{111}Sb	$<0.0012^a$	^{151}Pm	0.70 ± 0.07
121 Total Chain	$<0.0014^a$	^{152}Sm	0.52 ± 0.05
^{115}Sb	0.0067 ± 0.0013^d	^{154}Sm	0.73 ± 0.03
125 Total Chain	0.0168 ± 0.0029^e	^{154}Eu	0.19 ± 0.02

^aKr yields normalized at mass 83 to 0.116% (^{118}Br).

^bXe yields normalized at mass 132 to 4.27% (^{132}Te).

^cIndependent yield.

^dIsomer yield.

^eTotal chain yield determined by using the isomer ratio from ^{235}U (n,f).

Fig. III.1. Mass-Yield Curve for Spontaneous Fission of ^{244}Cm Compared with That for ^{252}Cf ANL Neg. No. 121-8246.

TABLE III.2. Fission Yields for Spontaneous Fission of ^{256}Fm

Fission Product	Number of Determinations	Fission Yield (%)	Fission Product	Number of Determinations	Fission Yield (%)
^{91}Sr	3	0.24 ± 0.03	^{131}I	1	2.6 ± 0.5
^{97}Zr	1	0.75 ± 0.15	^{132}Te	3	3.9 ± 0.5
^{103}Ru	2	3.1 ± 0.4	^{133}I	1	3.9 ± 0.8
^{107}Pd	1	3.6 ± 1.0	^{134}I	1	5.4 ± 1.0
^{111}Ag	4	5.4 ± 0.4	^{139}Ba	2	6.2 ± 0.8
^{113}Ag	4	4.7 ± 0.6	^{140}Ba	2	6.0 ± 0.5
$^{112}\text{Ag} (5.3\text{m})$	4	4.0 ± 0.3^b	^{141}La	1	7.1 ± 1.4
^{115}Cd	2	5.6 ± 0.5	^{143}Ce	3	6.1 ± 0.5
$^{115}\text{Total Chain}$		6.0 ± 0.6^b	^{145}Pr	1	5.2 ± 1.0
^{116}Cd	1	5.7 ± 1.0	^{148}Pm	3	2.7 ± 0.4
^{121}Sn	2	2.3 ± 0.2	^{151}Pm	2	2.2 ± 0.3
$^{121}\text{Total Chain}$		2.7 ± 0.3^b	^{153}Sm	1	1.4 ± 0.3
^{123}Sn	2	0.6 ± 0.2	^{154}Sm	1	0.7 ± 0.2
$^{125}\text{Total Chain}$		1.5 ± 0.5^b	^{157}Eu	2	0.53 ± 0.07
^{127}Sb	1	0.44 ± 0.08	^{159}Gd	2	0.50 ± 0.07
^{128}Sb	1	0.88 ± 0.15			

^aIsomer yield.

^bTotal chain yield determined by using isomer ratio from $^{235}\text{U}(n,f)$.

Fig. III.2. Mass-Yield Curve for Spontaneous Fission of ^{254}Fm Compared with That for ^{252}Cf . ANL Neg. No. 121-8247 Rev. 1.

Fig. III.3. Mass Distributions for Spontaneous Fission of ^{254}Cm (•), ^{252}Cf (---), and ^{254}Fm (•). ANL Neg. No. 121-8070.

Fig. III.4. Mass Distributions for Spontaneous Fission of ^{252}Cf , ^{254}Fm , and ^{256}Fm and Thermal-neutron-induced Fission of ^{257}Fm . ANL Neg. No. 121-8396.

average fragment-kinetic-energy release $\bar{E}_k$ in spontaneous fission of ^{248}Cm , ^{252}Cf , and ^{256}Fm are compared in Fig III 5 with the recommended values for neutron-induced fission [3] and some earlier data (of lesser accuracy) for spontaneous fission [4] by plotting $\bar{E}_k$ as a function of the coulombic repulsion parameter $Z^2/A^{1/3}$, where Z and A represent the nuclear charge and mass of the fissioning system. It is seen that $\bar{E}_k$ for spontaneous fission of ^{252}Cf and ^{256}Fm is about 5 MeV lower than the extrapolated curve for neutron-induced fission. This unexpected difference will be investigated further by measurements of $\bar{E}_k$ for spontaneous fission of ^{240}Pu , ^{242}Pu , and ^{244}Pu and thermal-neutron-induced fission of ^{235}Cm and ^{249}Cf .

2 The Distribution of Angular Momentum in Fission

(D C Aumann* and J E Gindler)

The role of angular momentum in the fission process has been examined by measuring the isomeric ratios of the fission products ^{111}Pd and ^{134}Cs formed in the $^{235}\text{U}(^4\text{He},f)$, $^{236}\text{U}(^3\text{He},f)$, and $^{237}\text{Np}(^2\text{H},f)$ reactions. In each of these reactions the compound nucleus formed is ^{239}Pu . The root-mean-square angular momentum $\sqrt{J^2}$ of the compound nucleus in each of the reactions is shown as a function of excitation energy E_x in Fig III 6. Values of $\sqrt{J^2}$ were calculated with the normalized-spin-distribution computer code of Hafner *et al* [5]. The transmission coefficients necessary for this code were computed [6] using optical-model parameters deduced from ^3He transfer reac-

Fig III 5 Comparison of the Total Average Fragment Kinetic Energy ($\bar{E}_k$) for Spontaneous Fission with That for Thermal-neutron-induced Fission. ANL Neg No 121-9181

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Fig III 6 Calculated Root-mean-square Angular Momentum of the Compound ^{239}Pu Nucleus as a Function of Excitation Energy for the Indicated Nuclear Reactions. ANL Neg No 121-8467

tions [7] and from total reaction cross sections [8,9]. The occurrence of direct interactions, especially in the $^{236}\text{U} + ^3\text{He}$ and $^{237}\text{Np} + ^2\text{H}$ reactions, causes effective angular momentum and excitation energy to be less than the calculated values.

The independent-yield isomeric ratio of fission products has been used by Warhanek and Vandenbosch [10] to deduce the root-mean-square angular momentum $\sqrt{J^2}$ of the initial spin distribution of fission fragments. Since the angular momentum of a nuclear reaction is conserved, a correlation between $\sqrt{J^2}$ and $\sqrt{J_f^2}$ or the independent-yield isomeric ratio of fission products is suggested.

In Fig III 7, the measured isomeric ratios $\sigma_m/(\sigma_m + \sigma_g)$ for ^{111}Pd and ^{134}Cs are given as open symbols. The nuclear spins of the metastable and ground states are, respectively, 11/2 and 3/2 for ^{111}Pd and 8 and 4 for ^{134}Cs . The measured isomeric ratios are for cumulative yields of ^{111}Pd and independent yields of ^{134}Cs . The former have been converted into independent-yield isomeric ratios by applying the ECD-G-I method of Wogman *et al* [11]. In this method, charge division is assumed to occur by equal charge displacement (ECD), masses are deduced from Green's (G) mass formula [12], and neutrons are assumed (I) to be emitted by the fission fragments in proportion to their masses. These calculated independent-yield isomeric ratios are given as solid symbols.

Fig. III.7. The ^{134}Cs and ^{111}Pd Isomeric Ratios $\sigma_m/(\sigma_m + \sigma_g)$ Determined as a Function of Excitation Energy for the Indicated Nuclear Reactions. The solid curves represent two-parameter least-squares fits to the data. ANL Neg. No. 121-8466.

and at one-half their values in Fig. III.7.

From the information presented in Fig. III.6 and III.7, no distinct correlation is observed between $\sqrt{I_f^2}$ and the independent-yield isomeric ratios as a function of E_x . At those excitation energies where ^{239}Pu can be formed in more than one nuclear reaction, there is no difference in the measured isomeric ratios within the experimental uncertainties of $\pm 15\%$. These results do not imply a violation of the principle of conservation of angular momentum since the intrinsic angular momentum of the complementary fission fragment and the orbital angular momentum between fragments are not accounted for in this experiment.

Saha and Yaffe [13] have extended the method of Warhanek and Vandenbosch [10] to higher excitation energies where multiple-chance fission becomes an important factor in the analysis of isomeric ratios. Their method has been applied to the data depicted in Fig. III.7 to give values of $\sqrt{I_f^2}$. For ^{134}Cs these values were found to vary between 12 and 20, and for ^{111}Pd , between 3 and 6. Depending on the accuracy of the analysis, these results indicate (1) that considerable angular momentum is generated in the fission process since the values of $\sqrt{I_f^2}$ deduced from the ^{134}Cs isomeric ratios are as great or greater than

$\sqrt{I_f^2}$ and (2) asymmetric fission fragments represented by ^{134}Cs are generated with greater angular momentum than are the more symmetric fragments represented by ^{111}Pd . These observations are in qualitative agreement with the results calculated by Hoffman [14] based on a model in which the angular momentum of the fragments is initiated in them by electrostatic forces acting through an average, nonsymmetric distortion which persists for 10^{-21} sec.

3. K X-ray Emission and the Distribution of Nuclear Charge and Mass in Fission (W. Reisdorf,* J. P. Unik, H. C. Griffin,** and L. E. Glendenin)

One of the most fundamental questions regarding the nuclear-fission process is the manner in which the mass and charge of the initial fissioning nucleus are distributed between the two resultant fission fragments. Much of the information that is currently available has been obtained indirectly from the results of radiochemical studies in which the yields of fission products (formed as a result of neutron and generally beta-particle emission from the primary fission fragments) are measured. Information regarding the fission process itself is generally difficult to obtain from these studies because of the experimental difficulties associated with the yield measurements of specific products and the uncertainties associated with the transformation of these final product yield distributions to the initial fragment distributions. In order to overcome these difficulties, an entirely physical method has been developed for the simultaneous determination of the masses and nuclear charges of the fragments. This method, referred to as the "K X-ray method," is based on the simultaneous measurement of the kinetic energies of the two fission fragments and the energies of the K X rays emitted in the first nanosecond after fission by the excited fragments. Through the laws of conservation of mass and linear momentum, the masses of the fragments can be determined from the measured kinetic energies with an accuracy of ± 0.2 atomic mass unit. The energies of the K X rays are characteristic for each element and thus identify the nuclear charges of the fragments. The K X-ray method, in its present state of development, has many advantages over existing methods used to study mass and charge distribution in nuclear fission, the principle advantage being the decreased time generally required to obtain complete mass and charge distributions for a given fissioning system. Also, the K X-ray method can inherently yield more information concerning the fission process itself. In addition to mass and charge distributions, information is also obtained on 1) the correlations between the masses of the fragments and their kinetic energies and 2) how the mass and charge

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distributions are dependent on the kinetic energies and internal excitation energies of the fragments

To date, the K X-ray method has been applied to the study of four different fissioning systems the thermal neutron-induced fission of ^{233}U , ^{235}U , and ^{239}Pu and the spontaneous fission of ^{252}Cf . As an example of a typical fragment mass-yield distribution, the preneutron-emission mass distribution obtained for $^{235}\text{U}(n,f)$ is shown in Fig III 8 as a dashed curve. Using the currently available data on neutron-emission probability for $^{235}\text{U}(n,f)$ as a function of fragment mass [$\nu(M)$ shown as points in Fig III 8] the preneutron mass distribution can be transformed to the postneutron mass distribution. Comparison of this transformed mass distribution (solid curve) in Fig III 8 with that obtained radiochemically (open circles) shows good agreement and demonstrates the accuracy with which the pre- and postneutron-emission fragment masses and yields can presently be measured by this method. The accuracy which can be obtained for these fragment mass and yield measurements will be further improved with the future availability of more accurate energy-calibration methods for the fission-fragment detectors and more accurate neutron-emission probability data.

For each fissioning system the most probable nuclear charge associated with each fragment of a given mass has been determined with an estimated accuracy of better than ± 0.15 nuclear charge unit. The charge-division results obtained for each fissioning system are shown in

Fig III 9–III 12, as linear functions with associated error bands (shaded areas). For comparison, the results obtained from radiochemical studies, as summarized in Refs 15–17, are also given for each fissioning system as individual data points with associated error flags. In order to obtain a more detailed and expanded graphical presentation of the charge-division results, the ordinates in Figs III 9–III 12, given as the parameter Δ , represent the difference between the measured most probable nuclear charge (Z_p) and that calculated on the basis that the charge density of the fragments (ratio of protons to nucleons) is the same as that of the fissioning nucleus. The subscripts L and H refer to the light and heavy mass fragments, respectively. From mass and charge conservation, the sum of the masses of the light and heavy fragments ($A_L + A_H$) is equal to that of the fissioning nucleus and $\Delta_L = -\Delta_H$. Therefore, for convenience the left ordinate and lower abscissa of each figure are for the heavy fragments and the right ordinate and upper abscissa can be used for the complementary light fragments. As can be seen from Figs III 9–III 12, the charge division for these fissioning systems is such that the light fragment has approximately 0.5 proton more and the heavy fragment approximately 0.5 proton less than expected on the basis of a fragment charge density equal to that of the fissioning nucleus ($\Delta = 0$). From Figs III 9–III 12, the agreement between the charge-division results of the K X ray method and those obtained radiochemically is seen to be quite good, generally, within 0.2 nuclear charge unit.

Fig III 8 $^{235}\text{U}(n,f)$ Mass Distributions ANL Neg
No 121 6266 Rev 1

Fig. III.9
Charge-division Results for $^{233}\text{U}(n,f)$.
ANL Neg. No. 121-8500.

Fig. III.10
Charge-division Results for $^{235}\text{U}(n,f)$.
ANL Neg. No. 121-8500.

Fig. III.11
Charge-division Results for $^{239}\text{Pu}(n,f)$.
ANL Neg. No. 121-8500.

Fig. III.12. Charge-division Results for $^{235}\text{U}(sf)$. ANL Neg. No. 121-8500.

Other important information regarding the nature of the fission process has also been obtained from these studies:

(1) The widths of the (Gaussian) charge distributions about the most probable values were found to have an average $\sigma = 0.44 \pm 0.05$ for all four fissioning systems. The value of $\sigma = 0.56 \pm 0.06$ obtained from radiochemical studies of $^{235}\text{U}(n,f)$ is slightly larger primarily due to the additional dispersive effect of neutron emission from the fragments.

(2) The charge division for these four fissioning systems was found to be, within an experimental error of 0.2 charge unit, independent of the proton pairing effect (the charge division functions for fission leading to formation of fragments with odd or even proton numbers is the same) and the excitation energies of the fragments.

(3) The fine structure in preneutron-emission mass distributions for fission taking place at low excitation energies (for example the peaks occurring at masses of approximately 92, 96, 102, 134, 140, and 144 in the dashed curve of Fig. III.3) has been shown experimentally to be due to a preferential formation of fragments with even (as opposed to odd numbers of protons in the fission process as previously suggested by Thomas and Vandenbosch [18]).

(4) The systematic behavior of K X-ray emission from highly excited fission fragments has been studied in detail as a function of fragment mass and nuclear charge for all four fissioning systems.

B. HIGH-ENERGY NUCLEAR CHEMISTRY

The interaction of high-energy protons with complex

nuclei produces a broad spectrum of reaction products resulting from a number of reaction mechanisms. The efforts of the High Energy Nuclear Chemistry group have been directed towards the elucidation of these mechanisms utilizing radiochemical and online fragment-counting techniques. Argonne's Zero Gradient Synchrotron has been the main source of energetic protons, providing beams up to 12 GeV, but other accelerators are also used in the primary and peripheral studies.

1. Secondary Nuclear Reactions of 11.5-GeV Protons on Uranium: A Search for the Production of Transcurium Actinide Elements (R. A. Esterlund,* A. F. Stehney,** and E. P. Steinberg)

One characteristic of the interaction of high-energy protons with complex nuclei is the emission from the target nucleus of particles and fragments with sufficient energy to induce reactions with other nuclei in the target matrix. Such particles are commonly called "secondaries," and reactions induced by them are known as "secondary nuclear reactions." Most work on such reactions has dealt with the production of transtarget species by secondary fragments with $Z < 4$; however, it is well known that large nuclei (^{24}Na , e.g.) are emitted with rather high kinetic

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energy in appreciable yields in high-energy bombardments [19]. Cumming and co-workers [20] determined the energy spectrum of ^{24}Na produced in the bombardment of bismuth with 2.9-GeV protons and observed kinetic energies as high as 120 MeV, significantly above the coulomb barrier for ^{24}Na nuclei incident on bismuth.

Poskanzer, Butler, and Hyde [21], using a counter-telescope technique, identified a number of isotopes of C, O, N, etc., emitted in the interaction of high-energy protons with uranium. Considerable numbers of these had energies in excess of the coulomb barrier for reaction with uranium and several species had neutron-to-proton ratios differing considerably from those of stable particles available as projectiles in heavy-ion accelerators. Thus, the direct observation of secondary products produced by such fragments might lead to the discovery of nuclides not readily produced by standard heavy-ion-bombardment techniques.

In the present work, we attempted to find direct evidence that heavy secondaries ($Z > 4$) reacted with uranium target nuclei and to evaluate the production cross section. Bombardments were carried out with the 11.5-GeV internal proton beam of the ZGS, and a search was made for transcurium elements formed as secondary products. The separation and identification procedures were directed mainly toward finding well-known and easily identifiable nuclides. Some of these (^{256}Fm , e.g.) fission spontaneously and can be detected with high sensitivity. A conceivable reaction channel for production of ^{256}Fm is:

where the notation indicates the primary reaction of a proton with ^{238}U and ejection of an energetic ^{20}O fragment which then reacts with the target matrix to produce ^{256}Fm .

Direct neutron counting of bombarded targets was carried out to detect any prompt, spontaneous fission neutrons after the decay of the well-known delayed-neutron periods (mainly, the 22- and 56-sec half-lives). Other targets were chemically separated to provide samples of actinide elements of $Z > 96$. Gamma spectra were obtained with a 5-cm³ Ge(Li) detector and alphas and fissions determined simultaneously using a Si surface-barrier detector.

No positive identification of known transcurium nuclides was possible, and upper limits were set for the production of 3.24-hr ^{254}Fm at 1.8×10^{-8} barn and 2.7-hr ^{256}Fm at 3.6×10^{-10} barn. It is obvious that much higher bombardment intensities and thicker targets will be required to produce a sufficient number of atoms of such species for observation.

2. Semiconductor Detector Studies of the Interaction of 11.5-GeV Protons with Uranium (M. J. Fluss,* S. B. Kaufman, E. P. Steinberg, and B. D. Wilkins)

The nuclear reactions induced in a target of high nuclear charge such as uranium are very complex and encompass the complete spectrum from the "simplest" (involving only a few nucleons and representing only small energy deposition in peripheral or surface collisions such as (p,2n) or (p,pn) reactions) to the most complex (involving deep spallation or cooperative phenomena, such as nuclear fission, with a broad spread in deposition energies). A variety of techniques have been applied to the understanding of the mechanisms of such reactions, each supplying answers to different aspects of the overall picture.

Radiochemical techniques give information on the mass and charge distributions of individual products and integral or differential energy and angular distributions. However, they do not provide data on event-by-event correlations of the products, i.e., on which products were formed in the same event, such as the partners in a binary or ternary fission. Track detectors (emulsions or dielectrics such as mica or Lexan) register correlated events as track pairs or multiprong stars. Features such as the cross sections for various types of events, track lengths, and angular correlations may be obtained with such detectors. Semiconductor detectors may be used to yield information on the energy, velocity, mass, and angular distributions of correlated as well as uncorrelated events and provide a powerful tool for the study of reaction mechanisms.

In the present investigation, semiconductor detectors of two types were utilized, one to provide an energy and time signal for a fragment emitted in the reaction (from which the velocity and mass could be calculated), the other a position-sensitive detector to provide an energy and position signal of any coincident event (from which angular correlations could be obtained). This experiment was carried out in a 50-cm-dia scatter chamber utilizing the external, 11.5-GeV proton beam of the ZGS. A similar experiment has been done at Brookhaven National Laboratory with the 2.9-GeV proton beam of the Cosmotron [22]. A position-sensitive detector was not employed in the latter experiment, but angular correlations were obtained (with somewhat poorer resolution) by positioning four semiconductor detectors at different angles. Moreover, the nature of the BNL experiment was such that only correlated events were recorded.

A schematic diagram of the experimental arrangement is shown in Fig. III.13, and a block diagram of the data-recording electronics is shown in Fig. III.14. The target was

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Fig. III.13. Schematic Diagram of the Experimental Arrangement. ANL Neg. No. 121-2836.

$\sim 80 \mu\text{g}/\text{cm}^2$ UF_4 vacuum deposited on an $\sim 30 \mu\text{g}/\text{cm}^2$ carbon film.

The energy and velocity data obtained from the time-of-flight arm (E_{90° detector) permit the calculation of the fragment mass. The time characteristics of pulses from the position detector (E_{pos} signal) are not amenable to an accurate velocity determination for the coincident events. However, an iterative calculation based on momentum conservation was carried out to give an approximate mass for this complementary fragment. The average total mass obtained from this calculation agrees very well with that obtained by taking twice the average measured mass for coincident events from the time-of-flight arm.

A comparison of some of the data on correlated events from the present experiment with those of the BNL experiment is given in Table III.3. (θ and ϕ are the in-plane and out-of-plane angles, respectively.)

The data indicate that the average fission fragment mass is about 7 amu less at 11.5 GeV than at 2.9 GeV. This represents about a 70-MeV greater deposition energy, on the average, for the 11.5-GeV reaction. Only about 2-MeV

Fig. III.14. Block Diagram of the Electronics. ANL Neg. No. 121-2837.

TABLE III.3. Comparison of 11.5-GeV (ANL) and 2.9-GeV (BNL) Proton Fission of Uranium

θ :	80°		90°		100°		Measured Quantity
	BNL	ANL	BNL	ANL	BNL	ANL	
ϕ							
0°	106.4	99.7	110.5	103.5	103.2	97.4	Ave. Fragment Mass
10°	99.2	-	110.2	100.5	-	-	
0°	154.2	150.9	162.0	159.7	148.1	151.1	Ave. Total Kinetic Energy
10°	149.1	-	153.5	153.0	-	-	

difference in the average total kinetic energy is observed. Moreover, the average in-plane angle for the BNL experiment was 89° , whereas that for the present experiment was 88° , showing only a slightly greater average forward-momentum transfer in the latter case. The ratio of asymmetric to symmetric binary fissions is also nearly the same in the two experiments.

These observations suggest that only a small fraction of the difference in bombarding energy between 2.9 and 11.5 GeV is reflected in differences in the binary fission events detected under the conditions of these experiments. If the cascade deposition energy at 11.5 GeV is much greater than at 2.9 GeV, it must be contributing to other processes.

An interesting feature of the present experiment is provided by a comparison of the singles (uncorrelated) and coincidence-gated (correlated) momentum spectra for various masses. Some of these are shown in Fig. III.15. The low momentum components (which are also observed in radiochemical experiments [23]) appear to be predominantly associated with processes not detected as binary fissions. The proportion of this component also appears to increase with decreasing mass.

Various correlations of the extensive data on masses, energies, velocities, and in-plane and out-of-plane angles are possible. However, many of these do not lend themselves to simple interpretation of a reaction mechanism. Further experiments and calculations are being carried out to help

clarify the nature of the interactions and reconcile them with the results of radiochemical and track-detector studies.

3. Excitation Function for the $^{209}\text{Bi}(p,2p5n)^{203}\text{Pb}$ Reaction from 0.15 to 11.5 GeV (A. H. Boos* and E. P. Steinberg)

Previous information on the excitation function for the spallation reaction $^{209}\text{Bi}(p,2p5n)^{203}\text{Pb}$ shows an indication of structure in the region of 500-MeV bombarding energy (Fig. III.16). A sudden increase in cross section of nearly a factor of ten in this energy region is difficult to understand. The present investigation was undertaken to check the cross section in the 100–500-MeV region and extend the known data to 11.5 GeV.

Bombardments were carried out at the Fermi Synchrocyclotron of The University of Chicago at proton energies of 150, 200, 300, and 450 MeV and at the Argonne ZGS at 11.5 GeV. Target stacks consisting of 1-mil Bi and 1-mil Al catcher and monitor foils were bombarded for about 10 min. Lead was chemically isolated from the target foils and the 279 keV γ ray of ^{203}Pb determined with a calibrated 3 X 3-in. NaI detector. Corrections were made for the growth of ^{203}Pb from ^{203}Bi produced in the $^{209}\text{Bi}(p,p6n)^{203}\text{Bi}$ reaction by timed separations of lead from bismuth. Replicate determinations were made at each bombarding energy. The proton intensity was determined from the $^{27}\text{Al}(p,3pn)^{24}\text{Na}$ reaction using the cross sections

Fig. III.15. Momentum Distributions for Selected Mass Ranges in High-energy Proton Fission of U. ANL Neg. No. 121-8454.

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Fig. III.16. Excitation Function for the Reaction $^{209}\text{Bi}(p,2p5n)^{193}\text{Pb}$.
ANL Neg. No. 121-8453.

given by Cumming [24]. The results are summarized in Table III.4.

These data show no indication of structure in the region of 0.45 GeV. A few more determinations are planned at bombarding energies of 0.66, 3.0, and 6.0 GeV to complete the excitation function and to establish whether the earlier indication of structure was simply in error.

4. The Response of Surface-barrier Detectors to Heavy Ions and Fission Fragments (M. J. Fluss,* C. E. Gross, S. B. Kaufman, E. P. Steinberg, and B. D. Wilkins)

Surface-barrier semiconductor detectors have been extensively used to detect and measure the energy of heavy ions and fission fragments. Their use is complicated by the fact that their response to heavy ions is different than to alpha particles, which are usually used to calibrate the

detectors. The pulse height produced by a heavy ion is smaller than that produced by an alpha particle of the same energy; if the alpha-particle calibration is used for the heavy ion, the energy is underestimated. We will use the term "pulse-height defect" (PHD) to mean the difference between the true energy of an ion and its apparent energy as given by the alpha-particle calibration. An example of this effect is shown in Fig. III.17 for a number of heavy ions; the magnitude of an ion's PHD increases with increasing energy and is larger, the heavier the ion.

As an outgrowth of the experiments on high-energy fission we were led to an examination of this effect. The response of a number of surface-barrier detectors to heavy ions was studied, and a simple model was developed which accounts for the data fairly well. A variety of heavy ions of known energy were produced by the elastic scattering of ^{16}O , ^{32}S , and ^{127}I beams on metallic targets. The experiments were carried out at the Tandem Van de Graaff accelerators at ANL and the University of Rochester.

All of the detectors with resistivity values in the range 300–450 ohm-cm, designed for use with heavy ions, showed nearly identical response characteristics. The PHD of a heavy ion in such a detector can be described as the sum of a simple energy loss in the gold surface layer, a calculated nuclear-stopping defect, and a defect due to recombination of electron-hole pairs in the plasma created by a heavily-ionizing particle. The latter defect appears to occur in a thin surface layer of the detector and is proportional to the difference between the electronic

TABLE III.4. $^{209}\text{Bi}(p,2p5n)^{193}\text{Pb}$
Cross Sections

Proton Energy (GeV)	σ (mb)
0.15	16.5 ± 1.7
0.20	10.9 ± 0.6
0.30	13.2 ± 1.0
0.45	9.5 ± 0.5
11.45	8.4 ± 0.5

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Fig. III.17. Energy of Ion Incident on Detector (E_i) as a Function of Pulse Height for Various Heavy Ions. The line through the He data is a least-squares fit. The other lines are meant only to guide the eye. ANL Neg. No. 121-7317.

stopping power of the ion in silicon and a "critical" value. The latter is a constant for all ions, and represents the electronic stopping power below which no recombination occurs. Detectors with higher resistivity values than these showed larger recombination defects.

When the PHD values are expressed in dimensionless energy units as defined by Lindhard *et al.* [25], it is found that data for all ions in a given detector lie close to a "universal" curve as a function of the ion energy, expressed in the same units. Figure III.18 shows the data in this form, along with separate scales in MeV for Ni, Ag, Au, and U. We are now testing the applicability of this curve to the calibration of detectors for heavy ions.

A number of problems important for a more fundamental understanding of the response of semiconductor detectors to heavy ions are being investigated by a Ph.D. thesis student from the University of Missouri at Rolla. These include studies of the bias dependency of the PHD and the effect of incident angle of the heavy ions.

5. Simple Nuclear Reactions at High Energies (P. A. Benioff and L. W. Person)

For some years we have been carrying out theoretical studies of (p,pn) and (p,2p) reactions at high bombarding energies (300 MeV and up). At such energies one makes the assumption, called the Distorted Wave Impulse Approximation, or DWIA, that the main contributing mechanism is

that in which the incident proton enters the target nucleus, strikes a bound nucleon and the two nucleons exit from the nucleus. The only other interactions allowed are those in which the incident and exit nucleus can scatter elastically off the target and product nucleus, respectively. This elastic scattering "distorts" the wavefunctions of the incident and exit nucleons.

One advantage of studying these reactions in the energy region where the DWIA is good, is that measurements of the differential reaction cross sections should give one information about the wavefunction of the struck nucleon. In particular, the momentum distribution of the recoiling product nucleus should give direct information about the momentum distribution of the target nucleon, provided one can unfold the effects of the distortion.

In order to study this possibility, calculations [26] were made of the differential recoil cross sections $d\sigma/d\Omega_k$ and $d^2\sigma/d\Omega_k dT_k$ for the $^{12}\text{C}(p,pn)^{11}\text{C}$ and $^{58}\text{Ni}(p,pn)^{57}\text{Ni}$ reactions at 450 MeV using the DWIA. The results showed that $d^2\sigma/d\Omega_k dT_k$, computed as a function of the recoil kinetic energy T_k for fixed recoil scattering angle θ_k , does give information about the radial momentum distribution of the struck neutron in the target nucleus. Since no $d^2\sigma/d\Omega_k dT_k$ experimental data were available, one had to be content with comparing the angular recoil distribution $d\sigma/d\Omega_k$, obtained by integrating $d^2\sigma/d\Omega_k dT_k$ over T_k , with experiment. Such a comparison for the $^{12}\text{C}(p,pn)^{11}\text{C}$ reaction gave good agreement except for $\theta_k > 120^\circ$ where the experimental data [27] decreased faster than the theoretical points.

An interesting effect appeared in the calculations done for target neutrons in the $2p_{3/2}$ shell of ^{58}Ni . This was that for $\theta_k = 90^\circ$, plots of $d^2\sigma/d\Omega_k dT_k$ against T_k showed the nodal structure present in the radial wavefunction, whereas for $\theta_k = 0$ and 180° similar plots showed complete suppression of the second maximum and no nodal structure. (Of course the nodes at $T_k = 0$ and ∞ were present.) The radial wavefunction $R_{nl}(r)$ for $n = 2$ and any l has nodes at $r = 0$, ∞ and at an intermediate value.

For further investigation of this and other effects, these calculations had some limitations. First, all the calculations were made using only the harmonic-oscillator (H.O.) form of the radial wavefunction. Thus the above nodal effect could be due to some peculiarity of the H.O. functions. Second, the form of the distorted wavefunction used widely in the literature was used in the above calculations, even though it is known to be invalid at large distances from the nucleus. This defect is ignored because the main contributions to the relevant matrix elements come from regions inside the nucleus. Since the nodal effects are due to interference between the distorted wavefunction and target nucleon wavefunction, the effect found above could be due to a peculiarity of the form used for the distorted wavefunction.

Finally, there is almost no experimental differential

Fig. 11.15. Pulse-height Defects in LSS Units ($\Delta\epsilon_2$) as a Function of Ion Energy in the Same Units (ϵ_2). The energy loss through the detector window has been subtracted from both quantities. The line represents the nuclear-stopping defect. Energy scales in MeV are also given for Ni, Ag, Au, and U. ANL Neg. No. 121-7318.

nuclear recoil data available. Furthermore, even if data were available, the nodal effect would be very hard to see. The reason is that experimental nuclear-recoil data always include a sum over all target nuclear shells for which a hole state is bound. Thus, large $n = 1$ contributions are mixed into small $n = 2$ contributions which essentially obliterate the $n = 2$ nodal effect.

To remedy these defects calculations were made [28] of $d^3\sigma/d\Omega_1 d\Omega_2 dE_1$ for individual target nuclear shells for the (p,2p) reactions on ^{12}C , ^{16}O , and ^{40}Ca at 460 MeV and were compared with experiment [29]. The DWIA was used along with the more realistic Woods-Saxon radial wavefunction and a more realistic form of the distorted wavefunction.

Comparison of the calculated values of $d^3\sigma/d\Omega_1 d\Omega_2 dE_1$ for the coplanar symmetric reaction (i.e., $\theta_1 = \theta_2$ as the variable, $\phi_2 = \phi_1 = 180^\circ$ and the recoil angle $\theta_k = 0$ or 180°) with experiment gave satisfactory agreement for the $2s^{1/2}$ shell of ^{40}Ca (where the agreement is very good), the $1d^{3/2}$ shell of ^{40}Ca , and the $1p^{3/2}$ shells of ^{16}O and ^{12}C . The agreement was not too good for the $1p^{1/2}$ shell of ^{16}O (the discrepancy here seems to be mainly a normalization effect) and the $1d^{5/2}$ shell of ^{40}Ca (the experimental data are quite poor). There are no adjustable parameters in our calculations to give better theory-experiment comparisons. For the ^{12}C and ^{16}O shells, for which other calculations were available, the above calculations agree with experiment as well as do other calculations reported in the literature.

Calculations were also made using the H.O. wave-

function and the standard form of the distorted wavefunction used in earlier work [26]. In general, the Woods-Saxon results agreed better with experiment than the H.O. results, and the more realistic form of the distorted wavefunction gave better agreement with experiment than did the standard form.

The close agreement between theory and experiment for the $2s^{1/2}$ shell of ^{40}Ca is noteworthy because both theory and experiment showed the strong suppression of the second maximum for the coplanar symmetric ($\theta_k = 0$ or 180°) cross section. Calculations made for the noncoplanar symmetric cross section ($d^3\sigma/d\Omega_1 d\Omega_2 dE_1$ with $\theta_1 = \theta_2$, $\phi_1 = \phi_2$ as the variable, and $\theta_k = 90^\circ$) for the same shell showed a strong second maximum. This gives support to the argument that this effect of the distortion in altering the momentum distribution of the target nucleon is not due to some peculiarity of the particular forms of the distorted and radial wavefunctions used, but is instead a general effect. Unfortunately there are no noncoplanar symmetric cross-section data available, so experimental confirmation or refutation of this difference between $\theta_k = 90^\circ$ and $\theta_k = 0$ or 180° data for $n = 2$ shells will have to wait.

6. Nuclear-chemistry Research Program at the National Accelerator Laboratory (NAL) (G. W. Butler, S. B. Kaufman, E. P. Steinberg, and B. D. Wilkins)

A consortium of high-energy nuclear chemists from several institutions (Argonne, Brookhaven, The University of Chicago, Carnegie-Mellon University, Purdue University,

and SUNY Buffalo) submitted an experimental proposal to NAL during 1970. This proposal outlined an experimental program to study the interactions of high-energy protons with complex nuclei. At the request of J. Sanford (NAL) we prepared a supplemental report to elucidate in more detail our proposal for a nuclear-chemistry research program at NAL. The NAL Program Advisory Committee then approved the nuclear-chemistry proposal, and, subsequently, NAL allocated \$50,000 in fiscal 1971 and another \$50,000 in fiscal 1972 for the purchase of suitable counting equipment for the nuclear-chemistry experiments. NAL Director R. R. Wilson selected the NAL Radiation Physics Group to be responsible for establishing a general-purpose counting laboratory and a nuclear-chemistry laboratory, both of which will be located in the NAL Village, which is approximately one mile from the experimental area. We have worked closely with the NAL Radiation Physics Group in establishing both of these laboratories.

Modern techniques of gamma-ray analysis will be used to establish representative formation cross sections of the broad spectrum of nuclides produced in these high-energy nuclear reactions, and therefore the following counting equipment has been or soon will be purchased by NAL for our experimental program: (1) two high-resolution, high-efficiency, cooled FET, coaxial Ge(Li) gamma-ray detectors; (2) a high-resolution, thin-window, planar, cooled FET high-purity Ge detector for X rays and low-energy gamma rays; (3) a data-acquisition system consisting of two 8192-channel ADC's, a two-parameter multiplexer, a 4096-channel pulse-height analyzer, a 4096-word, 16-bit computer (interfaced to the PHA), and an IBM computer-compatible magnetic tape transport; and (4) sufficient NIM electronic equipment to allow X-ray gamma-ray coincidence experiments. Several NaI(Tl) gamma-ray detectors, some surface-barrier alpha detectors, and a 4096-channel PHA are already part of the NAL Radiation Physics Group's equipment, and it will also be available for use by the nuclear chemists.

Equipment provided by Argonne for this nuclear-chemistry collaborative effort includes a Lucite target box that will be used for the foil-irradiation experiments, and a scintillation counter telescope, which will be used to determine the absolute cross section for the $^{12}\text{C}(p,pn)^{11}\text{C}$ reaction.

Some of the nuclear-chemistry experiments will be done in the diffracted proton beam of the NAL Meson Lab, which is designed for a maximum proton intensity of 10^{10} protons/pulse and a maximum proton energy of 200 GeV. Another series of experiments will be carried out in the NAL Proton Lab, which is designed for a maximum proton intensity of 10^{13} protons/pulse and a maximum beam energy of 500 GeV.

Currently it appears that it will be early 1972 before NAL will have a 200-GeV proton beam suitable for experiments.

C. A STUDY OF SPONTANEOUSLY FISSIONING ISOMERS (K. L. Wolf, J. P. Unik, D. Henderson, and A. Gorski)

For heavy elements a common mode of decay is spontaneous fission, which involves ground-state nuclei that quantum-mechanically tunnel through the fission barrier. Spontaneous-fission half-lives decrease with increasing atomic number from 10^{16} yrs for ^{238}U to approximately three hours for ^{256}Fm , which covers the range of actinides of interest here. It has been observed [30-32] that most actinide nuclei have isomeric states that decay by spontaneous fission with much shorter half-lives than the ground states, ranging from nanoseconds to milliseconds. These fissioning isomers exist at an excitation energy of two to four MeV above the ground state, have low spin, and are unusually stable toward other modes of decay such as gamma-ray emission. These properties of fissioning isomers can be explained if the fission barrier is double-humped, and the local minimum between the two barriers is sufficiently deep that the nucleus can form a metastable state in the minimum. Figure III.19 shows an example of such a fission barrier. Since the isomer has a deformation parameter ϵ of 0.5–0.6 in this model and the stable ground-state deformation is 0.2–0.25, the fissioning isomer is a "shape isomer" of the nucleus, analogous to molecular isomers. (The deformation can be expressed in terms of the ratios of the major axis to the minor axis of an ellipsoid, c/a . The deformation of the ground-state nucleus is approximately $c/a = 1.2$, and the isomer deformation is $c/a = 1.7$.) Gamma emission is hindered because the nucleus must penetrate the barrier on the left before the isomer can decay. Fission proceeds by penetrating the barrier on the right. The fission half-life is much shorter than the half-life of the ground state because the isomer has less barrier to

Fig. III.19. The Nuclear Potential Energy, Relative to the Ground State, vs Deformation toward Fission. Values of the barrier heights and the height of the secondary minimum are from a statistical model analysis of fission data for the nucleus ^{240}Pu , while values of the deformation coordinates for the isomer minimum and the saddle points are from theoretical calculations. ANL Neg. No. 121-8520.

penetrate. This interpretation of fissioning isomers was put on firm theoretical ground by Strutinski [33], who performed barrier calculations by making single-particle corrections to the liquid-drop model of the nucleus.

A number of phenomena observed in low-energy fission have been explained as quantum-mechanical effects arising from penetration of the double-humped fission barrier. Some examples are: 1) the intermediate-resonance structure of cross sections observed in neutron-induced fission [34,35], 2) the broad vibrational resonances found in fission cross sections for (n,f) and (d,pf) reactions [36], and 3) anomalous fission-fragment angular distributions measured for photofission [37]. In order to explain these phenomena quantitatively, detailed properties of the fission barriers need to be measured for many nuclei. Some of these properties are the heights and widths of the fission barriers and the height of the isomer minimum relative to the ground state. These quantities can be determined by making some simplifying assumptions and combining existing data for the ground-state fission half-life and fission threshold measurements with fissioning isomer half-life and cross-section measurements. The fission barrier shown in Fig. III.19 for the nucleus ^{240}Pu was constructed in this way.

The measurement of barrier parameters has another important application which is indirectly related to the possibility that superheavy elements exist. The same kind of calculation as that performed by Strutinski, which was mentioned previously, offers the only predictions about the stability of the superheavy elements. Good agreement of the calculations with experiment in the actinides would allow one to extrapolate the calculations to the mass region of the superheavies with less uncertainty than at present.

Thus, the purpose of the experimental study reported here is not only to discover new fissioning isomers, but also to accurately measure isomer half-lives and cross sections which can be used to help parameterize the potential energy surfaces of many actinides as has been done for ^{240}Pu .

In experiments performed at Argonne several new fissioning isomers have been discovered in the americium, curium, and berkelium isotopes as listed in Table III.5 [38,39]. Half-lives and cross sections are measured with a direct electronic method that allows data collection at a high rate in spite of the very low isomer

TABLE III.5. Fissioning Isomers Discovered at Argonne

Isomer	Half-life (seconds)	Production Reaction
$^{242}_{97}\text{Am}$	$(600 \pm 60) \times 10^{-9}$	$^{244}\text{Pu}(\alpha, p2n)$
$^{244}_{98}\text{Am}$	$(73 \pm 10) \times 10^{-9}$	$^{244}\text{Pu}(\alpha, pn)$
$^{246}_{98}\text{Cm}$	$(13.2 \pm 1.6) \times 10^{-9}$	$^{244}\text{Pu}(\alpha, 3n)$
$^{247}_{99}\text{Bk}$	$(9.5 \pm 2.0) \times 10^{-9}$	$^{241}\text{Am}(\alpha, 3n)$
$^{248}_{99}\text{Bk}$	$(600 \pm 100) \times 10^{-9}$	
$^{249}_{99}\text{Bk}$	$(820 \pm 60) \times 10^{-9}$	$^{243}\text{Am}(\alpha, 3n)$

cross sections ($0.1\text{--}30\text{ }\mu\text{b}$). The 46-MeV alpha-particle beam from the Argonne 60-in. cyclotron has been used for all measurements reported here. The alpha-particle energy is varied by use of degrader foils. Table III.6 shows some of the known isomers that have been studied in this laboratory. Two examples of the excitation functions that have been taken are shown in Fig. III.20. Statistical-model calculations are being performed in order to extract fission-barrier parameters from these data.

Plans for future experiments include a search for fissioning isomers in more berkelium isotopes and in einsteinium isotopes. Also, measurements of the gamma cascade in the isomer potential minimum are in progress.

D. ON THE EXISTENCE OF THE CHEMICALLY BOUND NEUTRON (S. Fried, A. Friedman, and M. Wahlgren)

Because of the great interest generated by the appearance of a paper by Grant and Cobble [40] who reported the delayed emission of neutrons from a cooled (4°K) crystal of LiF containing trapped electrons and which had been exposed to the neutron beam from a Cockcroft-Walton generator, it was decided to attempt to confirm their results.

Other workers in this field attempted to confirm this work but were unable to do so. However, the attempts at confirmation were open to the objection that the experiments did not exactly duplicate conditions used by Grant and Cobble. Specifically, the neutrons in one case were reactor-produced neutrons rather than those formed in the reaction

while another case used cyclotron-produced neutrons. No real effort was made to duplicate the geometry or temperature and thereby the spectrum of the neutrons.

With the cordial cooperation of Professor Cobble we were able to duplicate his conditions very closely. The only substantive difference in our experiment was the neutron-detection technique. We used a ^3He gas proportional counter rather than the ^6LiI scintillation counter used by Grant and Cobble. Our counters were chosen because of their superior characteristics, beta insensitivity, and counting efficiency.

TABLE III.6. Other Shape Isomers Studied at Argonne

Isomer	Half-life (seconds)	Isomer	Half-life (seconds)
$^{232}_{92}\text{U}$	110×10^{-9}	$^{243}_{95}\text{Am}$	14×10^{-3}
$^{235}_{92}\text{U}$	200×10^{-9}	$^{245}_{96}\text{Cm}$	6.5×10^{-6}
$^{238}_{94}\text{Pu}$	8×10^{-6}	$^{247}_{97}\text{Bk}$	1.1×10^{-3}
$^{240}_{96}\text{Pu}$	4×10^{-9}	$^{248}_{98}\text{Cm}$	40×10^{-9}
$^{241}_{97}\text{Am}$	0.9×10^{-3}

Fig. III.20. Isomer Cross Sections as a Function of Alpha-particle Bombarding Energy for the Isomers a) $^{239\text{m}}\text{Pu}$ and b) $^{244\text{m}}\text{Cm}$. ANL Neg. No. 121-8519.

No stored neutrons were found under the conditions of the experiment above those that could be ascribed to background. These background counts were found to be due to photoneutrons and mechanical electrical noise.

In Fig. III.21 it can be seen that the background and sample counting rate are equal within the statistical uncertainties and decay with the same rate.

E. MISCELLANEOUS RADIOACTIVITY STUDIES

A program of radioactivity studies and development of a variety of quantitative counting techniques has been in progress for many years. Counting techniques are utilized particularly in the heavy-element and nuclear programs, but these studies have been applied, for example, to the accurate determination of the decay characteristics of long-lived and naturally occurring radionuclides of importance to geochronology.

1. Absolute Counting of Low-energy β Emitters

(L. E. Glendenin, K. F. Flynn, and J. E. Gindler)

Development of an absolute counting technique for low-energy beta emitters was completed. Samples in a liquid scintillator are counted through light filters of various optical densities and results extrapolated to 100% detection efficiency. This method is more convenient and accurate than other methods in current use. Since the

Fig. III.21. Decay of Counts Observed in LiF Crystal in Chemically Bound Neutron Experiment. ANL Neg. No. 121-8502.

method works well for beta energies even as low as that of tritium, and involves only elementary techniques and apparatus, it should be widely applicable to many radiochemical and tracer problems.

The partial half-life for β^- decay of the long-lived isomer of ^{236}Np has been measured by observing the growth of its daughter ^{236}Pu over a period of four years. Preliminary calculations give a half-life of $(1.3 \pm 0.1) \times 10^6$ yrs.

2. Organic Scintillator Studies (D. L. Horrocks and J. B. Birks*)

Information on the fluorescence and scintillation properties of organic molecules is useful in the understanding of liquid scintillation counting systems and results obtained in radiation-chemistry studies. We have initiated a study of scintillations arising from high-energy ionizing radiation impinging upon organic molecules, using the Chemistry Division Van de Graaff generator as an intense source of 3-MeV electrons. Irradiations are made of various aromatic aliphatic hydrocarbons in which certain organic molecules had been dissolved. Scintillation results from low-intensity (radioactive sources) and high-intensity (Van de Graaff) ionizing irradiations have been correlated with results of photo-excitations with uv radiations (fluorescence). These scintillation studies make it possible to obtain information now unattainable from other experiments. Among the results of our continuing studies of the properties of various solvents and solutes in liquid scintillation counting, excimer formation and emission, and pulse-shape discrimination we have noted that the structural requirements for excimer formation and for self-quenching are the same. We have proposed, therefore, that these two processes occur via a common intermediate.

a. The Yield of Tritium in Fission

Associated with our studies on organic scintillation we have developed exceptionally sensitive facilities for counting tritium. The yield of tritium accompanying fission processes is of considerable interest and we have recently completed some additional studies.

Measurement of the yield of ^3H in the ternary (thermal-neutron) fission of ^{235}U has been completed, yielding the value $(1.10 \pm 0.07) \times 10^4$ fissions per tritium atom. A preliminary result for the tritium yield in thermal-neutron fission of ^{239}Pu is $(2.0 \pm 5.5) \times 10^3$ fissions per other tritium atom. These values, together with previously obtained values for other fissionable nuclides, have been correlated with a Z^2/A dependency similar to that obtained for the yield of alpha particles coincident with fission.

3. Application of Statistics to Nuclear Measurements (A. H. Jaffey)

Aside from the usual errors of measurement, nuclear measurements exhibit the randomness of counted data. Problems arise concerning efficient experimental design, consistency of data, attainable accuracies, backgrounds, deadtime losses, coincidence statistics, and many others. The particular problems considered have frequently been stimulated by questions arising in our own experimental work or in that of other members of the Division. Results of interest are then generalized sufficiently to warrant publication.

We have recently reviewed the statistical considerations entering into half-life estimation from data derived from decay measurement. These considerations may be of considerable importance when only a small number of decays are measured, as when new and difficultly made isotopes are formed.

We have started a study on the most suitable procedure to use for fitting a straight line to data in which the independent variable has statistical errors. This is a highly clouded subject, which we propose to make accessible to experimenters. This study will be carried on in FY 1972.

F. ISOTOPE SEPARATOR APPLICATIONS (J. L. Lerner)

The electromagnetic isotope separator is a basic tool for the study of the properties of individual nuclides. At Argonne it remains in heavy demand for four principal purposes: (1) isolation of transplutonium isotopes, (2) preparation of sources with negligible self-absorption for high-resolution alpha and beta spectrometers, (3) deposition of target materials on ultrathin backings for high-energy machines (i.e., Van de Graaff, cyclotron, ZGS, etc.), and (4) solid-state ion-implantation studies.

A new isotope separator is being assembled, intended primarily for use at the Zero Gradient Synchrotron. In addition to its use for studying reaction products generated at the ZGS beam, the new machine will be maintained as a relatively contamination-free instrument for investigating low-level radioactive samples.

G. ISOTOPIC NEUTRON SOURCES (D. C. Stewart, M. A. Wahlgren, E. P. Horwitz, and C. H. Youngquist)

The isotope ^{244}Cm will be produced abundantly as a byproduct from reprocessing of the high-burnup reactor fuels of the future. This potential availability in quantity, combined with the nuclide's 18-year half-life and other desirable nuclear properties, makes it a prime candidate for fabrication of (a,n) neutron sources. Construction of irradiation facilities based on such sources that avoid the restrictions of operating even a small reactor can be readily visualized. These would be useful to hospitals, crime

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laboratories, universities, and industrial laboratories, among others.

A prototype ^{244}Cm -Be neutron source has been fabricated. During last year, the gamma spectra from both the bare and water- or paraffin-moderated source have been measured, since these will be of importance in prompt-neutron-capture activation methods where they exist as background. Experimental detection sensitivities have been obtained for the light elements where (n,p) and (n, α)

reactions occur, and these results compared to those using a ^{252}Cf source of approximately the same intensity.

The ^{244}Cm -Be capsule is currently being used to evaluate its application in neutron radiography, although a somewhat more intense source will be required before definitive results in this area can be obtained. As more material becomes available, additional sources will be assembled and studied.

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Secondary Nuclear Reactions of 12-GeV Protons on Uranium: A Search for the Production of Transcurium Elements

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Pulse Height Response Characteristics for Heavy Ions in Silicon Surface Barrier Detectors

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Intensity Measurements by the Activation Method: Proton and γ Ion Beams

E. P. Steinberg
Contribution to LAMPF Summer Study Session,
Los Alamos, New Mexico, August 9-11, 1971

A Study of Fission Isomerism in Curium and Berkelium Isotopes

K. L. Wolf and J. P. Unik
Bull. Am. Phys. Soc. 16, 55 (February 1971)
Abstract

Charge Distribution and Nuclear Fission Based on the K X-ray Method and Interpretation of Mass Distribution Fine Structure

J. P. Unik
Bull. Am. Phys. Soc. 16, 98 (February 1971)
Abstract

Properties of Fissioning Isomers

K. L. Wolf and J. P. Unik
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Spontaneous Fission of ^{244}Cm , ^{248}Cm and ^{256}Fm

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IV. α , β , AND γ SPECTROSCOPY*

In radioactive decay, the emission of particles and photons is associated with energy-level changes in the nucleus, just as energy-level changes in the outer electron shell are reflected in the emission or absorption of discrete energy packets. The analysis of the spectrum associated with such radioactive decays is an important adjunct to the study of nuclear properties in general.

A. MAGNETIC ALPHA SPECTROMETRY (J. Milsted, N. J. Hansen, A. H. Jaffey, P. R. Fields, and R. G. Scott)

New or improved values for alpha energies, abundances, and decay schemes are now available for several transplutonium nuclides as a result of a research effort utilizing an electromagnetic isotope separator and a high-quality magnetic alpha spectrometer.

Alpha spectrometry is of primary importance in identifying rotational level structure in deformed nuclei because alpha-decay probability is relatively insensitive to angular momentum change. However, the observation of alpha transitions to higher-energy levels is limited by the very strong dependence on decay energy, and high sensitivity for the detection of weak alpha groups is of great importance. A magnetic spectrometer provides the highest available precision and resolution, and is not affected by beta particles or conversion electrons which frequently accompany alpha decay.

The Argonne Alpha Spectrometer [1] is a 30-in.-radius, double-focussing instrument with energy resolution from 4 to 6 keV at a transmission of about 0.1%. It has a unique detection system in which the usual photographic plate is replaced by an array of silicon surface-barrier detectors which provide live data acquisition and display. Apart from its obvious convenience, this system makes it possible not only to detect the arrival of an alpha particle at a given point in the focal plane, but to estimate its energy, and to reject the event if this energy differs considerably from the expected value. Thus, focussed alpha particles of well-defined energy can be distinguished from scattered or background particles of random energy. This energy-discrimination feature reduces low-energy "tail" by an order of magnitude or more, and gives a corresponding increase in sensitivity for detecting weak alpha groups. The electronic detection system is also readily adaptable to alpha-gamma and alpha-conversion electron measurements, which are generally essential to the establishment of a decay scheme.

The availability of the electromagnetic isotope separator greatly enhances the value of the alpha spectrometer, since isotopically separated sources can be prepared directly with

a recovery (a few percent) comparable to that obtainable by direct vacuum evaporation.

To date, the high-quality alpha singles spectra produced by the instrument have revealed previously unobserved alpha groups in most of the alpha emitters studied, and in conjunction with independent coincidence measurements have contributed to proposed decay schemes for ^{254}mEs and ^{255}Fm . In order to obtain accurate abundance measurements and to avoid possible spurious peaks, it is necessary to correct the spectra for the differences in counting efficiency among the 224 detector segments. This is done by measuring the continuous spectrum of an "infinitely thick" source, and using this as a reference spectrum to correct the observed spectra. These corrections, and also normalization for counting time and decay, are made by a computer program.

The spectrometer has been calibrated with accurately known standards over the energy range 4.8 to 7.7 MeV, and is capable of absolute energy measurements to a precision of ± 2 keV. As a result, new and improved values have been established for particle energies of several prominent alpha groups, e.g.,

^{253}Es	α_0	6.632 ± 0.002 MeV
^{254}Es	α_{86}	6.430 ± 0.002 MeV
^{255}Fm	α_{107}	7.022 ± 0.002 MeV

These values are from 5 to 8 keV lower than those quoted in Ref. 7. Results for individual nuclides are summarized below.

1. 39-hour ^{254}mEs

This nuclide decays primarily by β^- emission to ^{254}Fm with about 0.3% alpha branching to ^{250}Bk . It presents a rare example of alpha decay from a metastable isomer in an odd-proton, odd-neutron nucleus. The source was prepared in the isotope separator [2] from a sample of ^{253}Es which had been irradiated in the high neutron flux of HFIR. The ^{254}mEs alpha activity would not have been observable in the presence of the high alpha activity of the ^{253}Es , and after separation the source still contained considerable alpha activity due to ^{250}Es (276 days) and ^{254}Fm . Figure IV.1 shows a corrected and normalized spectrum measured in two overlapping sections; for clarity, the overlapping parts are not shown. The higher-energy section containing the ^{254}Fm groups was observed about 4 days after the start of measurements, and has been normalized for decay, to make it consistent with the lower energy section. The ten alpha groups labelled "A" in Fig. IV.1 were attributed to ^{254}mEs , and four of these were interpreted as populating a rotational band based on a (2, 2+) state, 212 keV above the ground state in ^{250}Bk .

*Chapter edited by: J. Milsted and M. S. Freedman.

Fig. IV.1. Alpha Spectrum of Mass 254 Fraction from Neutron-Irradiated ^{253}Es . ANL Neg. No. 121-8591.

The moment of inertia of this state has been calculated, and since alpha-gamma coincidence data were available, a decay scheme could be constructed [3]. Further details are given in Sect. I.B.

2. 20-hour ^{255}Fm

Energies and abundances for 20 alpha groups have been measured, confirming the previously suggested decay scheme [4] which was partially based on early results with this instrument. Two of these groups populate states not previously observed, which can be fitted into the proposed rotational bands.

3. 20-day ^{253}Es

At least 22 alpha groups have been detected, of which only 12 have previously been observed in singles measurements. Several of the new groups populate levels in ^{249}Bk which can readily be predicted from the previously proposed decay scheme [5]. Of the remaining low-abundance groups in the energy range 5.7 to 6.1 MeV, three agree fairly well with groups observed by Lederer [6,7] in coincidence with gamma rays.

4. 314-day ^{249}Bk and 345-year ^{249}Cf

^{249}Bk decays almost entirely by β^- emission to ^{249}Cf , a beta-stable alpha-emitter, but shows very weak alpha branching ($\alpha/\beta \sim 1.5 \times 10^{-5}$) [8]. This alpha decay is difficult to study with conventional detectors because of interference from the beta particles and rapid growth of ^{249}Cf alpha activity.

Measurements using a more intense source of ^{249}Bk than had previously been available, have revealed 8 new alpha groups with abundances less than 0.05% of the total alpha emission. Four of these populate levels at about 72,

124, 135, and 476 keV in ^{245}Am , which are in good agreement with levels observed in the β^- decay of ^{245}Pu [9]. In order to eliminate the possibility that the remaining groups, in the energy range 5.14 to 5.28 MeV, might be due to ^{249}Cf , a very intense source of this nuclide has been studied. Several new alpha groups were detected, populating high spin states in ^{245}Cm which can be predicted from the proposed decay scheme [10], and in addition a group at 5.23 MeV was observed, populating a level at 973 keV. The abundance of this latter group was insufficient to explain a group of similar energy observed in ^{249}Bk decay. Efforts are continuing to characterize the new alpha groups in ^{249}Bk and ^{249}Cf more precisely.

B. BETA- AND GAMMA-RAY SPECTROSCOPY

(M. S. Freedman, F. T. Porter, and F. Wagner)

Three distinct fields delineate the scope of our research interests.

1. Investigations of systematics and character of nuclear energy levels and transitions in radioactive decay, particularly in transuranic elements (in cooperation with the nuclear chemistry group). The unrivalled capabilities of the Argonne high-resolution, high-transmission toroidal beta-coincidence spectrometers, together with the electromagnetic isotope separator, are indispensable in the analysis of low-energy complexities unresolvable by γ and α spectroscopy.

2. Studies of the effects of atomic electron environment on radioactive decay. Such whole-atom effects include internal conversion, Auger spectra, precision electron binding energies, chemical effects, level widths, and high-order effects like electron shakeoff in beta decay and internal conversion, double internal conversion, and forbidden X-ray transitions.

3. Fundamental studies of the beta-decay process via precise shape studies of continuous beta spectra.

Data analysis of the electron spectrometry on ^{255}Fm was correlated with α - and γ -ray measurements in cooperation with I Ahmad *et al* [11] (cf Chapter I). In addition to a complete 2S-level, 6-band, 50-transition decay scheme with all accessible multipolar mixings established, significant revisions in most inner-shell electron binding energies in Cf were deduced, and a spectrum of high-Z L-Auger transitions (in Cf) was obtained.

The conversion electron spectrum of ^{250}Es was correlated with γ -ray spectroscopy (cf Chapter I, I Ahmad). Fourteen nuclear levels in 5 bands involving 23 transitions were identified, and all transition multipolarities below 300 keV were determined.

We plan to examine, by electron and α -e and γ -e coincidence spectroscopy, the decay schemes of ^{237}Am and ^{241}Cm . We also intend to study ^{249}Bk , in a search for a weak (3×10^{-5}) first-forbidden unique beta branch, and low levels in ^{245}Am following weak α -branching, and ^{249}Cf , studying low level and anomalous EI conversion in ^{245}Cm . In the more distant future, specific isotopes targeted for decay-scheme investigation, some already the subjects of substantial investment of our effort, are ^{229}Th , ^{237}Np , ^{227}Ac , and ^{106}Ru , α -decay of ^{252}Es and β -decay of ^{246}Am are new cases of interest.

2 Atomic Properties in Radioactive Decay

The past year has produced significant results in orbital electron ejection accompanying the nuclear processes of β -decay and internal conversion. These programs will hopefully continue for perhaps another year with some particularly interesting and difficult cases (e.g., ^{99}Tc as a case of a highly forbidden transition, ^{147}Pm and ^{63}Ni involving very low-energy processes, and the electron-capture case of ^{55}Fe). We have also measured precision electron binding energies in Cf and Fm, have studied chemical effects in internal conversion, and have uncovered evidence for the existence of K-L_i X-ray transitions.

a Orbital Electron Emission Accompanying Beta Decay

(H Fischbeck,* F Wagner, F T Porter, and M S Freedman)

The first precision measurement [12] of the composite (nuclear beta plus K-orbital-shakeoff electron) spectrum shape for a pure beta emitter has been made on the Argonne double-lens beta spectrometer. In the decay of ^{143}Pr , the electrons in coincidence with K X rays provide the first observation of the low energy rise on the composite spectrum (due to the emitted K electron) which is easily distinguishable from the broad continuum due

(mainly) to the accompanying nuclear beta. The maximum energy of this composite spectrum, which includes only K-orbital-shakeoff-accompanied events because of the requirement of K X-ray coincidence, is lower than the end point of the singles beta spectrum by 42 ± 5 keV. This 42-keV difference is in agreement with the 43.6-keV K binding energy of the Nd daughter. The composite spectrum shape approximately fits the prediction of a shakeoff theory (modified by an energy-dependent correction factor for which a theoretical justification has been given), but disagrees radically with the shape prediction of collision theory (see Fig. IV 2). Moreover, the experimental value for the probability of K shakeoff per normal beta decay, $(2.95 \pm 0.32) \times 10^{-4}$, agrees with relativistic self-consistent field (SCF) shakeoff calculations, 3.0×10^{-4} , collision theory predicts $\sim 10^{-5}$. Both shape and intensity thus clearly evidence the need for a whole-atom view of the beta transition.

Fig. IV 2 Experimental Momentum Plot [$N(p)$ = counts per unit momentum interval vs momentum] of the Composite Nuclear Beta plus K-Orbital Shakeoff Spectrum in Coincidence with K X rays. Theoretical spectra are given for a recent version of shakeoff theory (Stephens-Crazeemann), for our modification of that theory (including the separate nuclear and orbital theoretical components), and for the prediction of beta orbital electron collision theory (Fermi). ANL Neg No. 121 6917

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That beta decay is a whole-atom process, rather than a nuclear process, was established in 1952 in this Laboratory [13]; the nuclear beta and neutrino participate in the sharing of the total nuclear plus atomic energy release which includes the contribution of the changed orbital electron binding energy. The rare ejection of an inner orbital electron simultaneously with the beta-decay event, with the total atomic-energy release shared in a continuous fashion among the electron, beta, and neutrino, constitutes further evidence of the participation of the atom in the nuclear process. The manner of the energy sharing, i.e., the shape of the two ejected electron spectra, can show whether atom and nucleus participate as an integral unit in a single-step three-particle emission ("shakeoff"), or whether the nuclear beta decay is followed by beta-electron collision interaction.

Experimental precision in the spectrum shape determination was sufficient to establish significant residual deviations from the predictions of the modified shakeoff theory. Deviations from theory, but of a different character, have also been seen in other laboratories in shakeoff spectrum shapes accompanying electron capture, and in the probability of double-electron ejection as a function of the energy of a primary-incident electron. Such discrepancies between experiment and shakeoff theory in its current state of refinement are now being explored in other cases of β decay and electron capture which are chosen to emphasize uncertain aspects of the theory.

b. Orbital Electron Emission Accompanying Internal Conversion (F. T. Porter and M. S. Freedman)

Using the high-resolution capability of our toroidal beta spectrometer, we have observed structure [14] on the low-energy side of internal-conversion lines which constitutes the first evidence that an orbital-electron-shakeoff process can accompany internal conversion. These measurements, in addition to being of interest for an understanding of the shakeoff mechanism itself, also provide experimental values for the energy required to remove simultaneously two inner-shell electrons from the atom.

The process of orbital-electron shakeoff is generally associated with any atomic or nuclear process which results in a sudden change in the effective inner atomic electrostatic potential. It has been observed in connection with radioactive α , β , and electron-capture decay in which the nuclear charge changes; it has been observed accompanying the ejection of inner orbital electrons by the photoelectric process and by energetic external electrons, i.e., double-electron emission. Shakeoff probabilities per decay or scattering event are small for inner electrons, e.g., $\sim 10^{-4}$ per beta decay in medium-weight elements; but these probabilities rise to 10–20% for valence electrons. Only in

the cases of electron capture and beta decay (see above) have the shakeoff electrons been directly observed; the other evidence has been indirect, as by the detection of X rays, X-ray satellites, Auger satellites, multiply charged ions, or, in photoelectric shakeoff, the energy-loss spectrum of the companion photoelectrons which appear as satellites to the photoelectron line.

Here at Argonne, very low-intensity, near-lying satellite continua have been resolved from the tails of the K conversion lines of the 122- and 136-keV transitions in ^{57}Fe and the 661-keV transition in ^{137}Ba . In analogy to the photoelectric case, these satellite continua constitute the first evidence for shakeoff in the internal-conversion process (see Fig. IV.3). Satellite high-energy-threshold displacements from the main conversion line corresponding to the emission of a second K or an L electron have been seen in each case. These displacements are measured with sufficient accuracy to yield precise values of the binding energy of the emitted "shakeoff" electron in the K-ionized ion, i.e., the energy required to create a second inner orbital vacancy from the ion with a missing K electron. A priori, one might expect this ionization energy to be somewhat smaller than that required to ionize the corresponding "shakeoff" electron from the $Z+1$ neutral atom. This expectation arises from the less-than-perfect screening of the Z nuclear charges by K electrons; i.e., one expects an effective nuclear charge for the K-ionized atom to lie between Z and $Z+1$ (Slater screening constants for K electrons are less than unity). Surprisingly, our measured binding energies considerably exceed the known orbital binding energies for the $(Z+1)$ neutral atom. This constitutes a challenge to the ability of self-consistent field (SCF) calculations to predict these anomalous double-inner-shell ionization potentials.

The shakeoff and internal-conversion electrons share the total available energy continuously; i.e., the "shakeoff" electron spectrum shape must be the "mirror image" of that of the observed satellite conversion electron. Thus, the "shakeoff" electron has its maximum intensity at zero kinetic energy, and rapidly drops off at increasing energy. The satellite tails are sensibly above background down to ~ 2 keV below their thresholds (case of ^{57}Fe). The observed relative shakeoff probabilities are in the order of 9×10^{-3} (L shakeoff, ^{57}Fe); 1×10^{-3} (L shakeoff, ^{137}Cs); 2.3×10^{-5} (K shakeoff, ^{57}Fe or ^{137}Cs). All are per K conversion. SCF calculations are in agreement within 50% for L shakeoff, but are an order of magnitude too low for K shakeoff. A detailed theoretical prediction for such energy distributions has been successfully applied to the case of conversion shakeoff, but the theoretical predictions for the relative shakeoff probabilities (as a function of Z , orbital quantum numbers, and transition energy), particularly for K shakeoff, clearly needs inclusion of higher-order terms to effect agreement with the data.

Fig. IV.3. Beta-ray Spectrometer Measurement of the Structure at the Base of the K-shell Internal-conversion Line (115 keV) of the 122-keV Transition in ^{57}Fe following the Decay of ^{57}Co . The left upper insert shows a condensed view of the spectrum. The K conversion line at 78.6 potentiometer units extends to ~ 100 times the maximum ordinate shown. In the expanded view of the main figure, the back-scattering tail of the main K line has been sketched in (as a smooth continuation of the solid line through the circles), and the resulting continuum, obtained by subtraction, is indicated by + symbols. The resolution function of the spectrometer (shown as "line shape of K_{122} ") fits the high-energy edge of the continuum exactly. This exact fit indicates that the continuum begins abruptly at ~ 798 -eV energy below the K line. This energy displacement falls between the L_3 binding energies in $Z+1$ (779 eV) and $Z+2$ (855 eV), where Z is the atomic number of the atom in which the conversion takes place. This continuum is interpreted as the spectrum of the higher-energy partner emitted when both a K and an L electron are ejected in the internal conversion process. The ratio of the areas of this KL continuum to that of the main K line is indicated at the lower left. ANL Neg. No. 121-6356 Rev. 1.

c. Experimental Atomic-electron Binding Energies in Fermium and Californium (F. T. Porter and M. S. Freedman)

Because of the current activity in electron and X-ray spectroscopy in transplutonic elements (and even for specifically chemical and optical spectroscopic interest), and to facilitate precise extrapolation of atomic properties beyond the known species, we present experimental electron binding energies (K through P shells) for fermium [15] and californium [11]. These values are obtained solely via precision spectroscopy (0.05–0.3% resolution) of internal-conversion electrons. Recent binding-energy determinations [16] at $Z = 96$ used transition-energy and conversion-line-energy measurements.

To illustrate, the decay scheme to ^{254}Fm levels in Fig. IV.4 shows that the energy of the 40-, 45-, and 104-keV transitions can be determined from energy differences of high-energy transitions converting in the same

shell. All the lines used here were well resolved (see Fig. IV.5).

These transition energies and the associated conversion lines yielded the binding energies (except for the K shell) given in Table IV.1. All these lines were well resolved (peak/valley $> 3/1$) except for N_5 , O_1 , and $O_{4,5}$; these latter two, resulting in the least-certain line positions, are shown in Fig. IV.6.

We call attention to our low $P_{7,2}(6p_{1/2,3/2})$ binding energy, 24 ± 9 eV in Fm, and our similarly low value in ^{98}Cf , 5 ± 20 eV. A 6p binding energy of 24 ± 9 eV suggests unexpected possibilities for 6p involvement in chemical and optical spectroscopic interactions.

The binding (and transition) energies in californium were obtained by a least-squares adjustment with the conversion line energies and transition crossover-stopover energy sum relationships in the decay of ^{255}Fm & ^{251}Cf as input data. Table IV.2 gives the binding energies.

Fig. IV.5. The L_1 and L_2 Conversion Lines of the 694-keV Transition. This example is shown because the fractional momentum separation is the smallest of the high-energy $L_{1,2}$ pairs and because it is the only case in which there was incomplete resolution from a neighboring line, L_3 (689) (not used in the analysis). The assigned uncertainty in position ($\pm\sigma$) is shown above the lines. The background is the ~ 1100 -keV β continuum of ^{254}Es . ANL Neg. No. 121-8565.

Fig. IV.4. Decay Scheme of $39\text{-h } ^{254}\text{Es} \rightarrow ^{254}\text{Fm}$. Energies in keV (4σ). Shell designations indicate conversion lines scanned. No detailed conversion studies of the 39.9-, 45-, and 104-keV transitions have been reported before. All transitions are (mainly) E2 multipolarity. ANL Neg. No. 121-8565.

TABLE IV.1. Electron Binding Energies [keV (4σ)] to the Fermi Level of a Solid Source of Fermium Oxide

Shell	From 45-keV Transition	From 104-keV Transition	From 40-keV Transition	Weighted (1/σ ²) Average
L_1	27.570(10)	27.579(14)		27.573(8)
L_2	26.638(10)	26.646(14)	26.651(11)	26.644(7)
L_3	20.862(10)	20.868(14)	20.874(11)	20.868(7)
M_1	7.199(11)	7.203(16)		7.200(9)
M_2	6.772(11)	6.782(15)	6.785(11)	6.779(7)
M_3	5.401(11)	5.411(15)	5.414(11)	5.408(7)
M_4	4.746(11)			4.746(11)
M_5	4.484(11)			4.484(11)
N_1	1.940(11)			1.940(11)
N_2	1.740(11)	1.750(15)		1.743(9)
N_3	1.370(11)	1.373(15)		1.371(9)
N_4	1.059(11)			1.059(11)
N_5	0.989(11)			0.989(11)
$N_{6,7}$	0.639(15)			0.639(15)
O_1	0.450(15)			0.450(15)
O_2	0.365(11)	0.373(17)		0.367(9)
O_3	0.262(11)	0.272(18)		0.265(9)
$O_{4,5}$	0.145(14)			0.145(14)
$P_{3,4}$	0.019(11)		0.033(16)	0.024(9)

K Binding Energies from Lines: (141.000 keV subtracted)				
	Gamma	K and L_1	K and L_2	K and L_3
K	694	0.959(17)	0.954(17)	0.959(42)
	649	0.968(17)	0.971(17)	0.950(23)
	689	0.956(17)	0.975(17)	
	584	0.966(23)	0.962(23)	
				141.963(13)

Fig. IV.6. Conversion Lines of O_1 , O_2 , O_3 , $O_{4,5}$, and $P_{2,3}$ Shells of the 44.988-keV Transition. A background, determined on the continuum above the $P_{2,3}$ line (220 counts per 100 sec) has been subtracted from each experimental point. Horizontal error bars show assigned uncertainties of line positions. Statistical errors at top of main peaks are smaller than symbols. Shape of N_2 line (not shown) fits $P_{2,3}$ points but not O_2 or O_3 , which are fitted with the (same) wider line shape. The reason for this excess O_2 , O_3 width is not understood. Identification of lines is supported by agreement of intensities with theoretical internal-conversion coefficients. ANL Neg. No. 121-8566.

TABLE IV.2. Atomic-electron Binding Energies in Californium ($Z = 98$)

Shell	Present Work	Shell	Present Work
K	134.963 ± 0.025	M_3	5.089 ± 0.015
L_1	25.996 ± 0.013	N_1	1.799 ± 0.015
L_2	25.098 ± 0.013	N_2	1.609 ± 0.020
L_3	19.881 ± 0.013	N_3	1.288 ± 0.015
M_1	6.737 ± 0.010	$O_{2,3}$	0.299 ± 0.020
M_2	6.316 ± 0.012	$P_{2,3}$	0.005 ± 0.020

d. Outer-shell Internal Conversion of the 14.4-keV Transition in ^{57}Fe : Chemical Effects and Line-shape Differences (F. T. Porter and M. S. Freedman)

The effect of chemical state on internal conversion probability in outer (valence) shells has been reported [17] in ^{119}mSn and also [18] in ^{169}Tm . These observations were limited by relatively poor experimental resolution and by thick source effects so that, while the certainty of the phenomenon was established, unobservable systematic effects limited the accuracy of interpretation. To mitigate these limitations, the internal conversion of the 14.4-keV transition in the outer shells of ^{57}Fe following the decay of ^{57}Co has been examined [19] at 0.05% momentum resolution with less-than-monolayer isotope-separator-deposited sources. The intensity of the conversion in the outermost shell $N_1(4s)$ in the free atom, relative to that of the $M_1(3s)$ shell, shows a dependence on the chemical environment of the decaying ^{57}Co atom. (See Fig. IV.7.) ^{57}Co ions

Fig. IV.7. Outer-shell Conversion Lines of 14.4-keV Transition following the Decay of ^{57}Co from Sources Prepared in Metallic ("500"-volt ions) and Oxide ("0"-volt ions) States, on a Log Intensity Scale. Note energy ranges from 14.313 keV (M_1) to 14.402 keV (N_1), a span of only ~ 90 eV at ~ 14.4 keV. Curves are displaced vertically to show chemically induced N_1 intensity changes (A'/B') relative to M_1 (A/B). The indicated 30% lower N_1 (oxide) peak intensity fails to account for the N_1 line shape differences relative to associated M_1 lines. Properly accounting for line area ratios (which the earlier experimenters could not resolve) yields the N_1 ratio in the text. ANL Neg. No. 121-4235.

from an electromagnetic isotope separator were deposited at <25 eV on the surface ("oxide state") or were allowed at 500 eV to penetrate a natural-graphite crystal lattice ("metallic state") where oxidation could not occur. The chemical identifications were established by measurements of the associated "chemical" shifts in the core (1s,2s) binding energies as seen in the observed K and L_I conversion-line energies, and from the observed Mössbauer hyperfine patterns of the 14.4-keV gamma ray. The intensity ratio N_1/M_1 ("oxide") is 0.024 ± 0.002 , and N_1/M_1 ("metal") is 0.034 ± 0.003 , leading to a ratio

$$\frac{N_1(\text{"metal"})}{N_1(\text{"oxide"})} = \frac{|\psi(0)|^2_{\text{metal}}}{|\psi(0)|^2_{\text{oxide}}} = 1.42 \pm 0.21,$$

where $|\psi(0)|^2$ is the 4s electron density at the nucleus. As expected, that density is greater in the metallic than in the oxide state.

The N_1 -shell line shapes show less low-energy tail than the M_1 lines (which are only ~0.7% lower in energy), an effect probably due to less outer-shell electron shakeoff in the case of the N_1 lines. This result throws doubt on the accuracy of the analyses of the earlier experiments in which

the outermost-shell conversion lines were not well enough resolved to observe this effect and in which the assumption of similar line shapes was used.

e. Discovery of K-L_I Forbidden X-ray Transition

(R. K. Smither,* M. S. Freedman, and F. T. Porter)

K-L_I (2s-1s) radiative transitions are absolutely forbidden if the electron wavefunctions are pure $\ell = 0$ states. In heavy atoms, relativistic effects introduce small orbital angular-momentum admixtures into the whole-atom electron wavefunctions to permit an observable transition probability. Recent theoretical calculations [20] give K-L_I/K-L_{III} intensity ratios of e.g., 3.8×10^{-4} at Hf ($Z = 72$).

In cooperation with Smither [21], photon spectra from the ANL 7.7-meter bent crystal spectrometer were examined and a line was seen at the calculated energy for Hf, 54.080 keV, with an intensity ratio to the K-L_{III} ($K\alpha_1$) X ray of $1.8 \pm 0.8 \times 10^{-4}$, ~50 ± 25% of the predicted value. Subsequent work by Smither and others yield better agreement with the theoretical prediction.

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PUBLICATIONS

Composite (K-orbital Shakeoff Plus Nuclear) Electron Spectrum Shape Coincident with K X Rays in Pr^{143}

H. J. Fischbeck,* F. Wagner, F. T. Porter, and M. S. Freedman

Bull. Am. Phys. Soc. 15, 644 (April 1970)
Abstract

Intensity of K-L_I X-ray Transitions

R. K. Smither, M. S. Freedman, and F. T. Porter
Phys. Letters 32A, 405-407 (1970)

Spectrum Shape of K-orbital Shakeoff Electrons and Accompanying Nuclear Beta Particles in the Decay of Pr^{143}

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Phys. Rev. C3, 265 (1971)

Outer-shell Internal Conversion of the 14.4-keV Transition in Fe^{57} : Chemical Effects and Line-shape Differences

F. T. Porter and M. S. Freedman

Phys. Rev. C3, 2285-2292 (June 1971)

Ionization (Shakeoff) Accompanying K-shell Internal Conversion

F. T. Porter, M. S. Freedman, and F. Wagner, Jr.

Phys. Rev. C3, 2246-2259 (June 1971)

also: Bull. Am. Phys. Soc. 15, 644 (April 1970)

Abstract

Experimental Atomic Electron Binding Energies in Fermium ($Z = 100$)

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Phys. Rev. Letters 27, 293-297 (August 1971)

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V MOLECULAR BEAM STUDIES*

A considerable number of important chemical processes involve reactions which are endothermic or have substantial activation energy. In order to make progress in understanding these reactions, it is necessary to obtain detailed information concerning their reaction dynamics. This should include cross sections for elastic, inelastic, and reactive collisions as a function of translational and internal states of the colliding species. Such measurements can be carried out most unambiguously under the single-collision conditions of a crossed-molecular-beams apparatus. With beam techniques much information has already been obtained for the thermal-energy region, i.e., for exoergic and thermoneutral processes.

The energy range of interest for endoergic chemical processes reaches from thermal to tens of electron volts. For a successful experimental program, beam sources of suitable intensity and energy range are of crucial importance. The maximum useful beam energy of conventional thermal oven sources is limited by the melting point of available materials, and reaches at most a few tenths of an electron volt. There exist, however, three different and widely applicable methods of acceleration of atoms and molecules which span a broad range of species accelerated, kinetic energies attainable, and, in some cases, states of excitation achievable. Very promising is the seeded-supersonic-jet technique, which, however, also requires that the beam material be in the gas phase. Increased beam energy arises from velocity equilibration with a light propellant gas expanded to high mach number. Hence, the method is mainly suitable for producing energetic beams of heavy atoms and molecules. The enormous intensity advantage and comparative freedom from excited-state problems argues for the use of this beam source where possible. Another type of source, producing fast neutral beams by acceleration of ions and subsequent charge exchange, has long been useful at high energies. However, in the chemically interesting region below 100 eV it suffers from drastic reduction of intensity with decreasing energy. The problem of determining the state of neutral particles produced is also of concern since charge exchange can occur to an excited level of the neutral.

Intermediate in intensity between the seeded-jet and charge-exchange methods is the technique of fast-beam production by cathode sputtering. Ion impact on a crystalline target of the desired beam material leads to ejection of neutral species with a distribution of energies. Most of the particles have energies in the chemically interesting range of up to several tens of electron volts. A wide range of target substances can be used, including many from which beam production would be difficult or impossible by other methods. The sputtering technique also applies to light

species, for which only a small energy increase can be achieved with seeded jets.

A REACTION DYNAMICS USING ACCELERATED BEAMS PRODUCED BY SPUTTERING (C. E. Young and S. Wexler)

An apparatus employing sputtering for beam production has been constructed in this laboratory. A schematic diagram is shown in Fig. V 1. An intense Ar^+ ion beam at 5–10-kV energy is focused on a target. The neutral beam emanating from the sputtered target passes through collimating slits and then through a high-speed (900 Hz maximum) slotted disk-velocity selector which transmits beam particles of a desired speed. For initial experiments, velocity resolution has been set at 8.5%, giving a maximum transmitted velocity of 1.8×10^6 cm/sec. This gives adequate energy for a large number of experiments initially planned, and can be altered to fit requirements of special cases. The fast beam intersects a second beam of target molecules in the region labeled scattering center. The second beam ($\sim 10^{13}$ molecules steradian⁻¹sec⁻¹) is produced as an expanded jet from a high-pressure nozzle source. After passing through the scattering zone, most of the target molecules are collected in a beam trap consisting of a cold trap and diffusion pump. The nozzle-beam trap makes possible a maximum density of target particles at the scattering center while subsequently removing them to minimize interference from randomized background gas. A high-sensitivity mass spectrometer consisting of an electron-bombardment ionizer, quadrupole mass filter, and scintillation ion detector is mounted on a rotating turntable, enabling the angular distribution of scattered species to be determined. Two stages of ion and titanium sublimation pumping allows the total pressure in the ionizer region to be maintained in the region of 10^{-10} torr. Chopping the second beam permits elimination of background signal by use of a dual scaling system. A substantial additional measure of discrimination against ionized background gas has been achieved by utilizing the electron space charge in the bombarder. A description of a new ionizer developed in this laboratory to exploit this technique optimally is presented below (Sect. B 2).

1 Reaction Dynamics of Silver-Halogen Collisions and Study of Bond Energies in Silver Compounds

At present, all components of the apparatus are operating. For initial scattering experiments, silver is being used as fast beam material. With Ag, sputtering yields are among the most favorable, and velocity-selected beams corresponding to theoretical estimates ($\sim 10^6$ atoms/sec) have been generated. Initially, elastic and reactive scattering of

*Chapter edited by S. Wexler.

Fig. V.1. Schematic of Cathode-accelerator/Crossed-beam Apparatus. ANL Neg. No. 121-8295.

Ag atoms on halogen molecules is being investigated. Preliminary results show that the elastic scattering of fast silver atoms off Br_2 extends beyond 30° (relative to the direction of the Ag beam), a characteristic quite different from that of alkali atom-halogen molecule collisions. It is also of great interest to compare product angular distributions from reactions like

with corresponding patterns from the alkali-halogen reactions. The latter were among the first to be studied with molecular-beam techniques, and have yielded a wealth of dynamical information. The endothermic reactions

and

are of interest since the reaction threshold energies found by variation of the silver-beam velocities give information about the poorly known AgO and AgH bond strengths. Also, the close spacing of lowest P and D excited states for Ag atoms probably leads to anomalous excited-state potential curves for many of its diatomic compounds. Experiments performed so far indicate substantial quantities of excited Ag atoms can be produced by the sputtering

technique. It is hoped that detailed excited-state studies can be performed.

2. The Lithium-Deuterium Reaction

There is currently considerable interest in the relative effectiveness of internal versus kinetic energy in promoting endoergic reactions. A theoretically important case is the reaction

for which an accurate a priori potential energy surface is being calculated by Wahl. The present indications are that considerable stretching of the D_2 bond is required before reaction occurs. It is of interest to test whether a reactive configuration can be reached by energetic collision of Li on thermal D_2 or whether vibrational excitation of the D_2 bond is required. Lithium is a reasonable sputtering-target material, and the appropriate energy region can be reached with the velocity selector.

3. Some Other Planned Studies

For some endoergic reactions there presently exists information on the reverse process, for example the endothermic chemical change

Reaction 5 has been studied, in the reverse direction, in chemiluminescence investigations, and the application of detailed balance considerations to such data suggests that k_5 should increase drastically with increasing HCl vibrational excitation. However, the chemiluminescence studies start with thermal species, and thus detailed balance gives information only about collisions which leave HI and Cl in the thermal-translational and vibrational-energy range. This may account for only a small fraction of the reactions of $\text{HCl} + \text{I}$ (fast), however, and direct experimental evidence for reaction in the endothermic direction is clearly desirable.

A further direction in which some investigation is planned involves polar ionization, a process being studied with the aerodynamic accelerator in this laboratory (cf Sect B). Some of these experiments have shown an interesting dependence on the atom being used to produce dissociation. It would be of interest to extend such studies to include many collision partners of varying polarizability and electronic configuration. Many suitable fast atoms can be produced by sputtering. A second possible usefulness of the sputtering technique is to extend the energy range upward. The seeded beam apparatus is currently limited to about 20 eV of laboratory energy for Xe. There is no similar sharp cutoff in the sputtered atom energy distribution, which may consequently provide useful intensities at substantially higher energies.

B. AERODYNAMIC CHEMICAL ACCELERATOR

Little information exists on atomic and molecular collisions in the intermediate-energy range (0.5–20 eV in the center-of-mass coordinate system), where inelastic encounters giving rise to electronic excitation, ionization, and reaction are expected. One process, polar ionization, refers to the production of an unbound ion pair through an energetic collision with a third body, i.e., $\text{AB} + \text{M} \rightarrow \text{A}^+ + \text{B}^- + \text{M}$. The collision must be energetic for two reasons, first because the AB bond must be broken, and second because for all known diatomic molecules, more energy is required to pull an electron off A (referred to as the ionization potential of A) than that obtained in putting it on B (the electron affinity of B). The energy required before the reaction will proceed is called the endoergicity (or threshold energy), and is the order of six electron volts for compounds such as the thallium halides. As a result, such reactions do not occur at ordinary temperatures (where the average collision energy is less than 0.5 eV), but can be very important at temperatures obtained in a shock tube or a plasma. In these cases polar ionization and its reverse reaction, three-body ionic recombination, are important in determining the production and removal of charge species. The latter reaction is also an important mechanism in the removal of charge in the D region of the atmosphere.

The crossed-molecular-beam method provides the best means of obtaining detailed dynamical information on chemically reactive systems. But in order to study polar ionization by this method, one needs a "chemical accelerator." At Argonne we have built a chemical accelerator based on the "seeded-jet" principle developed by Fenn and his co-workers during the 1960's. The method can be used to produce accelerated beams of heavy species (we have obtained Xe beams with energies up to 15 eV and Kr beams up to 10 eV) with beam intensities 4 to 5 orders of magnitude greater than those obtained by the charge exchange method. This allows careful study of the threshold behavior and low-energy dependence of many reactions exhibiting polar ionization.

A schematic of the aerodynamic accelerator is shown in Fig. V.2. In the "seeded-jet" method a small percentage of Xe (or Kr) is entrained in a supersonic jet of H_2 expanding from a nozzle at high temperature and pressure. The core of the accelerated beam is skimmed off and collimated to 0.3° full width. Two types of detectors are used to characterize the accelerated beam, a flux detector to measure beam intensities and an electron-bombardment detector for time-of-flight measurements of the beam velocity. Intensity measurements on the thallium halide crossed beam (thermal source) are also made in order to determine absolute cross sections for polar ionization. The two beams cross in an electric field of 2000 V/cm, and the ions formed in the reaction are swept into two collection cylinders, the longer one of which forms the entrance to a time-of-flight mass spectrometer. In the other shorter cylinder (which can also be used for mass analysis), positive ions are focused into a scintillation ion detector and counted directly. In this way both total ion production as a function of relative energy as well as the masses and relative intensities of the various product ions (both positive and negative) can be determined.

1. Polar Ionization of Thallium Halides by Accelerated Xenon and Krypton Atoms (E. K. Parks, N. Hansen, and S. Wexler)

In Figs V.3–V.5 we give the total cross sections for polar ionization from thallium chloride, bromide and iodide from collisions with Xe and Kr. The abscissa is the relative translational energy in the center-of-mass coordinate system (assuming the target to be thallium halide monomer). The energy dependence of the cross section in the postthreshold region agrees well with recent theoretical work. The cross section in this region is found to be of the form $\sigma(E_{\text{tot}} - E_0)^{5/2} / E_{\text{tr}}$, where E_{tr} is the initial relative translational energy, E_{tot} is the total energy (translation + internal), and E_0 is the endoergicity (or threshold energy). The 5/2 power is a direct consequence of the presence of three particles in the final state.

The observed cross sections for polar ionization vary

Fig V 2 Schematic of Aerodynamic Chemical Accelerator ANL Neg No 121 7799

Fig V 3 Cross Section for Polar Ionization of Thallium Chloride by Accelerated Xe and Kr Atoms as a Function of Relative Kinetic Energy of the Collision Partners ANL Neg No 121 8119

Fig V 4 Excitation Function for Polar Ionization of TlBr by Fast Xe and Kr Atoms ANL Neg No 121 7797 Rev 3

Fig. V.5. Variation of Cross Section for Polar Ionization of TII by Accelerated Xe and Kr Atoms with Relative Kinetic Energy. ANL Neg. No. 121-811B.

from the order of 10^{-16} cm^2 for thallium chloride to 10^{-19} cm^2 for thallium iodide, the thallium bromide cross section being intermediate in value. In addition, only in thallium bromide is there a strong dependence on the projectile, Xe being about nine times more effective in total ion production than Kr.

Besides polar ionization, the thallium halides can undergo collision-induced dissociation to neutral atoms. The thresholds for these reactions are always lower than those of the corresponding polar ionization (the two thresholds differ by the difference between the ionization potential of thallium and the electron affinity of the halogen). The total cross sections for dissociation (neutrals + ions) are expected to be similar for the different halides and may be expected to be in the range $(1-10) \times 10^{-16} \text{ cm}^2$. From the magnitude of the polar ionization cross sections seen in Figs. V.3-V.5, we conclude that for thallium chloride ion production is one of the major dissociation processes while for thallium iodide and probably thallium bromide ion production is a minor dissociation process, dissociation to atoms being the predominant process. The ratio of ions to atoms in the final state is called the branching ratio and is seen to vary over three orders of magnitude in the thallium halides.

The branching ratio can be explained on the basis of the proximity of the two potential curves relating the ionic and covalent states of the diatomic molecule. The curves for the

three thallium halides are shown in Fig. V.6. Note that the ground states of the molecules are covalent, and thus an electronic transition to the excited ionic state is required for polar ionization. The probability of such a transition is related to how closely the curves approach each other (or actually cross). In thallium chloride the potential curves approach very closely (or cross to within experimental error), which should result in a strong probability for an electronic transition, while for thallium iodide the curves are separated by about 0.8 eV, and such a transition should be unlikely. This is in agreement with the present experimental results.

The large difference between the Xe and Kr cross sections in the case of TIBr can also be explained by including the effect of the charge-induced dipole attractive force between the thallium bromide ionic state and the Xe (or Kr) atom. This force results in the lowering of the ionic potential surface in certain regions, bringing the two surfaces (ionic and covalent) closer together. The effect of Xe in this respect is considerably larger than that of Kr (due to its larger polarizability), and can result in a crossing in the case of the Xe interaction but not in the case of Kr. Since for TlCl the two curves virtually cross, one would not

Fig. V.6. Potential Curves of the Ground (covalent) State and Lowest Ionic State of TlCl, TIBr, and TII. ANL Neg. No. 121-8219.

expect any effect due to the polarizability of the rare gas collidant, and indeed little if any difference between Xe and Kr is observed (see Fig. V.3).

Mass analysis has been completed in the case of thallium chloride, where the predominant ions are Tl^+ and Cl^- . No other negative ions other than Cl^- were observed. In addition to Tl^+ , however, $TlXe^+$ and $TlKr^+$ were observed in the corresponding studies with Xe and Kr. Their intensities, which were comparable to Tl^+ only near the onset of ion production, increased with relative energy up to approximately one volt above threshold, where they represented about 1% of the total ion signal. At higher energies their intensities remained fairly constant.

Preliminary mass analysis in the case of thallium bromide indicated the presence of Tl^+ , $TlXe^+$, and Tl_2Br^+ ions from collisions with Xe, and Tl^+ and Tl_2Br^+ ions from Kr. No $TlKr^+$ species were observed. The Tl_2Br^+ ion was shown to arise from a small percentage of dimer present in the thallium bromide crossed beam.

2. Electron-bombardment Ionizer for Accelerated Molecular Beams (E. K. Parks, C. E. Young, and S. Wexler)

In the course of implementing the program of fast-beam collision studies, a novel electron-bombardment ionizer was developed which achieves substantial suppression of background signal from ambient gas. Even with the most intense beams, densities of products and background in the ionizer region are comparable. Thus it is always necessary to contend with a large background ion signal.

The ionizer shown in Fig. V.7 was built after initial experiments with an earlier version had shown that the space charge potential well created by the bombarding electrons could be used to trap thermal ions, provided a sufficiently small ion-extraction potential was applied. In

the aerodynamic accelerator, ions from the light propellant gas, having a low energy, were also easily trapped. However, suitable extraction conditions could be found such that the heavy "seeded" beam component, with a few electron volts of kinetic energy, passed through the region of electron space charge potential and was detected. The Kr signal of Fig. V.8 illustrates operation of the ionizer in such a mode, whereas the $H_2 + Kr$ curve corresponds to the conventional technique where all ionic species are extracted. The latter signal is principally due to H_2 , the Kr component being a small shoulder. Such an extraction mode has usefulness in calibration of various parameters of the conditions for the nozzle operation.

Another operation mode consists of extracting essentially all the ions but subsequently applying retarding potentials sufficient to prevent transmission of all but the energetic seeded beam component. This approach, which depends on subsequent defocusing of the low-energy ions, has been found to work moderately well using a conventional Brink-type ionizer in the sputtered beam apparatus. There the use of a quadrupole mass filter provides that strongly defocused ions will have very small probability of being detected. However, in the aerodynamic accelerator the ion detector is in close proximity to the ionizer region, so that the discrimination technique previously described proved superior.

C. STUDIES OF CHEMICAL SPUTTERING OF SURFACES OF POTENTIAL USE IN THERMONUCLEAR REACTORS (S. Wexler)

Of immense importance in the production of power from thermonuclear reactors is the problem of removal of material from surfaces exposed to the contained plasma. It is estimated that relatively small amounts of impurities brought into the plasma by sputtering of the walls of the

Fig. V.7. Assembly of Ionizer for Fast Molecular Beams. ANL Neg. No. 121-7821.

Fig. V.8. Time-of-flight Velocity Distributions of $H_2 + Kr$ and of Kr with the H_2 Propellant Suppressed. ANL Neg. No. 121-7820.

containment vessel would seriously reduce the efficiency of the reactor for power production, and indeed may possibly jeopardize the success of the entire approach of obtaining vast amounts of electric energy from nuclear-fusion reactions. The fuel for these fusion reactions are molecular hydrogen, deuterium, and tritium. Ionic and neutral atomic and molecular species of these isotopes would be present in a thermonuclear reactor, and their kinetic energies are expected to be in the range from 0 to ~ 20 keV. Since hydrogen and its isotopes are chemically reactive entities, they may react efficiently with surfaces exposed to them under the operating conditions of the proposed reactor and remove material by chemical as well as physical sputtering. The chemical mode of sputtering is expected to be important when the energy of the impinging hydrogen species is less than 2 keV.

At present there exists no information on these phenomena at low energies at surfaces such as niobium or tantalum, which are of potential use as containment vessels or surface materials in proposed thermonuclear reactors. As a consequence of the great need for such basic information, the tritium "chemical accelerator" has been modified in order to carry out studies on chemical sputtering from heated surfaces. This accelerator is admirably suited for such investigations, since it can produce reasonably intense accelerated beams of both ionic and neutral atomic and

molecular hydrogen and its two heavier isotopes in the very region of kinetic energies of interest, i.e., from 5 to 2000 eV.

A schematic of the altered machine appears in Fig. V.9. H_2 or one of its isotopes enters the ion source B through A, where it is ionized in a low-voltage arc fed by electrons from a filament D. Ions are extracted through the aperture D and accelerated and focused by the two-element lens E. The desired ionic species are selected by the zero-deflection mass filter F and pass through the aperture G. The four pairs of deflection plates I serve to position the ionic beam. The energy of the mass-selected beam is then decreased to the desired value by the system of wide-aperture lens H, and the ions then pass through a neutralization chamber S, where they are partially neutralized by resonance or near-resonance charge exchange with an appropriate gas. The intensity of the fast neutralized species is determined by measuring the current to the chamber walls of slow ions formed in the charge-exchange process. Unneutralized fast ions are then repelled by a potential on the grid T. When a beam of ions rather than of neutrals is desired, no neutralizing gas is present in S, and T is at ground potential or is used to monitor the ionic beam. The fast hydrogen, deuterium, or tritium species impinges at 70° to the normal on the target O, which can be heated by coiled filaments to temperatures up to 1000°C . Ionic

Fig. V.9. Schematic of "Tritium Chemical Accelerator" Modified for Studies of Chemical Sputtering of Nb and Ta Surfaces. ANL Neg. No. 121-8366.

and neutral sputtered species are analyzed by an assembly M composed of a high-efficiency ionizer, quadrupole mass spectrometer, and electron multiplier. The analyzer (contrary to the schematic drawing) accepts species ejected at approximately 20° to the surface normal.

At the time of this report, the alterations of the accelerator have been completed, and preliminary testing and investigation of chemical sputtering of D_2^+ on niobium begun.

PUBLICATIONS

He-D₂ Total Cross Sections at Low Thermal Velocities

H. V. Lilenfeld,* N. C. Lang,* E. K. Parks, and
J. L. Kinsey*

Seventh Internat'l Conf. on the Physics of
Electronic and Atomic Collisions, Abstracts of
Papers, North Holland Publishing Co.,
Amsterdam, 1971

Electron Bombardment Ionizer for Accelerated Molecular Beams

E. K. Parks, C. E. Young, and S. Wexler
Rev. Sci. Instr. 42(10), 1405-1410 (1971)

Collisional Dissociative Ionization of TlBr by Accelerated Xe and Kr Atoms

E. K. Parks and S. Wexler
Chem. Phys. Letters 10, 245-250 (1971)

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VI. RADIATION CHEMISTRY AND PHOTOCHEMISTRY*

The production of ionizing radiation is an inevitable accompaniment of the generation of nuclear power. Consequently, understanding the effects of such radiation on materials, chemicals, and biological systems is inextricably a necessity for any rational development of nuclear-energy sources. Beyond this, ionizing radiation provides a marvelous probe for the study of chemical systems generally, and this is especially true with the development of the technique of pulse radiolysis.

Radiation chemistry dates back almost to the discovery of X rays. However, a surge of expanded interest occurred during and after World War II with the development of nuclear reactors, which made available radioactive sources such as ^{60}Co . A. O. Allen and M. Burton at the Metallurgical Laboratory began a tradition of excellence which has been the continuing model for research at the successor laboratory, ANL. Cobalt-60 gammas, polonium alphas, and mixed reactor radiation were used in the solution of many aqueous radiation chemical problems. In 1959, Argonne was one of four laboratories which pioneered in developing the powerful tool of pulse radiolysis [1]. With this technique many short-lived intermediates (such as H and OH radicals), which formerly were only postulates to explain overall kinetics and final products, could be studied directly. In 1962, Argonne scientists played a major role in the discovery and intensive investigation of the important entity, the hydrated electron [2], an entity now known to have a role in other areas as well as in radiation chemistry. With pulse radiolysis the Argonne radiation chemists have unraveled the course of radiation chemical systems on a shorter and shorter time scale and presently are working at the picosecond level. Radicals, organic ions, solvated electrons, metallic ions of unusual valency, and excited singlet and triplet molecules have been observed and their absolute rate constants determined in many reactions. These species and their quantitative behavior play a significant role in broad areas of chemistry beyond the bounds of radiation chemistry. There is strong evidence that the Argonne staff will continue its pioneering and preeminent role in radiation chemical research for many years.

A. RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS

Because of the broad, fundamental applications of the photochemistry and radiation chemistry of water to free radical chemistry, reactor chemistry, radiation biology, food processing, photosynthesis, and pollution, we continue to direct our main efforts to a study of the reactions

of irradiated water. The primary processes in each case involve the radicals found in irradiated water, so an understanding of the reactions taking place in water under photolysis and radiolysis is of considerable importance. Even after forty years of research, our knowledge of water radiolysis is incomplete. Each year significant discoveries involving new transient species are made, discoveries made possible through the use of newly developed equipment and improved analytical techniques. For example, microsecond pulse radiolysis ushered in the hydrated electron, and within the past few years nanosecond and picosecond pulse radiolysis revealed its precursor, the "dry" electron. Thus by shortening the time scale of experimental observation, our goal of studying the chemistry of the primary species becomes realized. And with the development of picosecond radiolysis not only can the study of the "dry" electron be carried out, but a new area of research, the study of concentrated solutions, becomes available. Realistic systems applicable to problems in radiation biology, food processing, and photosynthesis may be investigated.

1. Status of Picosecond-pulse Radiolysis (J. W. Hunt** and E. J. Hart)

Our new high-current, L-Band (1300-MHz) Linac is being used for studies on aqueous solutions. This variable-energy accelerator with its 22-MeV electron beam energy has a peak beam intensity of 20 A for a pulse duration of 2 nsec. We are utilizing the Linac's fine-structure (77-picosec) pulses for our studies which are designed to reveal the properties of transient chemical species formed during subnanosecond time periods. These fine-structure pulses are separated by 770 picosec. Our experimental arrangement utilizes a pulsed argon or krypton laser as the analyzing light source. These light pulses are synchronized with the electron beam pulses, and changes in optical absorption are detected by a high-voltage diode with a rise time of less than 100 picosec and displayed on a sampling oscilloscope. This information is stored in a 100-channel analyzer and the data read out on an XY recorder. Figure VI.1 shows the micropulses of a 6-nanosec electron pulse. Clearly visible are eight of these fine-structure pulses. These have been obtained by measuring the Cerenkov emission from a quartz bead. Note that the five central pulses are much larger than the end ones. It is possible to operate our accelerator in the "clipped" mode, whereby only the top portions of the principal pulses are used. However, even with this "clipped" mode sufficient dose is available for the study of e_{aq}^- formation. Figure VI.2 shows the effect of irradiating triply distilled water with a beam containing 4 micropulses. The 100% transmission level on the left

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Fig. VI.1. Fine-structure Pulses of ANL Linac as Revealed by Cerenkov Emission. ANL Neg. No. 121-6684.

Fig. VI.2. Fine-structure Pulses of ANL Linac as Revealed by Hydrated Electron Absorption in Irradiated Water. ANL Neg. No. 121-8300.

precedes 4 clearly defined absorption levels associated with $\bar{e}_{aq}$ formation. The total absorption for this pulse in a 4-cm cell is approximately 50%.

The fine-structure pulses may also be observed in the transient $\bar{e}_{aq}$ absorption generated in strong acids. The rapid rise of optical absorption is immediately followed by a rapid decay in a 0.3M HClO_4 solution. By further refinement of our techniques we expect to obtain rate constants even for the more rapid decay at molar concentrations of such strong acid solutions. In the future we hope to operate our accelerator with the electron beam bunched in such a way as to extract a single fine-structure pulse. This will greatly facilitate formation and decay of transient species in irradiated systems. A principal objective of these studies is to determine the yield of $\bar{e}_{aq}$ before spur recombination reactions become appreciable. Thus a critical test of "spur" theory is imminent [3].

2. Photodissociation of an $\bar{e}_{aq}$ Complex in H_2 -saturated Solutions (C. Gopinathan,* E. J. Hart, and K. H. Schmidt)

An unstable transient species (X^-), exists in photolyzed H_2 -saturated 0.001N NaOH solutions. This species forms $\bar{e}_{aq}$ on flash photolysis only when the solution is continuously photolyzed by light capable of producing $\bar{e}_{aq}$. $\text{X}^- \xrightarrow{h\nu} \text{X} + \bar{e}_{aq}$. Species X^- has a lifetime of about 180 sec and produces $\bar{e}_{aq}$ by a light flash at wavelengths in the range from 300 down to 235 nm. Impurity ions (Mg^{++} , Ni^{++}), pH changes, increase in Na^+ concentration, and light intensity are each without effect on the concentration of $\bar{e}_{aq}$ produced by the light flash. In this system $\bar{e}_{aq}$ is produced by the steady UV light, by the photoionization of the OH^- ion. In alkaline solutions the OH^- radical simultaneously produced with $\bar{e}_{aq}$ is converted to a second $\bar{e}_{aq}$ through the intermediate formation of an H-atom by OH^- reaction with H_2 . At present we have no knowledge of the structure of this $\bar{e}_{aq}$ complex.

3. Tritiated Water (S. Gordon, E. J. Hart, and W. A. Mulac)

Because of the present controversy regarding optical emissions from cosmic-ray or γ -ray irradiated water, we have undertaken an investigation of the radiations emanating from pure $^3\text{H}_2\text{O}$. Since the maximum energy of the electrons emitted by the decay of the tritium atom is only 18 keV, Cerenkov radiation does not interfere with our spectral measurements. This has been a complicating and troublesome factor in all previous work involving γ and cosmic rays. Earlier studies on tritium water were not sensitive enough to detect the small initial photon yield

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found. At least one band is observed. The intensity of this band rises rapidly from 400 to 250 nm. There is some evidence that this band has a peak or shoulder at 250 nm. This is being studied in greater detail.

4. Role of Excited-water Molecules in Aqueous Radiation Chemistry (C. Gopinthan, E. J. Hart, and G. C. Stevens[†])

Our recent results on the pulse radiolysis of uranyl sulfate and the effect of high-pressure oxygen on $G(H_2)$ and $G(H_2O_2)$ are providing evidence that excited water participates in the reactions of irradiated water. Studies of the radiation-induced excitation of UO_2SO_4 demonstrate that its fluorescence is not caused by the Cerenkov radiation, nor by the OH radical. The characteristic three-band fluorescence of UO_2^{++} has also been observed from uranyl sulfate solutions and their frozen glasses in concentrated H_2SO_4 containing 1 Ci/ml of tritiated water. See Fig. VI.3. Increasing the activity increases the intensity of fluorescence. A possible explanation of these results is that triplet water transfers its energy to the UO_2^{++} ion to form its triplet state. Additional results supporting the role of excited water have been obtained by measuring the effect of high-pressure O_2 on $G(H_2)$ and $G(H_2O_2)$ in the Br^-O_2 system. Similarly, studies of $G(Fe^{3+})$ and $G(H_2)$ in irradiated $FeSO_4-O_2$ solutions are in progress. In this latter work, scavenging of the H-atoms by O_2 from the reaction

or of the excited water (H_2O^*) by O_2 results in higher yields of H_2O_2 and ferric ion. Excited water has often been

Fig. VI.3. Uranyl Ion Emission from 0.12 M UO_2^{++} in Concentrated Sulfuric Acid Containing 1 curie/ml of Tritiated Water. ANL Neg. No. 121-8301.

suggested as participating in the primary reactions of irradiated water. However, proof of its role has not been convincingly demonstrated. In order to provide additional data on this important topic, we are looking for reactions and products that would not be expected from the currently accepted "spur" theory. Thus, transfer of triplet water energy to molecules such as UO_2^{++} and O_2 may produce new chemical effects and alter radiation chemistry yields.

5. Oxygen Atoms (E. Bjergbakke,^{††} W. Brown, and E. J. Hart)

Molecular oxygen forms in ^{60}Co γ -ray-irradiated $FeSO_4 + CuSO_4$ solutions. Our study of the mechanism of O_2 formation in this system has ruled out HO_2 , OH , H_2O_2 , and O_2 as precursors of O_2 . In order to explain our results, "spur" O atoms were postulated as a source of O_2 with a yield, $G(O)$, of 0.02.

Oxygen atoms have been reported to form by a direct action effect in γ -ray-irradiated concentrated aqueous $NaClO_4$ solutions, but no direct experimental evidence for O atoms has been obtained in irradiated solute-free water. We have unequivocally demonstrated O atoms by making use of the reaction

and analyzing for ethylene after irradiation. And confirming the report that the ClO_4^- ion liberates O atoms, the yield of ethylene is increased an order of magnitude when 4.0M $NaClO_4$ is irradiated. Because of the possibility that the OH radical may react with cyclopentene, irradiations were also carried out with methanol, an OH scavenger. Our data, shown in Table VI.1, demonstrate that 0.3M CH_3OH , which is capable of reducing the OH attack on cyclopentene by a factor of twenty, lowers the ethylene yield by only a factor of two. Furthermore, the relative effect of the methanol in lowering the ethylene yield is identical in the presence and absence of 4.0M $NaClO_4$. Although the yield of O atoms is small, the significance of this yield to the radiolysis of water is great since it reveals the contribution of the γ -ray-induced photodissociation of water to produce 3P , 1S , or 1D oxygen atoms.

TABLE VI.1. Ethylene Formation in Irradiated Aqueous 1.5 mM Cyclopentene Solutions

Additive	A	B	C	D
CH_3OH M	-	0.3	-	0.3
$NaClO_4$ M	-	-	4.0	4.0
$G(C_2H_4)$	0.00233	0.00093	0.0219	0.0095
	$B/A = 0.40$		$D/C = 0.43$	

[†]Postdoctoral appointee, London University, London, England.

^{††}Danish AEC Laboratories, Risø, Denmark (collaborative work).

6. *Nature of the Species Released on the Dissolution of Irradiated NaCl* (C. Gopinathan, E. J. Hart, and P. S. Damle*)

The emission of light during the dissolution of irradiated salt, such as NaCl, NaBr, and KBr, in water has been known for more than a decade. This phenomenon has recently been termed "aquoluminescence." Although probably not associated with the emission of light, e_{aq}^- has been postulated but not experimentally proved as a possible intermediate. We have studied the formation of nitrogen in N_2O aqueous solution in which irradiated NaCl is dissolved. The reaction is

and so the formation of N_2 provides evidence for e_{aq}^- formation. It is also known that the addition of e_{aq}^- scavengers diminishes the intensity of emitted light. In order to provide a more substantial foundation for the conclusion that e_{aq}^- is present in the aqueous solution from irradiated NaCl, we measured the relative rate of e_{aq}^- reactions with N_2O and with O_2 . We established that in a dilute O_2 solution the ratio of rate constants, as measured by the decline in N_2 formation with increasing O_2 concentration, is in fact the same ratio (2.8) as is obtained in γ -ray-irradiated N_2O - O_2 solutions. From this evidence we conclude that e_{aq}^- does, indeed, form from the trapped F-center. Much more interesting, however, is the result obtained in more concentrated O_2 - N_2O solutions. Under these conditions we find that the ratio $k(O_2)/k(N_2O)$ is an order of magnitude greater than that obtained in the dilute O_2 - N_2O blends. Thus a species of much greater reactivity than e_{aq}^- with O_2 is probably the precursor of e_{aq}^- . A possible interpretation of this result is that the electron-hole pair (F) possesses a transitory species (F') in the water-NaCl solution at the time of its dissolution. Our concept of the processes involved may be represented by the following reactions:

At sufficiently low O_2 concentrations F' produces only e_{aq}^- , but at higher concentrations O_2 may intercept the reaction of F' with water. After normal e_{aq}^- formation the

expected ratio of rate constants, k_4/k_3 , would be expected. Work is in progress to determine the possible role of these precursors of e_{aq}^- in irradiated water.

7. *Aqueous Oxygen Solutions* (E. J. Hart and K. H. Schmidt)

The transient species formed during the electron irradiation of aqueous alkaline-oxygen solutions are sufficiently long-lived so that their decay may be displayed on an XY recorder. Figure VI.4 shows the decay of O_2^- in an O_2 -saturated solution at pH 9.4. This decay curve was obtained on a modified double-beam Cary spectrophotometer. Our optical-absorption and electrical-conductivity studies on the effect of O_2 , H_2O_2 , and H^+ concentrations on the decay of this long-lived UV absorbing species confirms the work of previous investigators. Its spectrum and decay properties indicate that the absorbing species is probably O_2^- . An optical absorption has also been found in this spectral region in O_2 -free solutions irradiated by 75–100-krad electron pulses.

The extensive studies already made on alkaline-oxygen solutions have still not accounted for all the complex chemistry taking place in these solutions. While O_3^- is a well-established short-lived ion, a species living several seconds or even minutes has also been reported. Ozone has been ruled out as the stable intermediate observed because of its rapid decay rate at pHs in the range of 13. However, O_4^{2-} , O_2^{2-} , or O_2^- are other possible short-lived species.

Evidence is accumulating to show that O_2^- is in equilibrium with the ion, O_4^{2-} . The possible reactions are

This accounts for the first-order decay observed in these alkaline solutions.

Fig. VI.4. Decay of O_2^- at pH 9.40 in O_2 -saturated water. ANL Neg. No. 121-8299.

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8. Sulfonephthalein Dyes (E. J. Hart and B. L. Gupta*)

Although the sulfonephthalein dyes have been used as aqueous dosimeters, relatively little is known regarding the mechanisms of their decolorization. The decolorization yield is only of the order of 0.5. Previous work had shown that in aerated dyes, where the effects of e_{aq}^- are suppressed, the decolorization yield was higher than in air-free solutions.

Several hydrated-electron rate constants were measured for a number of sulfonephthalein dyes, and the absorption spectra obtained on the products of the e_{aq}^- reactions. These studies demonstrate that while the reaction of the dye with e_{aq}^- is very fast it produces little or no bleaching. On the other hand the hydroxyl radical is largely responsible for their decolorization. The reactions of the OH radical with the dyes were suppressed by carrying out the irradiations under high-pressure H_2 in alkaline solutions.

9. Aqueous Methane Solutions (E. J. Hart and G. C. Stevens)

The CH_3 and C_2H_5 radicals and CH_3OH have been identified as products of CH_4 radiolysis. The OH radical alone is responsible for these products. The hydrated electron and H atom show no reaction with CH_4 , but they do react rapidly with the CH_3 radical. The absorption spectra of the CH_3 radical and also of the C_2H_5 radical have been obtained in the 210–250-nm spectral region.

10. Development of Techniques (E. J. Hart, J. W. Hunt, A. Hutton,** K. H. Schmidt, and G. C. Stevens)

During FY 1971 a UV pulse-radiolysis apparatus, using an optical split-beam technique for canceling the effect of Cerenkov radiation, was completed and tested. Transient absorption measurements during the electron pulse at wavelengths lower than 200 nm can now be run. Also completed was a high-pressure unit for carrying out pulse radiolysis and transient spectral measurements up to 75,000 psi. Preliminary measurements of the effect of hydrostatic pressure on the spectrum of e_{aq}^- confirm previous reports of a UV shift in the spectrum. Equipment is being assembled for use with our 70-picosec electron pulse. Studies already completed indicate that the fine-structure components of a 6-nsec electron pulse can be detected by absorption due to e_{aq}^- as well as by Cerenkov radiation (see above). Most radiation-chemistry experiments are carried out at atmospheric pressure, and the spectra of the transients formed are normally limited to the range above 200–220 nm. We are moving beyond these limits. In order to provide a capability extending the optical

absorption range into the limit of transmission of water, an optical pulse radiolysis system is needed to eliminate the absorption of atmospheric oxygen along the optical path. And in view of the desirability of measuring transient absorptions during the electron pulse, the elimination or canceling of the Cerenkov radiation effect is also needed. Rate-constant and spectral measurements at elevated pressures will also provide data useful in determining the structure of intermediate species.

An improved version of the existing apparatus for measuring transient conductivity changes in irradiated aqueous solutions was constructed and adapted for a Febetron 705B accelerator. The essential feature of the new apparatus, besides improved sensitivity and stability, is the extension of the time range to about 20 sec. This allows one to study long-lived charged transients such as those produced in alkaline solutions of O_2 and H_2O_2 .

B. ORGANIC RADIATION CHEMISTRY—REACTIONS IN LIQUID CARBON DIOXIDE (W. G. Brown)

The utilization of gamma-ray sources to effect chemical reactions in organic materials is severely limited by the indiscriminate nature of the high-energy interactions (shot-gun effect). To achieve more selective, and, to some degree, more controllable, chemical effects, the organic material may be exposed as a solution or suspension in a solvent which serves as the primary energy absorber and which may generate reactive species which in turn may react with solutes. Numerous examples can be cited of highly selective reactions achieved in the radiolysis of aqueous solutions. However, water is a generally poor solvent for organic materials and also has the disadvantage that both oxidizing and reducing species are produced in radiolysis. It is the purpose of the present investigation to determine if liquid carbon dioxide, as a solvent in radiolysis experiments, would be advantageous on both counts and would perhaps have practical utility for large-scale operations.

Carbon dioxide has a liquid range from -56.6 to $+31.0^\circ C$ and is known from earlier engineering studies, mainly in the Socony-Vacuum Laboratories, to have good solvent properties for a wide range of organic materials. It is also an excellent cosolvent for nonpolar organics and highly polar liquids, including water. Radiolysis of pure liquid carbon dioxide causes decomposition to carbon monoxide, oxygen, and ozone, and it is likely that free oxygen atoms are the principal reactive species. In the radiolysis of organic solutions, it is, therefore, anticipated that solubility would not be a serious limitation and that reactions due to an oxidizing species, specifically oxygen atoms, might be realized. It is also a reasonable expectation that in favorable cases reactions of an ionic nature might be initiated.

The first phase of this study has been completed. Styrene, cyclohexene, and cyclopentene have been studied, and, in all cases, the principal product is the epoxide to be

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expected from the addition of oxygen atoms across the olefinic double bond together with minor amounts of isomeric aldehydes and ketones. The concluding experiments in this demonstration relate to the radiolysis of *cis*- and *trans*-butene-2 to determine if the same stereochemistry of oxygen addition prevails as with photochemically produced oxygen atoms.

This study has necessarily required extensive development work in connection with appropriate procedures for the analysis of mixtures of isomeric epoxides, aldehydes, and ketones.

A major activity has been the preparation of ultrapure organic compounds in connection with scintillation studies being done in this Division. These studies frequently demand purity beyond that ordinarily attainable, because impurities can sometimes give rise to dramatic but spurious effects. During this time, 9-methylfluorene and pyrene have been supplied at a level of purity far beyond that hitherto available to workers in this field.

The continuation of the exploratory studies on carbon dioxide solutions next year will attempt to develop three aspects: (a) the possibility of radiolytic induction of ionic chain reactions in favorable cases, (b) a survey of oxygen atom reactions with functional groups not previously studied, and (c) demonstration of free oxygen atom production in the radiolysis of water.

Under (a), experiments are planned with solutions of isobutylene, which is known to be capable of fast ionic polymerization at low temperatures by means of conventional catalysts. Under (b), observations on many different kinds of functional groups will be under consideration with special attention to those which might provide a point to attack, in polymeric materials, for cross-linking or other modification of polymer structure. For example, if a silane function, Si-H, in a silicone is converted by oxygen atoms to a silanol function, Si-OH, cross-linking will inevitably occur. The program under (c), being undertaken in collaboration with Dr E. Hart, is a result of preliminary observations in support of the prediction by Bjergbakke and Hart that free O atoms are produced in the radiolysis of liquid water.

C PULSE RADIOLYSIS OF GASEOUS SYSTEMS

(S. Gordon, M. Sauer, W. Mulac, J. Warman,*
P. Nangia,** R. Cooper,† and G. Bullock†)

Studies on the fundamental processes occurring when gases are ionized and excited by radiation are being carried out using the technique of pulse radiolysis. The use of pulse

radiolysis has the particular advantage in gaseous systems in that one can identify the radical species and ions by their optical spectra using fast reaction techniques. The spectra of molecules in the gaseous state are better defined and show more structure than in condensed media. This enables one to correlate the spectra with the structure and energy states of the transient species produced in the radiolysis and to gain a greater insight into how these species are produced and how they react. Aside from the fundamental information to be gained by this research, the data concerning the rate constants and the reactivities of many of the species observed are of interest in allied fields. As examples, the NH and NH_2 radicals are of interest in rocket technology since hydrazine is an important rocket fuel. Reactions of the OH radical are of great interest in air-pollution studies. As a further example, the rates of recombination of electrons with ions, the absolute rate constants of electrons with various molecules, and electron thermalization times are of fundamental interest in plasma studies.

The following list describes recent developments and accomplishments, and plans for future work.

1. New Irradiation Cell (S. Gordon and W. Mulac)

A new irradiation cell was constructed for use with our Febatron 705 pulsed electron accelerator. With this cell we can study the reactions of intermediate transient species at temperatures ranging from room temperature to 250°C. This will enable us to determine activation energies for the reactions of transient species as well as to study a greater variety of gases. For example, we can now study the reactions of the OH radical produced in pure water vapor at pressures ranging from a few tenths of an atmosphere to several atmospheres and over a range of temperatures.

2. Thermalization and Reactions of Electrons (J. Warman and M. Sauer)

A microwave apparatus for detecting gaseous electrons (which was constructed and put into operation in FY 1970) was used extensively to study the reactions of electrons produced by 3-nsec pulses of X-rays from a model 706 Febatron accelerator.

Using this apparatus, a series of experiments on electron thermalization was successfully completed. The purpose of these experiments was to determine the efficiencies of a number of gases in a representative series for thermalizing electrons produced by radiation. These results have been reported in a preliminary publication [4], and a complete report on the 18 gases studied is being prepared. The results allow one to estimate the length of time necessary for the radiation-produced electrons to reach kinetic energies characteristic of the gas temperature. This is of direct interest in other pulse radiolysis studies (and radiation chemistry of gases in general) because the length of time

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necessary to thermalize the electron would be expected to affect the kinetics and/or the nature of its reactions

Also, rate constants are being studied as a function of temperature and inert-gas pressures for the reactions of electrons with various gases, using the microwave apparatus. Some of these results are in the process of publication [5]. The method is quite straightforward and reliable

3 Ion Recombination and Formation of Excited States (M. Sauer and W. Mulac)

An experimental apparatus for studying pulse radiolysis of gases (25–250°C) using the new linear accelerator has been put into operation. Using electron pulses in the range of 4–40 nsec, ion-recombination reactions with initial half-times in the range of 10 nsec and longer are being studied. We have found it possible to determine rate constants for such recombination processes by analyzing the light emitted in certain chemical systems [6]. The technique is based on the fact that when positive and negative ions (or electrons) combine, the product molecules are often in excited states. Observation of the light emitted from these excited states allow us to follow the course of the reaction. Reactions currently being examined are $e + N_2^+$, $An^- + An^+$, and $e + Nap^+$, where An and Nap represent anthracene and naphthalene, respectively.

Optical absorption spectrophotometry will be used to study further the production (by ionizing radiation) of the lowest triplet states of naphthalene and anthracene. Results already obtained indicated that these triplet states are produced directly in the ion-recombination processes ($e + Nap^+$ or $An^- + An^+$) as well as by intersystem crossing from the singlet states. A complete examination of these processes will increase our understanding of the way in which energy absorbed from the high-energy electron beam is partitioned between ionized and excited species.

4 Pulse Radiolysis of Ammonia (S. Gordon, W. Mulac, and P. Nangia)

The results of the pulse-radiolysis study of ammonia vapor at ambient temperature were analyzed. The relative contribution of ions and excited states to the formation of the NH_2 radical was determined. Absolute rate constants for the reactions between two NH_2 radicals and between an NH_2 radical and an H atom were determined at a variety of ammonia pressures. In addition, absolute rate constants for the reactions between the NH_2 and NH radicals with a number of compounds were determined [7].

5 Rate Constants for OH Radical Reactions (W. Mulac and S. Gordon)

Rate constants and activation energies for the reaction of OH radicals with various organic compounds in the gas

phase have been determined by following the change in OH optical absorption with time [8]. The effect of deuteration on the rate constant has been determined for the series CH_4 , CH_3D , CH_2D_2 , CHD_3 , and CD_4 . We plan to study the reactions of OH with inorganic gases (such as SO_2). Such reactions have importance in the chemistry of polluted atmospheres.

6 Improvements in Time Resolution (S. Gordon, W. Mulac, and M. Sauer)

Some of our current work is aimed at extending our techniques to be able to look at reactions on shorter time scales, using the 3-nsec pulse from the Febetron 706, and the fine structure pulses (about 0.1 nsec) of the new linear accelerator. It is hoped that we will be able to follow ionic reactions by means of optical absorption spectroscopy and spectrophotometry.

7 Reactions of CN Radicals (G. Bullock, R. Cooper, S. Gordon, and W. Mulac)

Rate constants and activation energies for reactions of CN radicals with various organic and inorganic gases were determined for several vibrationally excited levels of the CN radical by following the optical absorption of this radical as a function of time.*

D ION CYCLOTRON RESONANCE STUDIES OF IONIC REACTIONS IN GASEOUS SYSTEMS (L. G. Pobo, S. Caronna, and S. Wexler)

A substantial part of the radiation chemistry of gases and of the chemistry of recoil species from nuclear reactions may be interpreted in terms of elementary ion-molecule reactions. Because of the need to understand the microscopic reactions in order to understand the radiation-chemical and "hot-atom" effects in the macroscopic or bulk gaseous systems, a great amount of effort has been devoted to investigations of ionic reactions.

The recently developed technique known as ion cyclotron resonance spectroscopy has been applied in a wide variety of studies. Besides its very high sensitivity and the in situ nature of the technique that preserves precious or radioactive material, its main advantage over conventional mass spectrometry is its ability to elucidate unambiguously the mechanisms of ion-molecule reactions.

The program of research by the Chemistry Division in this area has been going forward over a few years, and during the past year the method has been used in two avenues of research—the determination of the nature of the ions formed in sequential reactions in gaseous systems

*Program of G. Bullock and R. Cooper, experimental work performed at Argonne

ionized by electron impact, and the study of the species formed as transients and their subsequent reactions following the nuclear transformation by beta decay to ^3He of tritium incorporated in specific molecules. Under the former group of investigations were those involving ionization of gaseous cyclopentane and those on nucleophilic substitution into the benzene ring in methyl bromide-benzene and methyl bromide-toluene systems. Among the β^- -decay studies were those on $\text{T}_2\text{-D}_2$ and $\text{T}_2\text{-CD}_4$ mixtures and on tritium-labeled cyclopentane. The mixtures of T_2 with substrate gases were investigated to gain knowledge of the mechanisms of "Wilzbach labeling," a simple and widely used method of tagging molecules of biological and medical interest.

1. The Ion Chemistry of Cyclopentane

In Fig. VI.5 are presented the abundances of the most common ions observed on electron impact of cyclopentane plotted as a function of the cell pressure. The shapes of the curves show that $\text{C}_5\text{H}_{10}^+$ and C_3H_6^+ are reactive primary ions, C_5H_9^+ , C_5H_8^+ , and $\text{C}_7\text{H}_{10}^+$ are secondary species, and C_4H_9^+ a tertiary ion. The principal ion-molecule reactions observed with this cyclic compound are listed in Table VI.2. Inspection of the table reveals that hydride and H_2^+ transfer and condensation reactions occur most frequently, reactions similar to those which take place in straight chain hydrocarbon compounds.

TABLE VI.2. Principal Reactions in Cyclopentane

$\text{C}_5\text{H}_{10}^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_5\text{H}_9^+ + \text{C}_5\text{H}_{11}$
$\text{C}_5\text{H}_{10}^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_4\text{H}_7^+ + \text{C}_6\text{H}_{11}$
$\text{C}_5\text{H}_9^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_4\text{H}_9^+ + \text{C}_6\text{H}_{10}$
$\text{C}_5\text{H}_9^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_5\text{H}_8^+ + \text{C}_5\text{H}_8$
$\text{C}_5\text{H}_8^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_7\text{H}_{10}^+ + \text{C}_5\text{H}_8$
$\text{C}_5\text{H}_9^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_{10}\text{H}_{17}^+ + \text{H}$
$\text{C}_5\text{H}_7^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_5\text{H}_7^+ + \text{CH}_4$
$\text{C}_5\text{H}_7^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_{10}\text{H}_{16}^+ + \text{H}$
$\text{C}_5\text{H}_7^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_8\text{H}_{11}^+ + \text{C}_5\text{H}_6$
$\text{C}_4\text{H}_7^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_4\text{H}_7^+ + \text{C}_1\text{H}_6$
$\text{C}_4\text{H}_7^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_8\text{H}_{11}^+ + \text{C}_5\text{H}_6$
$\text{C}_2\text{H}_6^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_2\text{H}_6^+ + \text{C}_5\text{H}_8$
$\text{C}_3\text{H}_4^+ + \text{c-C}_5\text{H}_{10} \rightarrow \text{C}_4\text{H}_9^+ + \text{C}_1\text{H}_7$

2. Electrophilic Substitution in Aromatic Rings

Electrophilic substitution into the benzene ring has been the subject of a voluminous literature in the organic chemistry of aromatic compounds and their radiation chemistry. Of particular interest are the existence and reactions of the so-called tropylium ion C_7H_7^+ , a

Fig. VI.5. Relative Abundances of Prominent Ions in Cyclopentane as Functions of Cell Pressure in the Ion Cyclotron Resonance Spectrometer. ANL Neg. No. 121-8429.

symmetrical seven-membered ring structure in which the carbon and hydrogen atoms are respectively indistinguishable. This species has been shown to be formed by dissociation and rearrangement following ionization of toluene and related organic molecules, and has been claimed to be the product of substitution into benzene.

Unequivocal evidence from ion cyclotron resonance studies in $\text{CH}_3\text{Br} + \text{C}_6\text{H}_6$ mixtures has shown that a C_7H_7^+ ion is formed mainly by the reactions

and

Similar studies on CH_3Br -toluene blends revealed that the homologous C_8H_9^+ ion was a prominent product, and was formed by reactions analogous to Eqs. 1-3 and by the reaction

The C_7H_7^+ reactant in Eq. 4 is a primary ion produced by ionization and dissociation of a toluene molecule. It has been shown by several other investigators to possess the tropylium structure. Since it is reactive toward CH_3Br (Eq. 4), whereas the C_7H_7^+ products of Eqs. 1-3 are not reactive with this molecule, it is concluded that these latter ionic species are not characterized by the tropylium structure.

3. Tritium Decay Studies

By storing the weak signals of mass spectra obtained with the ion cyclotron resonance spectrometer in a time-averaging computer, it has been possible to study the ion chemistry of recoil species formed following beta decay of tritium in T_2 - D_2 and T_2 - CD_4 mixtures and in tritium-labeled cyclopentane. Previous investigations by the technique of charge spectrometry demonstrated that the principal species formed on beta decay of T_2 was the ion $(\text{T}^3\text{He})^+$. However, following β decay of a tritium atom incorporated in an organic molecule, RT , the main recoil species was the radical ion R^+ , the C^3He bond having broken.

In Fig. VI.6 are shown the yields of ionic species observed in T_2 - D_2 blends as a function of the pressure of D_2 when the pressure of T_2 is held fixed at 2.4×10^{-4} torr. Note that four species are observed, T_3^+ , T_2D^+ , TD_2^+ , and D_3^+ , whose yields are strongly dependent on the relative concentrations of T_2 and D_2 . The positions and shapes of the curves are reminiscent of the abundances of radioactive

Fig. VI.6. Variations of Abundances of Ions Observed following β Decay in T_2 - D_2 Mixtures with Pressure of D_2 . The pressure of T_2 was held constant at 2.4×10^{-4} torr. ANL Neg. No. 121-6306.

nuclides in chains of nuclear decays. The behaviors of the species and other experimental evidence suggest that following the nuclear transition the triton from $(\text{T}^3\text{He})^+$ is transferred to T_2 or D_2 , and this is followed by chains of consecutive triton or deuteron transfer.

The ion chemistry of the recoil species in T_2 - CD_4 mixtures is more complex. The studies reveal that the $(\text{T}^3\text{He})^+$ transfers a triton to T_2 or CD_4 , forming T_3^+ and CD_4T^+ or CD_2T^+ , respectively. The important ionic reactions following these are

and

Reactions 5 and 6 are of considerable interest because they were previously proposed in two differing mechanisms for the Wülbach labeling of methane. The present results suggest that both reactions lead to CD_3T , the first directly and the second by electron neutralization of $\text{C}_2\text{D}_4\text{T}^+$ to give $\text{CD}_2\text{T} + \text{CD}_2$, followed by abstraction of a deuterium atom from methane by CD_2T .

Illustrative mass spectra of positive ions observed in studies on cyclopentane tagged with tritium in very high specific activity (the syntheses produced mixtures composed of $1/2$ $\text{c-C}_5\text{H}_{10}$, $1/3$ $\text{c-C}_5\text{H}_9\text{T}$ and $1/6$ $\text{c-C}_5\text{H}_8\text{T}_2$) are shown in Fig. VI.7. It is seen that at this pressure of gas in the instrument the principal species are C_4H_7^+ , $\text{C}_4\text{H}_6\text{T}^+$,

Fig VI 7 Single resonance Mass Spectra of Positive Ions in Cyclopentane after Beta Decay of Incorporated Tritium. The total pressure of gas in the spectrometer cell was 1.5×10^{-4} torr. ANL Neg No. 121 8237

$C_5H_9^+$, $C_5H_8T^+$, $C_5H_7T_2^+$, $C_6H_9^+$, $C_6H_8T^+$, $C_6H_7T_2^+$, $C_6H_{11}^+$, $C_6H_{10}T^+$, and $C_6H_9T_2^+$. Further experiments revealed that the principal ionic reactions in pure $c\text{-C}_5\text{H}_9\text{T}$ would be

It is of interest that the tritiated analogs of the neutral products of Reactions 9–12 are just those which are the products observed following nuclear decay of $c\text{-C}_5\text{H}_8\text{T}_2$ in gaseous cyclopentane at normal pressures. In a recent investigation by another group, the main product was tritiated 1-pentene (cf Eq 9), while smaller yields of tritiated butane, butene, and propylene were found.

E. PHOTOCHEMISTRY OF AROMATIC COMPOUNDS

The apparent stability of aromatic hydrocarbons and some of their heterocyclic analogs toward radiation, both ionizing and ultraviolet, has been shown to result in large part from rearomatization of highly strained products formed by molecular rearrangements from excited states of the parent compounds. Benzene, for example, is isomerized to the tricyclic benzvalene, while pyridine is converted to a very reactive bicyclic isomer. The studies summarized below include a reaction which has been shown to involve benzvalene as an intermediate, and others which appear to arise directly from singlet-excited benzene.

1. Photochemical 1,2 and 1,4 Cycloadditions of Benzene to Olefins (K. E. Wilzbach and L. Kaplan)

Ultraviolet irradiations of benzene in the presence of olefins had previously been shown [9] to yield tricyclo[3.3.0]oct-3-enes (1) by 1,3 cycloaddition. It has now been found that bicyclo[4.2.0]octa-2,4-dienes (2) and bicyclo[2.2.2]octa-2,5-dienes (3) are also formed by 1,2 and 1,4 cycloadditions.

Although quantum yields for the 1,4 additions are relatively small (~ 0.01 to 0.02), the quantum yield for 1,2 addition to tetramethylethylene is close to 0.5. The 1,2 adducts do not accumulate, however, because their high extinction coefficients favor secondary photolysis to yield either the starting materials or open-chain tetraenes. Like the 1,3 adducts, the 1,2 and 1,4 adducts appear to result from addition of singlet-excited (${}^1B_{2u}$) benzene to the ground-state olefin. With *cis* or *trans*-2-butene, the configuration of the olefin is retained in each of the cycloadducts. This stereospecificity is expected, on the basis of orbital symmetry considerations, for the 1,3 addition, but not for 1,2 or 1,4 addition. The apparent relaxation of the orbital symmetry restrictions may be attributable to the intervention of an excited complex of ${}^1B_{2u}$ benzene and ground-state olefin.

2. *The Photooxidation of Aqueous Benzene* (L. Kaplan, L. A. Wendling, and K. E. Wilzbach)

The ultraviolet irradiation of benzene in aerated water has been reported [10,11] to yield a strongly absorbing conjugated aldehyde, which was assigned the structure 4-H-pyran-2-carboxaldehyde ($C_6H_6O_2$), and was assumed to be formed by addition of a molecule of oxygen to excited benzene or a species derived therefrom. A reinvestigation of this reaction has demonstrated that the product is, in fact, 1,3-cyclopentadiene-1-carboxaldehyde (C_6H_6O), identical in every respect to the compound synthesized by reaction of sodium cyclopentadienide with ethyl formate. The photoaldehyde is derived, in a dark reaction, from benzvalene, the tricyclic photoisomer of benzene, and water. In the absence of oxygen, at pH 4 to 12, one molecule of benzvalene is oxidized to the aldehyde while another is reduced to 1,4-cyclohexadiene.

In the presence of O_2 , cyclohexadiene is not formed, but a peroxide is generated in an amount comparable to that of the aldehyde. Although the detailed mechanisms of these reactions are not yet clear, radical chain processes seem to be involved.

F. *VIBRATIONAL AND ELECTRONIC ENERGY RELAXATION IN THE XYLENES* (W. A. Noyes, Jr., and D. A. Harter)

Very complete data on the photochemistry of the three xylenes have been accumulated. Since the xylenes isomerize with yields which vary with wavelength as well as with pressure, it is possible to relate in at least a qualitative way the effect of vibrational level in excited singlet and triplet states to the rates of isomerization. It has become increasingly evident that yields of triplet-state formation are not known with any accuracy because the methods for such determinations are not theoretically sound. The investigation of these methods has provided interesting data on problems of energy transfer from different vibronic states.

The following data on the xylenes have essentially been obtained: a) isomerization yields at several wavelengths and pressures; b) fluorescence yields over the same range of conditions; c) quenching data on fluorescence as a function of added biacetyl pressure and of added oxygen pressure; d) nature of biacetyl emission following energy transfer from the xylenes; e) the effect of adding *cis*-2-butene to the xylene-biacetyl systems, thus removing triplet state xylene

molecules. The mechanism has been elaborated in some detail, and no further research in this area is currently planned.

G. *ELECTRON PARAMAGNETIC RESONANCE AND RADIATION EFFECTS IN QUARTZ* (J. A. Weil and H. H. Rinneberg)

Crystalline quartz is an important substance in numerous industrial and scientific applications. However, comparatively little has been accomplished, so far, in reaching an understanding of the microscopic defect structure arising from radiation damage and presence of foreign ions in the quartz lattice. Yet these centers affect the electroacoustical and optical quality factors, as well as the semiconductor properties, quite sensitively.

An especially suitable tool for investigation of the quartz system is electron paramagnetic resonance, which has the sensitivity and the discriminatory capability to measure details of the sites, thermal stabilities, and mobilities of defect centers in the one-ppm (center:Si) range. Under X-ray irradiation, chemical charge-transfer reactions take place in the lattice and create paramagnetic sites observable by epr. For example, aluminum ions are thought to act as donors of both electrons and cations. We have studied and identified acceptor sites in irradiated quartz; i.e., electrons and small cations migrate to such ions as germanium $4+$ and titanium $4+$ in the lattice:

We have also observed that hydrogen atoms are created in the crystal by irradiation, and that these are held fixed in several types of (as yet unknown) sites at low temperatures. As the crystal is warmed, the H atoms begin to diffuse, and it has been observed that these atoms too can act as electron donors and acceptors. Furthermore, it is clear from the epr measurements that the quartz lattice is capable of stabilizing some very unusual oxidation states of various elements. Thus Ge^{3+} is created by irradiation, and it was observed that this ion occurs as both an uncompensated form of low stability, and as a charge-compensated form which is quite stable. Similarly, it was found that the unusual state Ti^{3+} of titanium is formed and stabilized by interstitial cations.

In FY 1971, the calculations and interpretation of experimental epr spectra were completed for the GeHLi_2 center created by X irradiation. This paramagnetic center is now seen to contain Ge^{3+} , with nearby charge-compensating ions 2Li^+ and H^- . It appears to be created by diffusion of atomic hydrogen to substitutional Ge^{2+} sites in the lattice, followed by electron-transfer to form the hydride ion. These deductions have led to a possible general mode of how divalent ions can occur substitutionally for Si^{4+} ions in the quartz lattice.

The understanding of the radiation chemistry of tita-

niun in quartz also has advanced substantially in this period. It has been found that the Ti^{3+}H^+ centers occur as paired sets (A-Ti-H and B-Ti-H), formed by migration of atomic hydrogen to either of the opposite sides of the Ti^{4+} site, followed by charge-transfer. The center B-Ti-H is stable only at low temperatures, transforming into A-Ti-H above 120°K, presumably by a proton-site interchange. The spin Hamiltonians of both centers were carefully measured and, as a result, detailed information about the orbital containing the unpaired 3d¹ electron has become available.

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 $H_2-C_2D_6$ Mixtures*

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VII ACCELERATOR IMPROVEMENT*

(J. Aron, R. Benaroya, A. Jaffey, K. Johnson, T. Khoe, J. Livingood, J. Nixon, G. Parker, W. Ramler, and W. Weslowski)

The Chemistry Division has a long-standing dependence on closely coupled accelerator facilities. Indeed it is rather unusual in that an important accelerator facility is both administratively and scientifically an integral part of the Division. The 60-in cyclotron, which accelerates protons, deuterons, ^3He , and ^4He ions to maximum energies of 11.4, 22.8, 35.6, and 45.8 MeV, respectively, is perhaps the first such instrument constructed for and dedicated to research on chemical processes rather than the physical aspects alone.

Our linear electron accelerator is rather new and provides a 22-MeV, 20-ampere pulsed beam with 10-nsec pulses. Even shorter pulses of high intensity are sought by our radiation chemists, and improvements in this direction are to be expected.

A Cockcroft-Walton accelerator is also available to provide low-energy heavy ions (1–150 keV) and 14-MeV neutrons.

Research in the heavy-element region would be greatly aided by the availability of a heavy-ion accelerator, and together with the Physics Division, we have sought authorization for a new machine and greatly improved capability in this region.

In addition to the injector-sector-focused cyclotron arrangements, we are investigating the possibility of making a superconducting radiofrequency (rf) helix linear accelerator capable of bringing uranium ions up to 10 MeV per nucleon. It is a theoretically very attractive design, primarily because of the potential savings in both capital and operating costs. However, because the technology of using superconducting niobium in rf fields is still very new, we must explore several problems before the feasibility is clear. It is now evident that the treatment of the niobium surface is a critical feature (see Sect. B following).

A. ELECTRON ACCELERATOR (K. Johnson, G. Mavrogenes, G. Parker and W. Ramler)

Modifications now make possible a beam pulse of one nanosecond. A fine structure pulse was achieved experimentally. We are working on a subharmonic prebuncher which will be tandem-coupled to the existing accelerator to produce a single fine-structure pulse of 70-picosec duration, 100-Å magnitude, which will allow extension of radiation chemical experiments to the very short-time reaction region.

B. SUPERCONDUCTING HELIX RF CAVITY (R. Benaroya, A. Jaffey, K. Johnson, T. Khoe, J. Livingood, J. Nixon, and W. Ramler)

The possibility of using a helical conductor as a slow-wave structure for the acceleration of heavy ions has

led to the design and construction of a superconducting niobium helix rf cavity to investigate the partial magnitude of the axial electric fields, the Q factor, and surface impedance as a function of the treatment and surface condition of the material. Other objectives of the program are to determine fabrication problems, to gain operational experience with rf cavities at 4.2 and 1.8°K, and to determine the effect of vibration on these high-Q cavities.

The cavity has been fabricated by electron-beam welding. It consists of a cylinder 19.5 cm ID $\times$ 20 cm long, in which a helix is coaxially mounted. The helix is made of 11 turns of 1/4-in OD Niobium tubing formed to a 6.5-cm mean diameter on a 1-cm pitch. The cavity is suspended in a helium dewar, which is surrounded by two magnetic shields that reduce the ambient field to about 3 mG, minimizing the possibility of flux trapping during cool-down through the transition temperature.

Radiofrequency power is supplied by a 40-W, 100-MHz amplifier through a coupling probe. The cavity is evacuated by a high-vacuum ion pumping system. A blower pumped system is provided to reduce pressure over the liquid helium to 12.5 torr for 1.8°K operation.

The testing program is underway, and the first series of tests indicated an almost insurmountable problem in realizing a stable Nb surface. Recently, the helix had been chemically treated to produce a Nb₂O₅ surface. The results have been excellent, an axial electric field of about 2.5 MV/meter being achieved with an associated magnetic field of about 600 G and a Q of about 8×10^7 . The helix after being exposed to air is stable and these data repeatable. We must now try to understand why these tests were limited to these magnitudes. In addition, the ultimate success of this accelerator concept depends on satisfactory answers to several candid questions. These include mechanical vibrations where tolerable limits must be determined and maintained, a determination of the purity, homogeneity, and surface treatment required for the superconducting niobium, and a development of fabrication techniques for tubing (homogeneity of section, welding characteristics, etc.) which will govern the permissible limits of the design.

PUBLICATION

A High Current Electron Linac

W. Gallagher, K. Johnson, G. Mavrogenes, and W. Ramler
Presented at the Particle Accelerator Conference,
Chicago, Illinois, March 1–3, 1971

*Chapter edited by W. Ramler

VIII ISOTOPE STUDIES (WITH PARTICULAR EMPHASIS ON BIOLOGICALLY INTERESTING SYSTEMS)*

The complete replacement in living organisms of ^1H and ^{12}C by the rare, stable, heavy isotopes ^2H and ^{13}C was first achieved in this laboratory. Organisms of unusual isotopic composition, and compounds such as proteins and photosynthetic pigments, which can be isolated from them, have been demonstrated to have great utility in magnetic-resonance spectroscopy because the magnetic properties of ^1H and ^2H , and ^{12}C and ^{13}C are very different. Thus, the availability of complex compounds of biological importance with a variety of unusual isotopic compositions in conjunction with nuclear-magnetic-resonance (NMR) and electron-spin-resonance (ESR) spectroscopy provides a powerful, versatile tool for the investigation of chemical structure, molecular interactions, biosynthetic pathways, and free radical intermediates in biologically important oxidation-reduction reactions. Of the many problems now amenable to investigation, we have concentrated on (a) the role of chlorophyll in the light conversion step in photosynthesis, and (b) protein structure and function. A common factor in these investigations is the use of NMR and ESR in conjunction with biologically important compounds containing high concentrations of ^2H and ^{13}C .

A ESR OF CHLOROPHYLL AND THE NATURE OF THE PHOTOSYNTHETIC REACTION CENTER (J. J. Katz, J. R. Norris, and R. A. Uphaus)

The way in which the energy of light is converted to chemical energy is perhaps the least understood aspect of photosynthesis. Our recent ESR studies now make it possible to propose a new model for the photosynthetic reaction center.

In 1956, Commoner and co-workers [1] discovered that free radical signals could be elicited by light from photosynthetic organisms or chloroplast preparations. The most prominent of the photo-ESR signals (Signal I) was reversible, had a g value of 2.0025, very near the free electron value, and showed no hyperfine structure. The line shape was Gaussian, with a peak-to-peak line width near 7 G. It is now generally accepted that the signal originates in a special photo-oxidized chlorophyll molecule that occurs in the photosynthetic reaction center. This special chlorophyll is believed to be responsible for the unusual long-wavelength light absorption characteristic of the photosynthetic reaction center (P700). It is quite certain that the special chlorophyll has the same chemical structure as ordinary chlorophyll a , but what is otherwise special about it has so far remained mysterious, despite an immense amount of work [2].

Over the past several years we have been able to

characterize by infrared and NMR spectroscopy a number of well-defined chlorophyll a species in vitro. These include the dimer, $(\text{Chl}_2)_2$, the oligomer, $(\text{Chl}_2)_n$, and a chlorophyll-water adduct, $(\text{Chl} \cdot \text{H}_2\text{O})_n$. The latter shows a remarkably narrow, reversible ESR signal on irradiation with red light, thus species is also strongly red-shifted, with an absorption maximum at 740 nm. The monomer, dimer, and oligomer are not photoactive, however, a free radical signal can be generated in these species by chemical or electrochemical oxidation (Table VIII 1). The $(\text{Chl} \cdot \text{H}_2\text{O})_n$ species is photoactive, and irradiation with red light produces a reversible ESR photo-signal [3,4].

Although the g values of the ESR signals produced in any of these species are remarkably similar, the line widths vary greatly. Whereas the free radical engendered in monomeric chlorophyll a has a line width ~ 10 G, the photo signal in the $(\text{Chl} \cdot \text{H}_2\text{O})_n$ species has a line width nearer 1 G in width. The extreme narrowness of this signal can be explained on the basis of spin exchange, i.e., the unpaired electron is delocalized over the entire $(\text{Chl} \cdot \text{H}_2\text{O})_n$ micelle. The unpaired electron (or positive hole) migrates from chlorophyll to chlorophyll, and if the migration rate is sufficiently rapid, line narrowing results. Relative to the photosynthetic reaction center in green plants, however, the chlorophyll water adduct free radical is too red-shifted and yields too narrow a signal.

Considerations of line shape make it possible to advance a plausible interpretation of the line shape of Signal I seen in the living plant. Line shapes are most conveniently considered in terms of second moments. A straightforward theoretical analysis of the line width to be expected when a free electron is delocalized over 1, 2, ..., N identical molecules yields the relationship $\Delta H_N = \Delta H_M / \sqrt{N}$, where N = number of molecules over which delocalization occurs, ΔH_N is the expected line width for an aggregate of N members, and ΔH_M is the line width for the monomer free radical. This theory is based on second moment calculations for a Gaussian line broadened by hyperfine interactions and is supported by the excellent agreement of the calculated values with those found for dimer cations of anthracene and pyrene.

TABLE VIII 1 Line Widths (ΔH) of In Vitro Chlorophyll ESR Signals

System(a)	Solvent	λ_{max}	Oxidant(b)	ΔH (c) (G)
^1H Chl a	CH_3OH	663	$\text{FeCl}_3 \cdot \text{I}_2$	9.3 ± 0.3
^2H Chl a	CH_3OH	663	$\text{FeCl}_3 \cdot \text{I}_2$	3.8 ± 0.2
Chl_2	CCl_4	665, 678	I_2	9.0 ± 0.5
$(\text{Chl}_2)_n$	$\text{C}_{12}\text{H}_{14}$	665, 678	I_2	9.0 ± 0.5
$(\text{Chl} \cdot \text{H}_2\text{O})_n$	Film	743	Light	1.8 ± 0.2
$(\text{Chl} \cdot \text{H}_2\text{O})_n$	$\text{C}_{12}\text{H}_{14}$	743	Light	0.8 ± 0.2

(a) ^1H , ordinary hydrogen; ^2H , fully deuterated

(b) Oxidant and chlorophyll concentrations, 10^{-4} – 10^{-5} M

(c) Spectra recorded at liquid N_2 temperatures

*Chapter edited by J. J. Katz

Values for the line widths of in vivo ESR signals are shown in Table VIII.2. With remarkable accuracy, the in vivo signals are related to the line width of the monomer signal by $1/\sqrt{2}$. That is to say, delocalization of the free electron over the entity $(\text{CHH}_2\text{OCH})^+$ accounts very well for the characteristics of the in vivo signal. The optical properties of such an arrangement of two chlorophyll molecules appear to be compatible with an absorption maximum at 700 nm. The validity of these considerations is strongly reinforced by experiments with fully deuterated chlorophylls and organisms (Table VIII.2). The narrowing expected for the deuterium cases follows the $1/\sqrt{2}$ relationship as precisely as it does for the ordinary ^1H case.

We believe that the model of the photosynthetic reaction center in plants provided by this work is the first one proposed that is compatible with both the optical and ESR properties observed in photosynthetic organisms.

B. HIGH-RESOLUTION PROTON-MAGNETIC-RESONANCE STUDIES WITH ^1H - ^2H ISOTOPE HYBRID ALGAL PROTEINS (H. L. Crespi and J. J. Katz)

Proteins and enzymes constitute some of the most important molecules of chemical and biological interest. Nuclear-magnetic resonance offers a new and powerful method for the study of the fine structure of these complicated molecules. However, proteins generally are very high-molecular-weight substances that contain hundreds of hydrogen and carbon atoms, and means must be found to simplify the highly complex proton-magnetic-resonance (PMR) and ^{13}C magnetic-resonance spectra these substances normally yield in order that resonance lines can be identified. We have developed a technique, which we call isotope hybridization, to achieve this goal. Protons (^1H) can be back-incorporated into fully deuterated (^2H) proteins at known positions in the molecule either by exchange or by biosynthesis. The magnetic-resonance lines associated with these protons can then be assigned to protons in

specific molecular sites in the protein, with the desired result that conformational changes and short-range interactions at these sites in the protein molecule can then be studied. Detailed information about the folding of proteins and the binding of substrates and prosthetic groups to proteins and enzymes thus can be gathered.

In order to study deuterated and isotope hybrid proteins of biological importance, it is necessary to grow large quantities of deuterated organisms because most proteins and enzymes are present in tissues in small amounts. During the past year, our 160-liter algae growth tank has been used to produce several pounds (about 2500 g, dry weight) of fully deuterated and isotope hybrid blue-green algae. This yield was obtained by using a recycling technique for the $^2\text{H}_2\text{O}$ and only a single charge of heavy water was required. The deuterated and isotope hybrid algae have been used for the extraction, purification, and characterization of three proteins: an algal cytochrome *c*, a ferredoxin, and a flavoprotein, all of which have been used in high-resolution proton-magnetic-resonance studies.

Fully deuterated flavoprotein has a prosthetic group, flavin mononucleotide (FMN), that is tightly bound to the apoprotein moiety. However, the binding does not involve covalent bonds, so that the bound FMN can be liberated by heating the protein at 70°C with a solution of ^1H -FMN. By adding a large excess of ordinary ^1H -FMN to the solution, the ^2H -FMN of ^2H -flavoprotein can be exchanged for ^1H -FMN, and we have thus produced the isotope hybrid ^2H -flavoprotein (^1H -FMN). Figure VIII.1 shows the result of this experiment. The individual PMR lines of protein-bound ^1H -FMN are clearly visible and occur at different positions in the spectrum from ^1H -FMN itself dissolved in water. The data indicate that the FMN is well-buried in the apoprotein, and is closely associated with amino acids that have aromatic sidechains. Electron-spin-resonance studies with the semiquinone free radical generated from ^2H -flavoprotein (^1H -FMN) show that very little if any of the free-electron-spin density from the flavin free radical is delocalized into the apoprotein.

TABLE VIII.2. Observed and Calculated Line Widths (ΔH) of ESR Signal I in Plants

Organism ^a	In Vivo, ΔH (G)		R ^d
	Observed ^b	Calculated ^c	
^1H - <i>Synechococcus lividus</i>	7.1 ± 0.2	6.6 ± 0.3	1.08 ± 0.06
^1H - <i>S. lividus</i>	2.95 ± 0.1	2.7 ± 0.1	1.10 ± 0.05
^1H - <i>Chlorella vulgaris</i>	7.0 ± 0.2	6.6 ± 0.3	1.06 ± 0.05
^1H - <i>C. vulgaris</i>	2.7 ± 0.1	2.7 ± 0.1	1.00 ± 0.05
^1H - <i>Scenedesmus obliquus</i>	7.1 ± 0.2	6.6 ± 0.3	1.08 ± 0.06
^1H - <i>S. obliquus</i>	2.7 ± 0.1	2.7 ± 0.1	1.00 ± 0.05

^aWhole cells.

^bAll line shapes are Gaussian.

^cCalculated by the equation $\Delta H = 1/\sqrt{2} \cdot \Delta H_M$, where ΔH_M is the line width for monomer chlorophyll from Table VIII.1, i.e., 9.3 ± 0.3 G for ^1H -Chl *a*, 3.6 ± 0.2 for ^2H -Chl *a*.

^dRatio of $\Delta H_{\text{in vivo}}/\Delta H_M/\sqrt{2}$.

Fig VIII 1 The Proton-magnetic resonance (PMR) Spectra of ^1H flavoprotein and the Isotope Hybrid Protein ^2H flavoprotein. Top The PMR spectrum of ^1H flavoprotein. From the hundreds of protons present in this protein (molecular weight, 17,000), only a few resolved lines appear, and assignment of lines is essentially impossible. Bottom The PMR spectrum of the isotope hybrid protein ^2H -flavoprotein (^1H flavinmononucleotide). Lines 1 through 6 (3 appears as a shoulder) are generated by protein bound flavinmononucleotide (FMN). Lines a through e are generated by FMN added to the solution. It is only in the hybridized flavoprotein that the protons of the prosthetic group are amenable to study by PMR techniques. ANL Neg No. 121 7746 Rev 2

Figure VIII 2 illustrates the results of PMR analysis of ^2H -ferredoxin (^1H -phenylalanine). A fraction (about half) of a phenyl group appears as a single line. Consequently, this phenylalanine residue must occur in at least two, and probably only two, conformational states of the ferredoxin. This type of observation is highly pertinent to the long-standing question of the number of protein states that are involved in protein denaturation. In addition to the lines from the protons in the phenylalanine, Fig VIII 2 also shows resonance lines from amide protons (N^1H groups) that are "buried" in the ferredoxin. These amide groups were originally N^2H , but the deuterons have been exchanged for protons during work-up in ordinary H_2O , and these lines can now be assigned and used as PMR probes of exchange rates and conformational interchange. Studies of these and other protein isotope hybrids are continuing.

C ON-LINE ^1H FOURIER-TRANSFORM SPECTROSCOPY AT UNNATURAL ABUNDANCES (J J Katz, P P Day, and H L Crespi)

The advantages of pulse and Fourier-transform (FT) techniques for recording NMR spectra are widely appre-

ciated. The great improvement in sensitivity obtained by the use of pulse techniques permits the study of solutions much more dilute than those that can be usefully investigated by continuous-wave spectroscopy, even with time-averaging techniques. Fourier-transform methods have probably found their best use in the NMR spectroscopy of ^{13}C in compounds containing ^{13}C at the natural abundance of 1.1%. Carbon-13 spectra at natural abundance are free of ^{13}C - ^{13}C spin interactions, which results in much simpler and more readily interpretable spectra.

Because the ^1H content of many living organisms can be reduced to a very low level by cultivation in 99.8% $^2\text{H}_2\text{O}$, the same advantages that can be realized for the NMR spectroscopy of ^{13}C at natural abundance can, in principle, be contemplated for ^1H NMR. If algae are cultured in a 99% $^2\text{H}_2\text{O}$ -1% $^1\text{H}_2\text{O}$ mixture, the resulting organisms, and the compounds that can be extracted from them, will contain 1% ^1H . In these compounds the ^1H is distributed at random, and ^1H - ^1H spin interactions will be minimal, as in general any ^1H will not have another ^1H as an immediate neighbor. The ^2H atoms in the molecule will have to be decoupled from the ^1H atoms in recording an ^1H spectrum to further minimize spin-spin interactions, but this is a much easier task in terms of rf requirements than to decouple ^1H from ^{13}C . ^1H nuclei are more sensitive to detection than is ^{13}C , which is a considerable advantage when samples are limited in size, and the data-acquisition rates are considerably more rapid for equivalent concentrations of ^1H than for ^{13}C . For compounds of biological importance, then, ^1H FT spectroscopy at unnatural abundance would thus appear to merit study. Such experiments have now been carried out, and the anticipated advantages can, in fact, be realized.

The apparatus used for the experiments consists of a Varian HA-100 NMR spectrometer converted to pulse operation by a Varian V4357 pulse unit. The probe is a standard Varian 5-mm probe, double-tuned for ^1H and ^2H . The ^2H decoupling frequency is supplied by a Nuclear Magnetic Resonance Specialties SD-60 oscillator and a diode random-noise generator. Data acquisition is by a Fabri-tek 1074 unit with a 4K memory. The Fabri-tek acts as a buffer and is interfaced to the central XDS Sigma 5 computer which is used in a time-sharing mode to control a large number of experiments in the Chemistry Division at the Argonne National Laboratory. The computer is programmed to read the Fabri-tek memory, to control the pulsing, and to make all the computations. The large memory and the 32-bit word of the Sigma 5 provide a huge dynamic range, permitting the acquisition of a great number of scans where necessary.

Figure VIII 3 shows a FT spectrum of isotope hybrid ^2H -chlorophyll *a* (2% ^1H). The chlorophyll concentration is 0.095M, so that the nominal ^1H concentration is about 0.002M. The spectrum was collected in 15 min. The top spectrum is recorded without ^2H decoupling, the bottom

Fig. VIII.2. The Downfield Portion of the PMR Spectrum of the Reduced Form of ^2H -ferredoxin (^1H -phenylalanine). Lines A through L and P are slowly exchangeable "core" protons that can be introduced by exchange into the protein. Lines M, N, and O are phenyl lines from the three phenylalanine sidechains of ferredoxin, as no aromatic protons from tyrosine or histidine sidechains are present in this isotope hybrid molecule. Since line O represents only 0.5 phenyl group, the protein must be in at least two slowly interchanging conformations. ANL Neg. No. 121-8369.

spectrum is with the ^2H decoupled. The high field peaks originate predominantly from the phytyl residue in the chlorophyll. The ^1H spectrum of the phytyl moiety at unnatural abundance clearly contains much more spectral information than is the case for the ^1H spectrum collected at natural abundance (Fig. VIII.4).

Fig. VIII.3. ^1H FT Spectra of 0.095M ^2H -chlorophyll a (2% ^1H) in Benzene- d_6 . The ^2H concentration is approximately 0.0019M. The bottom spectrum is with ^2H decoupled. 1000 pulses, 7- μs pulse width, 0.9-sec pulse intervals. ANL Neg. No. 121-7993 Rev. 1.

Our preliminary results thus indicate that ^1H Fourier-transform spectroscopy at unnatural abundance has considerable promise for the study of lipids and other compounds that contain large amounts of C-H bonds that have very similar chemical-shift characteristics.

D. PREPARATION OF ISOTOPICALLY ALTERED COMPOUNDS (J. J. Katz, H. L. Crespi, H. F. DaBoll, and E. Flaumenhaft*)

Large-scale cultivation of deuterated organisms is now a routine operation on the 160-liter scale. We have extended our ^{13}C studies and have grown sizable amounts of ^{13}C organisms for ESR studies and for the extraction of ^{13}C -chlorophylls and carotenoids. Not only is the large-scale apparatus highly satisfactory for culturing isotopically altered organisms, it is also very useful for investigations of algal physiology. Blue-green algae produce CO when they synthesize photosynthetic pigments. We are studying the algal contribution to CO in the biosphere and plan to investigate utilization of CO by various algal species that we grow routinely (cf. Chapter XIX, Analytical Chemistry).

E. MOLECULAR STRUCTURE OF CHLOROPLAST XANTHOPHYLLS (H. H. Strain, J. J. Katz, B. C. Cope, Jr., H. L. Crespi, M. C. Grandolfo, A. L. Harkness, G. McDonald, W. A. Svec, F. L. Benton,** and K. Aitzetmuller†)

In addition to the green chlorophylls, all autotrophic plants contain yellow carotenoid pigments. These latter pigments include the polyene hydrocarbon β -carotene and several oxygen-containing polyenes called xanthophylls. All

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Fig VIII 4 ^1H FT Spectrum (high field portion corresponding to region marked in Fig VIII 3) of $0.004M$ ^1H phytol in CCl_4 , 768 pulses, $10\text{-}\mu\text{s}$ pulse width, 1.7 sec pulse intervals. ANL Nag No 121-8030 Rev 1

these pigments are indispensable parts of the photosynthetic apparatus

The molecular structures of a number of the more complex xanthophylls have now been worked out at Argonne. The results of these studies have revealed unique relationships among the essential chloroplast pigments and have increased our understanding of the biological systems of autotrophic organisms. Additionally, they reflect the taxonomy or evolutionary history of the plants themselves, and they reveal new aspects of Nature's delicate ecological balance.

As indicated by the large number of collaborators, progress in these investigations has resulted, to a large degree, from the hybridization of the skills and experience of specialists in diverse fields. Much of our progress in the structural determinations and in their interpretation has been the result of this collaborative interdisciplinary approach.

For most of our studies, the pigments must first be isolated in quantities of 0.01 to 0.1 g and in a state of high purity. To this end, extensive use has been made of chromatographic and crystallization methods developed at this laboratory [5]. Chemical properties have usually been determined by the formation of such derivatives as acetates, ethers, and partial hydrogenation products, all purified, in turn, by chromatography.

Much use has been made of high-resolution mass spectroscopy. The mass spectrometer (AEI, MS 902), coupled on line with a computerized data-acquisition and -analysis system, provides the molecular weight (M) and atomic composition of the pigments and their derivatives. It also provides the composition of the molecular fragments formed in the mass spectrometer. From these observations, the molecular structure of the pigments may often be deduced [6,7]. Further details of the structure are revealed by the nuclear magnetic resonance, the electronic spectra, especially in the visible region of the spectrum, and the chromatographic behavior in relation to pigments of known structure.

In chromatographic columns of powdered sugar, the carotenoid pigments of seed plants, spore-producing plants, and green algae (Chlorophyceae) separate in the sequence

Neoxanthin (most sorbed)
Violaxanthin
Lutein $\pm$ traces of zeaxanthin
 β -Carotene (nonsorbed)

Many green algae yield an additional xanthophyll, called loroxanthin, which is sorbed between neoxanthin and violaxanthin. We have now established the structure of loroxanthin, which is shown with those previously established for neoxanthin, violaxanthin, and lutein [6].

One special group of green algae, the Siphonales, contain a unique, strongly sorbed carotenoid pigment called siphonaxanthin. This xanthophyll has now been found to be a carbonyl derivative of loroxanthin, as indicated by its structural formula [7].

The yellow-green algae (Heterokontae) examined here contain three xanthophylls with an unusual structural feature. Each of these pigments, diatoxanthin, diadinoxanthin, and heteroxanthin, contains a triple bond in addition to the usual conjugated double bonds, as shown by the structural formulas [8,9].

Algae of yet another major taxonomic plant group, the Pyrrophyta or dinoflagellates, contain a unique xanthophyll called peridinin. The structural formula of this pigment, recently established by the cooperative effort of workers from three other laboratories, is described in the next section.

All these and many other investigations show that xanthophylls of differing molecular structure are included in the photosynthetic apparatus of various kinds of plants.

Particular pigments are usually restricted to plants of particular taxonomic groups. Consequently, the pathways for carotenoid synthesis were fixed very early in the evolution of the plant species known today. The diversity of the structure of the chloroplast xanthophylls relative to that of the principal carotene (β -carotene) shows that the biosynthetic pathways for xanthophylls must be very divergent from those for β -carotene. Because all these pigments are essential components of the photosynthetic apparatus, they are functionally important in the maintenance of Nature's environment and in the ecological balance of the earth.

F. THE STRUCTURE OF PERIDININ, THE CHARACTERISTIC DINOFLAGELLATE CAROTENOID

(H. H. Strain, W. A. Svec, K. Aitzetmüller, M. C. Grandolfo, and J. J. Katz*)

The principal carotenoid pigment of dinoflagellates (class, Dinophyceae; division, Pyrrophyta) is an important substance in the carbon economy and ecology of the world [10]. Like diatoms, dinoflagellates are relatively abundant and widely distributed in the oceans. Their unique xanthophyll, first isolated and named peridinin by F. Schütt in 1890 [11], has since been isolated from various marine and fresh-water species [12,13].

Peridinin is an orange-red pigment [$\lambda_{\max}$ (hexane) 455, 485 nm; (ethanol) 475 nm], Ref. 14, readily separable from other carotenoids by chromatography [14,15]. It absorbs light in a wider spectral region than does any other major chloroplast carotenoid, its absorption extending from the blue region almost to the red. It is decolorized by alkalis [13,16] and reacts slowly with acids, the absorption maxima being shifted 20 nm [13] toward shorter wavelength. Our high-resolution mass spectrometry had established the molecular formula as $C_{39}H_{50}O_7$ (630.3529) [15].

For our current collaborative studies, which were carried out cooperatively in four laboratories, peridinin with identical properties was isolated from the zooxanthellae of the Pacific Coast sea anemone [14], *Bunodactis* (now *Anthopleura*) *xanthogrammica*, from a natural bloom or red tide of dinoflagellates, greater than 98% *Gonyaulax polyedra*, and from cultures of *Cachonina niei* and *Amphidinium operculatum*. The determination of the structure necessarily involved a very substantial number of different investigations. A detailed analysis of the mass spectrum of peridinin and a number of its derivatives was most helpful. Chemical reactions and identification of some cleavage products with those of other pigments defined certain

portions of the molecule. An analysis of the proton-magnetic-resonance spectrum, taking advantage of such recently developed techniques as the chemical shift observed on addition of paramagnetic $Eu(dpm)_3$ [16] and the ^{13}C -resonance spectrum of peridinin p-bromobenzoate, was extremely important in identifying the arrangement of the hydrocarbon skeleton.

From these investigations, the structure of peridinin was established, as indicated by the structural formula. Peridinin, a natural monoacetate, is a bicyclic carotenoid. It has a C_{37} skeleton in contrast to the usual C_{40} skeletons of the common carotenoid pigments. (See Fig. VIII.5.) Two

Fig. VIII.5. The Structure of Peridinin and Other Carotenoids. Peridinin has a C_{37} skeleton. All the other carotenoids have a C_{40} skeleton. ANL Neg. No. 121-8481.

*With collaboration of H. Kjøsen, S. Norgard, and S. Låsen-Jensen, Norwegian Institute of Technology, Trondheim, Norway; F. T. Haxo, Scripps Institution of Oceanography, La Jolla, California; and P. Wegfahrt and H. Rapoport, Department of Chemistry, University of California, Berkeley, California.

terminal rings are linked by a chain differing from the usual carotenoid structure by the absence of two in-chain carbons and two branching methyl groups. One of the latter is replaced by a carboxylic function in the form of a butenolide unit, which forms part of the chromophore.

In spite of its unusual molecular structure, peridinin occurs together with carotenoids, such as β -carotene, which possess the ordinary isoprenoid C_{40} -type skeleton. The biosynthetic formation of its unusual C_{37} skeleton may be

rationalized in terms of oxidation of the 20-methyl group, which by analogy with carotenoids of the rhodospinal series [17] would result in inversion of the adjacent double bond to the *cis* configuration, thereby facilitating rearrangement and elimination of a C_3 -acetylenic moiety [18].

The variety of techniques utilized in dealing with the problem, the number of specialists involved, and the diverse location of the laboratories collaborating in the research are not the least noteworthy aspect of this research.

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IX. HIGH-TEMPERATURE CHEMISTRY*

The thermodynamic investigations of inorganic materials at high temperatures (500–2500°C) are directed towards the following objectives: (1) The thermochemistry of the evaporation processes with emphasis on precise measurements of vapor pressures and partial vapor pressures. (2) The use of the derived thermochemical quantities, partial molar enthalpies and entropies, and auxiliary information to study (a) the role of valence states and lattice defects in the solid-state chemistry of inorganic compounds and particularly nonstoichiometric phases and (b) the systematic thermochemistry of simple gaseous molecules. (3) The theoretical studies pertinent to these items including statistical thermodynamic analyses of molecular clusters in nonstoichiometric phases, equations of state of solids with defects, chemical bonding in simple molecules, systematic trends throughout the periodic table, and systematic errors. (4) Relation of equilibrium thermochemical properties to the atomic transport in solids via nonequilibrium thermodynamics.

All these objectives are parts of an integrated program intended to furnish information (a) regarding the complex processes which occur in reactor fuels in which gradients in

temperature, composition, and electrical potential can exist and (b) regarding the prediction of thermochemical properties of compounds of rare-earth, actinide, and superheavy elements.

A. APPARATUS DEVELOPMENT (R. J. Thorn, J. R. McCreary, and E. G. Rauh)

To determine the partial vapor pressures more directly via mass spectrometry, two developments have been accomplished. Collectors have been added to the Bendix time-of-flight mass spectrometer on which the effusate from a Knudsen cell is condensed. This condensate can then be analyzed by neutron activation or a similar technique. Another apparatus consisting of a vacuum balance and a quadrupole mass spectrometer has been assembled and tested to permit the simultaneous determination at the high temperatures of interest in our work of the rate of mass-effusion and a mass-spectrometric analysis of the effusate from a Knudsen cell suspended on the vacuum balance. (See Fig. IX.1.) Heretofore these two measurements, mass-effusion and mass-spectrometric analysis, have

Fig. IX.1. Equipment for the Simultaneous Measurement of Mass-effusion and Mass-spectrometric Analysis of Effusate from Knudsen Cell. ANL Neg. No. 121-7794.

*Chapter edited by: R. J. Thorn.

been accomplished separately. This second apparatus is evacuated with ion pumps through high-vacuum gate valves so that the working volume contains an extremely small number and amount of residual gaseous species and the time required to attain 10^{-8} torr can be of the order of an hour. The quadrupole mass spectrometer is contained inside one of the ion pumps which is connected to the vacuum balance via a gate valve so that the mass spectrometer is always evacuated at 10^{-8} torr or less, even when the vacuum balance is at atmospheric pressure. Thus the sensitivity of the mass spectrometer should remain constant; furthermore the unit consisting of the ion pump and the mass spectrometer evacuated to 10^{-8} torr can be readily carried from one experimental configuration to another.

To obtain atomic and molecular information pertinent to our research, we have explored the utility of two types of commercially available instruments. One of these involves photoelectron spectroscopy (ESCA), which may be used to determine the distribution of orbital electrons and therefore valence states in solids. This is especially interesting in nonstoichiometric phases of practical interest such as the U-Pu-O contemplated in a fast-breeder-reactor fuel. We are also interested in its potential use in determining orbital energies in molecules existing in vapors at high temperatures. The other device would permit the study of inelastic scattering of electrons by gaseous molecules such as UO, UO₂, and UO₃ and other actinide and rare-earth oxides with the objective of determining separately the electronic, vibrational, and rotational contributions to the entropy. Both of these are expected to furnish information pertinent to extrapolation of known thermochemical properties to the experimentally inaccessible superheavy elements.

B. LANTHANIDE AND ACTINIDE OXIDE STUDIES

(R. J. Ackermann, E. G. Rauh, and G. H. Winslow)

With the Bendix mass spectrometer, the thermodynamic behavior of the lanthanum and the cerium oxygen systems have been studied more thoroughly than heretofore. The properties measured are the congruently subliming composition, the lower phase boundary, and the free energy of formation of the gaseous monoxides. One of the reasons for establishing reliable thermochemical quantities for lanthanum monoxide is that it can be used as a reference for reactions like $\text{LaO(g)} + \text{Ac(g)} \rightarrow \text{AcO(g)} + \text{La(g)}$ to determine the properties of the actinide monoxides.

The insoluble material resulting from the reaction between thorium metal and hydrochloric acid has been examined. The results reported by Katzin [1] have been confirmed in that the product is a complex of ThO, H₂O, and HCl. Removal of the last two components and an examination by X-ray diffraction in vacuum have yielded a lattice parameter of 5.307 Å for ThO.

A model which contains Schottky defects was employed to derive an equation of state in ThO₂. As the defect

density increases with increasing temperature, the most marked effect of the additional internal pressure attributable to the defects is a drop in the bulk modulus, well below that to be expected were such defects absent, or were the energy to generate them independent of the volume. An effect on the expansion of the lattice parameter can be shown as well, and a basis is developed by which the effects of quenched-in Schottky defects on the room-temperature lattice parameter and the measured enthalpic increments can be discussed. A test of the goodness of the basic model has been made by calculating the lattice parameters of ThO₂ and UO₂ as functions of temperature from room-temperature values of the parameters and the bulk moduli and directly measured enthalpic increments, $H_T - H_{298}$. The results are equivalent to any direct measurements not specifically directed toward examining interrelations between the lattice parameter and the enthalpy on the same sample.

A critical review of the thermochemical properties of the actinide metal-oxide systems at high temperature has been accomplished.

C. SOME THEORETICAL CONSIDERATIONS

(R. J. Thorn and J. R. McCreary)

Theoretical studies based essentially on statistical thermodynamics have developed two principles useful to this program.

(1) It has been shown that the principle of unattainability can be extended to the high-temperature limit of $T = \infty$ (in addition to the usual limit of $T = 0$) and that provided the energy of a pure phase space remains bound, the entropy approaches limiting values because of the required monotonicity of $S(E)$. These limiting values for entropy correspond to situations described by various random-probability density functions of statistics or of wave mechanics. One result of this principle is that the partition function for a canonical ensemble is expressible in the form of a theorem:

$$Q(\beta) = e^{S_{\infty}} e^{-\beta E(\beta)}$$

in which $\beta = (kT)^{-1}$ and

$$S_{\infty} = \ln \int_0^{\infty} g(\epsilon) d\epsilon$$

and

$$E(\beta) = -\frac{1}{\beta} \ln \sum_r \int_0^{\infty} \epsilon^r g(\epsilon) d\epsilon \frac{(-\beta)^r}{r!}.$$

In these equations ϵ is the energy of the microstates. Thus both the preexponential factor and the exponential energy are determined by the probability density function $g(\epsilon)$. This theorem furnishes a rationale for a large number of empirical observations wherein the logarithm of the

preexponential factors is a linear function of the energy. The concepts involved in this principle should be useful in identifying the quantitative significance of atomic-electron configuration interaction in molecular orbital calculations and in furnishing a statistical thermodynamic basis for its incorporation in ab initio calculations.

(2) Although the monotonic character of $\Delta S(\Delta H)$ for a sequence of chemical reactions cannot be readily derived from the monotonic character of $S(H)$ for two pure phase spaces in thermal equilibrium, empirical studies enable one to postulate that for a sequence of reactions wherein orbital symmetry is conserved, two monotonic branches may occur: one with $d^2\Delta S/d\Delta H^2 < 0$ and one with $d^2\Delta S/d\Delta H^2 > 0$. An extension of the theory of the correlation of entropic and enthalpic effects, i.e., $\Delta S(\Delta H)$, has been applied to systematic and random errors contained in the multivariate normal distribution with linear regression. This has served to clarify the confusion concerning the

role of errors in these correlations and linear free-energy relations. In a sense this formalism represents an extension of the analysis of covariance as a test of reproducibility. This principle has been applied to an analysis of the measurements of the vapor pressure of magnesium. Further extensions can be accomplished on a statistical thermodynamic basis for the systematic variation of the thermochemical properties throughout the periodic table and thereby for extrapolations to superheavy elements, especially when the theory is supplemented by wave mechanics of chemical bonding and measurements of orbital energies by photoelectron spectroscopy. The concepts involved in these two principles have rather extensive implications with regard to theory of errors, information theory, and systems analysis in that a correlation of entropic and energetic effects represents the introduction of systematic effects on a random situation.

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*Not a member of the Chemistry Division.

X LOW-TEMPERATURE CALORIMETRY*

Heat-capacity measurements on pure elements and compounds, extended to low temperatures, are important for chemical thermodynamics. From heat-capacity data and from determinations (made in the course of the heat-capacity studies) of the temperature and heat of any phase change that occurs between low temperature and room temperature, various thermodynamic properties are obtained, such as the entropy, enthalpy increments, and Gibbs energy increments. These results can be combined with measurements of the heat of reaction (made elsewhere) in order to predict equilibrium constants and electrode potentials that may be difficult or impossible to measure directly.

In addition to giving data that are of practical value in chemical calculations, low temperature calorimetry may provide information of interest in solid-state physics and in theoretical chemistry. To cite a few samples, Schottky anomalies and λ anomalies may occur in the heat-capacity curve which can be correlated with other properties such as magnetic susceptibility or which can yield the low-lying energy levels in the solid. Solid-solid transitions may be discovered and studied. The heat-capacity curve may supplement results obtained from theoretical lattice dynamics or from inelastic neutron scattering or from velocity-of-sound measurements. Finally, a comparison of the entropy calculated from the calorimetric data with that calculated from statistical mechanics can often be used to test a molecular model or to evaluate a missing vibrational frequency or to determine a barrier hindering internal rotations in the molecules.

A CALORIMETRIC STUDY OF IODINE PENTAFLUORIDE HEAT CAPACITY BETWEEN 5 AND 350°K, ENTHALPY OF FUSION AND VAPORIZATION, STANDARD ENTROPY OF THE VAPOR, AND OTHER THERMODYNAMIC PROPERTIES (D. W. Osborne, F. Schreiner,** and H. Selig†)

As a result of a recent electron-diffraction study in another laboratory [1] the structure of IF_5 in the gaseous phase is well established. The molecule has C_{4v} symmetry, and the six atoms occupy the corners of a distorted octahedron. One fluorine atom and the iodine atom are on the fourfold axis, and the other four fluorine atoms occupy the corners of a square in a plane normal to the fourfold axis. The distance between the iodine atom and any one of the azimuthal fluorine atoms is $\text{I-F}_{\text{az}} = 1.827 \pm 0.007 \text{ \AA}$, and that between the iodine atom and

the axial fluorine atom is $\text{I-F}_{\text{ax}} = 1.867 \pm 0.003 \text{ \AA}$. The angle $\text{F}_{\text{az}}\text{-I-F}_{\text{ax}}$ is $82.2 \pm 0.3^\circ$.

Although the structure is known, there was some question about the fundamental vibrational frequencies. It was therefore decided to make low-temperature heat-capacity measurements and other measurements sufficient to determine the standard entropy of the vapor. A comparison of the entropy calculated from the thermal data with that calculated by means of statistical mechanics from the structural data and from the assignment of the vibrational frequencies affords a check of the latter.

Heat capacity measurements on a highly purified sample of iodine pentafluoride were made between 5 and 350°K in an adiabatic system. Temperatures were measured with a calibrated platinum resistance thermometer. In the course of the heat-capacity measurements, the change in the melting temperature with fraction melted was observed, and from these observations the fraction of liquid-soluble, solid-insoluble impurity was calculated to be 0.015 mol %. The triple point of pure IF_5 was found to be $282.553 \pm 0.01^\circ\text{K}$ and the melting point at 1 atm total pressure $282.571 \pm 0.01^\circ\text{K}$. The enthalpy of fusion was determined to be $11,222 \pm 11 \text{ J mol}^{-1}$.

In order to obtain the enthalpy and entropy of vaporization, the vapor pressure was measured between 282.23 and 378.20°K. The results are represented by

$$\log_{10} P_{\text{torr}} = (3090.14/T) - 6.96834 \log_{10} T + 29.02167 \quad (1)$$

Also, vapor densities were measured at two temperatures at pressures slightly below saturation, from which the second virial coefficient $B(T)$ for use in the equation of state

$$PV = RT + B(T)P \quad (2)$$

was calculated to be

$$B(T) = 15,227 + 37.62T \text{ cm}^3 \text{ mol}^{-1} \quad (3)$$

from 330 to 372°K. The variation of B with temperature was assumed to be linear with temperature for the purpose of interpolation. Further, the molal volume of the liquid was represented by

$$V = 43.093 + 0.08784T \text{ cm}^3 \text{ mol}^{-1} \quad (4)$$

The entropy of vaporization ΔS_{vap} was then calculated from the thermodynamic relation

$$\Delta S_{\text{vap}} = (V_{\text{gas}} - V_{\text{liq}})(dP/dT) \quad (5)$$

and Eqs. 1-4

The calculation of the standard entropy S° of iodine pentafluoride vapor at 330°K is summarized in Table X.1. The temperature 330°K was chosen for the comparison of entropies from thermal and molecular data because it is

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TABLE X.1. Calculation of the Standard Entropy S° of IF_5 Vapor at 330°K . in $\text{J}^\circ\text{K}^{-1}\text{mol}^{-1}$

0 to 6°K , T^3 extrapolation	0.34
6 to 282.571°K , $\int(C_p^\circ/T) dT$	175.41
Fusion at m.p., $11222/282.571$	39.71
282.571 to 330°K , $\int(C_p^\circ/T) dT$	27.07
S° of liquid at 330°K	242.53 ± 0.24
Correction to vapor pressure	0.01
ΔS_{vap} at 330°K	119.15 ± 0.60
Correction to ideal state	0.64
Compression to 1 atm	-14.80
$S^\circ(\text{IF}_5, g, 330^\circ\text{K})$ from thermal data	347.53 ± 0.84

approximately the average temperature in the range of the vapor-pressure measurements, where the slope needed in Eq. 5 can be expected to be most reliable. In this table C_p° is the heat capacity at a constant pressure of 1 atm. The correction of the entropy to the ideal state is given by

$$S_{\text{ideal}} - S_{\text{real}} = \int_0^P \left(\frac{dB}{dT} \right) dP, \quad (6)$$

where P is the vapor pressure, 128.16 torr at 330°K .

The standard entropy was also calculated from molecular data by means of statistical mechanics, on the basis of the harmonic-oscillator, rigid-rotator approximation. The moments of inertia were calculated from the electron-diffraction results of Hewitt *et al.* [1]. The symmetry number is four, and the ground electronic state is nondegenerate. The fundamental vibrational frequencies ν_1 , ν_3 , ν_7 , and ν_9 were taken from the infrared absorption spectrum of the vapor observed by Begun *et al.* [2] to be 710, 318, 640, and 372 cm^{-1} , respectively; the values for ν_2 , ν_4 , and ν_6 were taken from the Raman spectrum of the vapor observed by Selig and Holzman [3] to be 616, 604, and 276 cm^{-1} , respectively. The infrared absorption spectrum of the vapor was examined in the present work between 140 and 340 cm^{-1} , and the ν_9 band was found at $189.0 \pm 0.7\text{ cm}^{-1}$. One frequency, ν_5 , has not been observed, although it should be Raman-active; however, a force-constant calculation by Begun *et al.* [2] led to the value $\nu_5 = 257\text{ cm}^{-1}$. The vibrational modes ν_7 , ν_8 , and ν_9 are doubly degenerate, and the rest are nondegenerate.

From these molecular data the standard entropy S° of IF_5 vapor at 330°K was calculated to be $344.81 \pm 0.14\text{ J}^\circ\text{K}^{-1}\text{mol}^{-1}$. This value differs from the S° from thermal data, $347.53 \pm 0.84\text{ J}^\circ\text{K}^{-1}\text{mol}^{-1}$, by more than the sum of the estimated uncertainties. It was concluded that, in order to bring the S° calculated from molecular data into satisfactory agreement with the S° from thermal data, the unobserved frequency ν_5 must be $181 \pm 20\text{ cm}^{-1}$ rather than 257 cm^{-1} .

B. THORIUM MONOSULFIDE: HEAT CAPACITY AND THERMODYNAMIC PROPERTIES FROM 1 TO 350°K . REEVALUATION OF THE MAGNETIC ENTROPY OF URANIUM MONOSULFIDE.

(H. E. Flotow, D. W. Osborne, and R. R. Walters)

A carefully prepared sample of thorium monosulfide has been characterized and its heat capacity measured. The results have been used to calculate some thermodynamic properties of thorium monosulfide and to reevaluate the magnetic entropy of uranium monosulfide.

Thorium monosulfide and uranium monosulfide are isostructural [4], are metallic-type conductors [5,6], and are refractory substances with melting points above 2300°C [5]. The heat capacity of uranium monosulfide has been measured from 1.5 to 350°K [7]. It shows a lambda-type anomaly which peaks at 180.1°K and which is associated with a ferromagnetic transition. Since thorium monosulfide is nonmagnetic, it is of interest to compare the thermodynamic properties of these two magnetically dissimilar isostructural compounds. Further, the heat capacity of thorium monosulfide can be used as a basis to estimate the lattice heat capacity of uranium monosulfide, which in turn will permit a new, and perhaps more reliable, estimate of the magnetic entropy of uranium monosulfide than the value previously reported [7].

The sample was synthesized from 99.9+% thorium metal converted to hydride and then to the overall composition ThS , as indicated by the gain in weight, by reaction with H_2S ($<0.1\% \text{ H}_2\text{O}$, $<0.1\% \text{ CO}_2$). It was then repeatedly ground and vacuum-annealed at 1850°C to prepare a homogeneous sample. Chemical analyses showed the following impurities (in ppm): C, 88; H, 4; N, 15; O, 950. In addition, extensive chemical analyses were made for sulfur and thorium. The ratio S/Th computed from these results is 1.043 ± 0.005 . X-ray powder patterns indicated at least two impurity phases; one set of impurity lines was ascribed to Th_2S_3 , and no evidence of ThO_2 , ThOS , or ThS_2 was found. Heat-capacity values for the sample composition $\text{ThS}_{1.043}$ were corrected to $\text{ThS}_{1.0}$ by assuming the excess sulfur was present as Th_2S_3 . This correction varied from -0.4% below 35°K to -2.0% above 150°K .

The heat capacity of thorium monosulfide was determined between 1 and 22°K by an isoperibol method using a germanium resistance thermometer and between 8 and 350°K by an adiabatic method using a platinum resistance thermometer. Below 4.2°K the heat capacity is represented by

$$C_p = 3.70 \times 10^{-3} T + 3.98 \times 10^{-4} T^3 \text{ J}^\circ\text{K}^{-1}\text{mol}^{-1}, \quad (7)$$

where the first term is the conduction-electron contribution and the second term the lattice contribution to the heat capacity. Values for the thermodynamic quantities C_p° , S° , $(H^\circ - H_0^\circ)/T$, and $(G^\circ - H_0^\circ)/T$ at 298.15°K are 47.72 ± 0.24 ,

69.81 ± 0.35 , 32.60 ± 0.16 , and $-37.21 \pm 0.19 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$, respectively. The standard entropy of formation at 298.15°K , calculated from this value of S° and from the values of the entropies of thorium and sulfur in the literature, is $-15.46 \pm 0.47 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$, and an estimated value for the standard Gibbs energy of formation at 298.15°K is -430 kJ mol^{-1} . After the measurements of the enthalpy of formation currently being made in the Chemical Engineering Division are completed it will be possible to calculate a more reliable value for the Gibbs energy of formation.

For either thorium monosulfide or uranium monosulfide, the measured heat capacity at constant pressure, C_p , is given by the equation

$$C_p = C_{\text{lat}} + C_{\text{cond}} + C_{\text{mag}} + C_{\text{el}} + C_{\text{nuc}} + (C_p - C_v), \quad (8)$$

where C_{lat} is the lattice contribution to the heat capacity at constant volume, C_{cond} is the contribution of the conduction electrons, C_{mag} is the magnetic contribution, C_{el} is the contribution of excited electronic states, C_{nuc} is the nuclear contribution, and C_v is the heat capacity at constant volume. In the subsequent argument, C_{el} and C_{nuc} can be ignored, and C_{mag} is significant for the uranium monosulfide only.

The lattice heat capacity of the uranium compound at constant pressure, $C_{\text{lat}} + (C_p - C_v)$, was calculated from the heat capacity of the thorium compound and a corresponding-state calculation. For US below the Curie temperature (180.1°K), C_{cond} is $23.26 \times 10^{-3} T \text{ J}^\circ\text{K}^{-1}$

mol^{-1} , as determined from an analysis of the heat capacity below 9°K ; above the Curie temperature it was evaluated to be $13.8 \times 10^{-3} T \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$ on the basis that the calculated C_{mag} should always be positive and should approach zero at 350°K . $C_{\text{mag}}(\text{US}, T)$ was then calculated from Eq. 8, and $S_{\text{mag}}(\text{US}, T)$ was obtained from the integral $\int_0^T (C_{\text{mag}}/T) dT$. The results are shown in Fig. X.1. The magnetic entropy of uranium monosulfide associated with the ferromagnetic transition at 180.1°K determined in this manner is $8.64 \pm 0.40 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$ at 350°K . An analogous corresponding-states calculation based directly upon entropies gave a magnetic entropy for uranium monosulfide of $8.97 \pm 0.40 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$, in good agreement with the method based upon heat capacities. The average of these two entropy values is $8.8 \pm 0.4 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$; this value is significantly higher than the previous estimate [7] of $6.8 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$.

C. ENTHALPY OF FORMATION OF DISODIUM ACETYLIDE AND OF MONOSODIUM ACETYLIDE AT 298.15°K , HEAT CAPACITY OF DISODIUM ACETYLIDE FROM 5 TO 350°K , AND SOME DERIVED THERMODYNAMIC PROPERTIES
(G. K. Johnson,* E. H. Van Deventer,* J. P. Ackerman, Jr.,* W. N. Hubbard,* D. W. Osborne, and H. E. Flotow)

The thermodynamic properties of disodium acetylide, Na_2C_2 , are of interest in connection with the use of liquid sodium as a coolant in the Liquid Metal Fast Breeder Reactor Program. Na_2C_2 has been postulated as the species responsible for the transport of carbon from ferritic to austenitic steels in the coolant loop of the reactor. The present research was undertaken to obtain the basic data necessary to evaluate the standard Gibbs energy of formation of Na_2C_2 , $\Delta G_f^\circ(\text{Na}_2\text{C}_2, c, 298.15^\circ\text{K})$. The previous values for the enthalpy of formation in the literature were considered to be unreliable, and no heat-capacity data could be found.

The standard enthalpies of formation of Na_2C_2 and of the related compound NaHC_2 were determined in the Chemical Engineering Division from measurements of the enthalpies of reaction with water. The results were:

$$\Delta H_f^\circ(\text{Na}_2\text{C}_2, c, 298.15^\circ\text{K}) = 4.80 \pm 0.40 \text{ kcal mol}^{-1}$$

and

$$\Delta H_f^\circ(\text{NaHC}_2, c, 298.15^\circ\text{K}) = 23.12 \pm 0.27 \text{ kcal mol}^{-1}.$$

(1 cal = 4.184 J).

The heat capacity of Na_2C_2 was measured in the Chemistry Division between 5 and 350°K . No heat-capacity

Fig. X.1. Plot of the Magnetic Heat Capacity (solid curve) and Magnetic Entropy (dashed curve) of Uranium Monosulfide, Based on a Corresponding-states Calculation Involving the Heat Capacity of Thorium Monosulfide. ANL Neg. No. 121-7229.

*Chemical Engineering Division.

measurements were made on NaHC_2 . Thermodynamic functions of Na_2C_2 were calculated from the heat capacity at various temperatures up to 350°K . The results at 298.15°K were: heat capacity $C_p^\circ = 90.98 \pm 0.27 \text{ J } ^\circ\text{K}^{-1} \text{ mol}^{-1}$, entropy $S^\circ = 111.24 \pm 0.33 \text{ J } ^\circ\text{K}^{-1} \text{ mol}^{-1}$, enthalpy increment $H^\circ - H_0^\circ = 17,389 \pm 52 \text{ J mol}^{-1}$, and $(G^\circ - H_0^\circ)/T = -52.92 \pm 0.16 \text{ J } ^\circ\text{K}^{-1} \text{ mol}^{-1}$.

The standard entropy of formation ΔS_f° of Na_2C_2 at 298.15°K was calculated from the above value for the standard entropy of Na_2C_2 and from literature values for the standard entropies of Na and of C (graphite). The values actually used were $S^\circ(\text{Na}, 298.15^\circ\text{K}) = 12.298 \pm 0.12 \text{ cal } ^\circ\text{K}^{-1} \text{ mol}^{-1}$ [8] and $S^\circ(\text{C, graphite}, 298.15^\circ\text{K}) = 1.359 \pm 0.02 \text{ cal } ^\circ\text{K}^{-1} \text{ mol}^{-1}$ [9]. The result was $\Delta S_f^\circ(\text{Na}_2\text{C}_2, 298.15^\circ\text{K}) = -0.727 \pm 0.34 \text{ cal } ^\circ\text{K}^{-1} \text{ mol}^{-1}$.

From the standard enthalpy of formation and the standard entropy of formation, the standard Gibbs energy of formation of Na_2C_2 at 298.15°K was calculated to be $\Delta G_f^\circ(\text{Na}_2\text{C}_2, 298.15^\circ\text{K}) = 5.02 \pm 0.41 \text{ kcal mol}^{-1}$.

For reactor applications the Gibbs energy is needed at temperatures up to 1000°K . If high-temperature heat capacities or enthalpy increments were available, the calculation of the change in the Gibbs energy between 298.15°K and higher temperatures would be straightforward. Unfortunately, such data are lacking. However, an extrapolation which is probably adequate for the purpose was made in the following manner: The heat capacity of Na_2C_2 between 250 and 350°K was fitted by least squares to an equation of a form often used in high-temperature work,

$$C_p^\circ = 17.61 + 1.604 \times 10^{-2}T - 5.78 \times 10^{-4}T^2 \text{ cal } ^\circ\text{K}^{-1} \text{ mol}^{-1} \quad (9)$$

Equation 9 was assumed to hold from 250 to 1000°K . Na_2C_2 is known to undergo a transition at 546°K from body-centered tetragonal to face-centered cubic [10]. The entropy change for the transition was assumed to be the same as for CaC_2 , namely, $\Delta S_{tr} = 1.847 \text{ cal } ^\circ\text{K}^{-1} \text{ mol}^{-1}$ [11]. The enthalpy change for the transition was assumed to be $\Delta H_{tr} = T_{tr}\Delta S_{tr} = 1008 \text{ cal mol}^{-1}$ for Na_2C_2 at $T_{tr} = 546^\circ\text{K}$. With these assumptions and the values of S° , $H^\circ - H_0^\circ$, and $(G^\circ - H_0^\circ)/T$ from the low-temperature heat capacity, the thermodynamic function $(G^\circ - H_0^\circ)/T$ was calculated and tabulated in column 2 of Table X.2. Combination of the numbers in column 2 with literature values of $(G^\circ - H_0^\circ)/T$ for sodium [8] and graphite [9] and with the standard enthalpy of formation of Na_2C_2 at 298.15°K yielded the numbers in column 3, the standard Gibbs energy of formation of Na_2C_2 at T . This is the Gibbs-energy change for the reaction

TABLE X.2. Extrapolated Thermodynamic Properties of Na_2C_2

T (°K)	$\frac{G^\circ - H_0^\circ}{T}$ (cal °K ⁻¹ mol ⁻¹)	ΔG_f° (kcal mol ⁻¹)	K_f
400	27.46	5.13 ± 0.5	1.57×10^{-3}
500	29.18	5.40 ± 0.5	4.36×10^{-3}
600	31.46	5.43 ± 0.6	1.05×10^{-2}
700	33.76	5.35 ± 0.7	2.14×10^{-2}
800	36.00	5.20 ± 0.8	3.80×10^{-2}
900	38.15	4.96 ± 0.9	6.25×10^{-2}
1000	40.24	4.62 ± 1.0	9.78×10^{-2}

with each of the substances in its standard state, that is, the state stable at 1 atm total pressure at the temperature in column 1. Thus, the standard state for sodium is the liquid at temperatures above 370.98°K . The standard state for Na_2C_2 is the body-centered tetragonal crystal below 546°K and the face-centered cubic crystal above 546°K .

The positive values of ΔG_f° for all temperatures between 400 and 1000°K mean that solid Na_2C_2 cannot be formed from liquid sodium and graphite in this temperature range. However, it is thermodynamically possible for a solution of Na_2C_2 to be formed in accordance with

and the equilibrium constant K_f for this reaction is given by

$$\log_{10} K_f = -\frac{\Delta G_f^\circ}{RT \ln 10}, \quad (12)$$

where R is the gas constant. Values of the equilibrium constant calculated from Eq. 12 are given in column 4 of Table X.2. The estimated uncertainties in ΔG_f° cause the values of K_f to be uncertain by a factor of 1.8 at 400°K and by a factor of 1.5 at 1000°K .

The equilibrium constant is related to the activities of Na and of Na_2C_2 by

$$K_f = \frac{a_{\text{Na}_2\text{C}_2}}{a_{\text{Na}}^2}. \quad (13)$$

If Na_2C_2 is not dissociated in liquid sodium solution, the activity of Na_2C_2 is given by the relation

$$a_{\text{Na}_2\text{C}_2} = \frac{x}{x_{\text{sat}}}, \quad (14)$$

where x is the mole fraction of Na_2C_2 when reaction 11 is at equilibrium, and x_{sat} is the mole fraction of Na_2C_2 when the following reaction is at equilibrium:

Since the solution is very dilute, $a_{\text{Na}} \approx 1$. Therefore we have

$$x = x_{\text{sat}} K_f \quad (16)$$

The values of x_{sat} needed for further calculations are being measured in the Chemical Engineering Division

D XENON TETRAFLUORIDE HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS FROM 5 TO 350°K RECONCILIATION OF THE ENTROPIES FROM MOLECULAR AND THERMAL DATA
(D W Osborne, F Schreiner, H E Flotow, and J G Malm)

The heat capacity of xenon tetrafluoride, XeF_4 , was measured by Johnston *et al* [12] from 20 to 300°K, and they calculated the entropy of solid XeF_4 to be $35.0 \pm 1.0 \text{ cal}^\circ\text{K}^{-1} \text{ mol}^{-1}$ or $146.4 \pm 4.2 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$ at 298.15°K. Schreiner *et al* [13] used this entropy plus the entropies of sublimation and compression derived from vapor-pressure measurements to obtain $305.2 \pm 10 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$ for the standard entropy of XeF_4 gas at 298.15°K. They also calculated the same quantity from the available molecular data, obtaining $316.6 \pm 1.5 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$. More recently, Tsao *et al* [14] have observed the Raman spectrum of gaseous XeF_4 , and on the basis of their data and previous infrared data they have reported a new set of fundamental vibrational frequencies for gaseous XeF_4 . Two of the low frequencies, which are important in the entropy calculations, were observed only as weak overtones. They calculated a value of $324.0 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$ for the standard entropy of gaseous XeF_4 at 298.15°K from the molecular data, which is considerably higher than the value from the thermal data.

Since the heat-capacity results of Johnston *et al* [12] were obtained on a small sample (1.8727 g) of unspecified purity, it seemed important to remeasure the heat capacity of XeF_4 on a large sample of known high purity and to extend the measurements to lower temperatures to reduce the uncertainty of extrapolation to 0°K. Therefore a very pure sample of XeF_4 (less than 0.1 mol% of XeF_2 or XeF_6) was prepared, and the heat capacity of a 65.948 g portion was measured between 5 and 350°K. The heat-capacity curve, shown in Fig X 2, had the normal sigmoid shape, except for a small irregularity near 205°K that was ascribed to a small amount of impurity. The heat-capacity results reported by Johnston *et al* [12], shown as the dotted curve in Fig X 2, agree with the present results only near 300°K and are much lower at all other temperatures. The present results are considered to be much more reliable, not only because the sample was quite pure and fairly large (thereby reducing the effect of the corrections for deviations from strictly adiabatic conditions) but also because the measurement technique is well established, having been verified by measurements on a Calommetry Conference sample of pure benzoic acid. From the present heat-capacity results and from the vapor-pressure results of

Fig X 2 Heat Capacity of Xenon Tetrafluoride at Constant Pressure. Circles show the experimental results of Osborne, Schreiner, Flotow, and Malm; a few experimental points below 30°K have been omitted to avoid overcrowding the figure. The dotted curve represents the results reported by Johnston, Filipovich, and Sheehan (Ref. 1) for $C_{p, \text{sat}}$ of xenon tetrafluoride; the correction to C_p is negligible. ANL Neg. No. 121-8307.

Schreiner *et al* [13] the standard entropy S° of XeF_4 at 298.15°K has been calculated to be $325.8 \pm 5.9 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$, as summarized in Table X 3. Since the vapor pressure at 298.15°K is only 2.55 torr, the correction for nonideality of the vapor is negligible. The agreement with S° calculated from structural data and the vibrational frequency assignment of Tsao *et al* [14], $324.0 \text{ J}^\circ\text{K}^{-1} \text{ mol}^{-1}$, is seen to be excellent and affords strong support to that assignment.

E A ^3He DILUTION REFRIGERATOR FOR HEAT-CAPACITY STUDIES (H E Flotow, M J McDermott,* and D W Osborne)

Our present apparatus does not allow heat-capacity measurements below 1°K, and in the case of uranium compounds 1.5°K is usually the lowest temperature for

TABLE X 3 Calculation of the Standard Entropy S° of XeF_4 at 298.15°K, in Units of $\text{J}^\circ\text{K}^{-1} \text{ mol}^{-1}$, from Thermal Data

0 to 6°K, T^3 extrapolation	0.10
6 to 298.15°K, $\int (C_p^\circ/T) dT$	166.90
$S^\circ(\text{XeF}_4, \text{c}, 298.15^\circ\text{K})$	167.00 ± 0.17
ΔS of sublimation	206.2 ± 5.0
ΔS of compression	47.4 ± 0.7
$S^\circ(\text{XeF}_4, \text{g}, 298.15^\circ\text{K})$ from thermal data	325.8 ± 5.9

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measurements. To provide the refrigeration necessary to cool about one mole of a uranium compound to 0.1°K or lower, a new cryogenic apparatus has been built which incorporates a ^3He dilution refrigerator capable of operation as low as 0.03°K. Figure X.3 shows the main components of the dilution refrigerator. The refrigerator is enclosed in a vacuum jacket which is immersed in a liquid-helium bath at 4.2°K. The liquid in the refrigerator is a mixture consisting of 30 mol % ^3He and 70 mol % ^4He . The main cooling process involves the circulation of 2×10^5 moles of ^3He per sec, which is evaporated preferentially from the still at 0.7°K and returned by an external pump to the condenser at 1°K. The liquid ^3He then passes

Fig. X.3. ^3He Dilution Refrigerator for Heat-capacity Measurements down to 0.03°K. The support for the specimen is not shown. The apparatus is evacuated and immersed in a ^4He bath at 4.2°K. ANL Neg. No. 121-5432 Rev. 1.

through the heat exchangers to the mixer and returns to the still through the dilute ^3He solution in the heat exchangers. The liquid helium in the mixer consists of two phases, the upper being essentially pure liquid ^3He and the lower a 6 mol % solution of ^3He in ^4He . The movement of ^3He across the phase boundary as ^3He is removed from the still causes the mixer to cool. Attached to the bottom of the mixer is a mechanical heat switch with gold-plated jaws that can be clamped to a copper wire or gold foil attached to the specimen to be cooled. The refrigerator is located between the poles of an electromagnet, so that heat-capacity measurements can be made in a magnetic field if desired.

The refrigerator has been tested and found to operate successfully down to 0.03°K. Preparations are being made to calibrate several germanium resistance thermometers between 0.05 and 30°K accurately enough for heat-capacity measurements.

The chief use of this apparatus will be to extend the heat-capacity measurements on uranium compounds to well below 1°K, in order to determine what happens to the magnetic entropy as the temperature is lowered. This information is needed for reliable extrapolations to absolute zero in calculating the entropy.

F. FUTURE HEAT-CAPACITY STUDIES (D. W. Osborne and H. E. Flotow)

In the near future, measurements will be made on Na_2UO_4 , which is of interest in the Liquid Metal Fast Breeder Reactor Program, and on XeF_2 . It is planned to make measurements on uranium disulfide, uranium trisulfide, and uranium diselenide, to study magnetic ordering in these compounds below 20°K and to obtain more reliable values for the entropy. Further studies will be made of the anomaly in the heat capacity of rhenium hexafluoride near 1°K. This anomaly, which is probably due to magnetic ordering, could not be studied down to sufficiently low temperatures in the apparatus available heretofore. Plans are being made for studies of the low-temperature heat capacity of a number of ^{242}Pu compounds. Because of the longer half-life, ^{242}Pu compounds suffer less radiation damage and can be measured to lower temperatures than ^{239}Pu compounds. Therefore, it is expected that better thermodynamic values can be obtained with ^{242}Pu . Even better results will be obtained with the longer-lived isotope ^{244}Pu , which it is hoped will soon be available in sufficient quantity for low-temperature heat-capacity work.

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Heat Capacity from 1 to 350°K and Enthalpy of Formation at 298.15 K of Uranium Diboride

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D. W. Osborne, and J. L. Settle*

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Thorium Monosulfide: Heat Capacity and Thermodynamic Properties from 1 to 350°K. Re-evaluation of the Magnetic Entropy of Uranium Monosulfide.

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J. Chem. Phys. **55**, 880–886 (1971)

The Heat Capacity of Potassium Perbromate, KBrO₄, between 5 and 350°K

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Calorimetric Study of Iodine Pentafluoride: Heat Capacity between 5 and 350°K, Enthalpy of Fusion and Vaporization, Standard Entropy of the Vapor, and Other Thermodynamic Properties

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Magnetic Anomaly in the Heat Capacity of TcF₆ at 3.12 K

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Heat Capacity, Enthalpy of Fusion, and Thermodynamic Properties of NpF₆ from 7 to 350°K

D. W. Osborne, B. Weinstock, and J. H. Burns

J. Chem. Phys. **52**, 1803–1810 (February 15, 1970)

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XI. PHYSICAL CHEMISTRY*

Physical Chemistry, as a general descriptive title, could blanket a major fraction of the research going on in the Division.

We have separated out those topics where the interest is focused on the substances being studied (e.g., Chapter I, Heavy-element Chemistry) or where the specific method of study offers a convenient method of organization (e.g., Chapter XV, Molecular Spectroscopy).

In this chapter we have in fact left only three interesting problems where the emphasis is on understanding a system. While the substances being studied are in each case interesting and important materials, and the techniques themselves develop some complexity and perhaps some novelty, the thrust of the program in each case is to go beyond either technique or substance to illuminate a principle or understand a general phenomena. The first involves research at low temperatures and the properties of liquid helium, the second the structure of liquids, more explicitly water and the modification of this water structure in solutions of electrolytes, the third the behavior of hydrogen in metal hydrides.

A. LOW-TEMPERATURE PHYSICAL CHEMISTRY

1. Quantum Fluids: Properties of Liquid Helium

(B. M. Abraham, D. W. Osborne, J. B. Ketterson,** and P. Roach**)

Much of modern physics is concerned with some aspect of the many-body problem; in particular, the calculation of properties of quantum fluids which are only weakly excited above the ground state. Well-known examples of such fluids are: electrons in metals, neutron stars, nuclear matter, and liquid helium. The simplifications introduced into the theoretical treatment by the fact that helium is neutral and isotropic makes it an ideal proving ground for the various theories. The experimentalist is also assisted by the fact that ^3He is the only Fermi system which can be held in a simple container to be probed by a variety of techniques and ^4He is the only Bose system with a finite rest mass. Further, certain theorists [1] regard ^3He - ^4He solutions as analogues to pulsars so that experiments with solutions can provide laboratory tests for theories of neutron stars. However, the temperature range for the helium systems to behave in a weakly excited manner, i.e., to be in the degenerate region, lies below 1 K. Therefore an elaborate low-temperature facility is required for investigations of liquid ^3He , ^4He , and solutions.

Although temperatures as low as 2.5 mK have been

obtained when the specific heat of cerous magnesium nitrate (CMN) was measured in order to establish certain corrections to the temperature scale [2], the minimum temperature to which we have refrigerated helium is 30 mK. During the past year one of the adiabatic demagnetization cryostats has been modified to extend the temperature range to 10 mK. Modification and testing have not yet been completed.

We have also, during the past year, determined the equation of state, $\rho(P,T)$, for liquid ^3He from the vapor pressure to 24 atm and from 35 mK to 1.2 K (ρ = density at the pressure P and absolute temperature T). This work was undertaken primarily to supply information needed to analyze a previous experiment [3]; at the same time, the temperature and pressure range was extended beyond that of work which had appeared in the literature. In addition, measurements of the compressibility below 500 mK, which were absent from the literature, have now been provided through the published account of this work [4]. An unexpected result was to find that the velocity of sound, v , exhibited a maximum, Fig. XI.1. Since v was determined by differentiating the equation of state, $v^2 = (\partial P / \partial \rho)_S$, a 0.1% error in ρ becomes magnified to greater than 1% in v . An experiment was designed and executed to measure the velocity of sound in liquid ^3He directly with an acoustic interferometer [7,8]. The maximum was confirmed, Fig. XI.2, although of smaller magnitude than obtained from the indirect measurements. At the same time the velocity was measured, the attenuation was also measured. In the hydrodynamic region the attenuation, α , is related to the viscosity, η , by the equation

$$\alpha = 2\omega^2 \eta / 3\rho v^3$$

where ω is the angular frequency and the other symbols

Fig. XI.1. The Adiabatic Sound Velocity in Liquid ^3He as a Function of Temperature and Pressure. ANL Neg. No. 121-7631 Rev. 1.

*Chapter edited by: B. M. Abraham, J. C. Hindman, and H. E. Plotow.

**Solid State Sciences Division.

Fig. XI.2. The Velocity of Sound in Liquid ^3He as a Function of Temperature. These values are determined with an acoustic interferometer. Measurements are at the vapor pressure. ANL Neg. No. 121-8205

have been defined. A measurement of the attenuation in the hydrodynamic region is then equivalent to a measurement of the viscosity. At very low temperatures the mode of sound propagation changes from a classical hydrodynamic mode to a quantum mode; the temperature at which the transition occurs varies with the frequency. No amplification will be given other than to say that the conditions for being in the hydrodynamic region have been adequately fulfilled. While the observed temperature dependence of the attenuation is in agreement with other work appearing in the literature [9], the magnitude is lower. When our attenuation results and others are normalized to higher-temperature viscosity measurements (550 mK), it is found that the temperature dependence of the viscosity below 80 mK is $T^{-2.4}$, rather than T^{-2} as expected from Fermi liquid theory. Fermi liquid theory is fairly well established, and any disagreement between theory and experiment is very disturbing. A more comprehensive investigation of acoustic transmission in liquid ^3He is being planned.

It has been established for some time [10] that theories of sound propagation in liquid ^4He which are based on Landau's model for the energy spectrum do not agree with experiment, although the higher momentum part of the spectrum has been confirmed by neutron scattering [11,12]. Recent theoretical work [13] has suggested a modification to the spectrum which could resolve the difficulty. If the modified spectrum is correct, then verification is barely within the realm of current technical capability. There is a general interest in the low-momentum end of the energy-dispersion relation in liquid ^4He among many-body theoreticians, and the dispersion relation is regarded as an important theoretical problem. Consequently, it is also an important experimental problem. We have made some preliminary attempts at measuring the dispersion but so far with ambiguous results. At the

moment there is considerable doubt of success, even though the ultrasonic capabilities at ANL are uniquely favorable.

2. The Low-temperature Scale (2–20 mK) (B. Abraham)

We have also been concerned with the temperature scale at very low temperatures which is based on the magnetic susceptibility of cerous magnesium nitrate (CMN). An earlier investigation of ours which involved comparing the specific heat of a sphere and a cylinder showed the need for a correction to the temperature scale which had long been neglected [2]. We have recently completed a series of susceptibility measurements on a compacted sphere of powdered CMN in the presence of a magnetic field applied at right angles to the measuring field. This was done in order to establish the necessary corrections to make temperature measurements in the presence of an applied magnetic field. Because of the magnetic anisotropy of CMN, the analysis becomes complicated and has not yet been completed.

B. STRUCTURE AND MOLECULAR INTERACTIONS IN THE LIQUID STATE AND IN SOLUTIONS OF ELECTROLYTES (J. C. Hindman, A. J. Zielen, M. Wood, and A. Svirnickas)

Studies on water structure and water-solute interactions have received increasing attention in recent years. This can be directly related to the fact that a knowledge of the behavior of water in a variety of systems is not only of direct concern to chemists and biologists but to those engaged in the investigation of a number of practical problems such as water desalination and pollution control. Despite the large number of new publications that appear each year, our knowledge is still fragmentary. Even relatively simple questions have not received definitive answers. Are there free water molecules in liquid water? How many hydrogen bonds are present in water at a given temperature? Is water a continuum or a mixture? To what extent is liquid water structured? Are bent and/or stretched hydrogen bonds present? In addition, there are many, more complex, problems of vital interest. For example, it is important to determine the nature of the diffusional process in water in order to determine whether osmotic transport across membranes (important in desalination) involved single water molecules or association complexes (2–3 water molecules). In biological systems, water plays a vital but little understood role in many processes. Such questions as the nature of water-macromolecule interactions, the role of water in enzymatic reactions, and, in fact, the fundamental question of the nature of the structure in cellular water and the influence of such structure on transport properties of electrolytes, all remain to be answered. Our understanding of the nature of these interactions is dependent on the degree to which we

understand the behavior of water itself. It is because of the difficulty in finding experimental methods that yield significant information, that these and many other questions remain unanswered.

The goal in our research has been to find new experimental approaches that will yield significant and useful information with respect to the nature of the equilibria and transport process in aqueous solutions. Our initial approach involved the study of nuclear magnetic chemical shifts in water [14] and water-electrolyte solutions [15]. Although it was found that a reasonable interpretation of the results for water could be given in terms of a simple model involving an equilibrium between a hydrogen-bonded "ice-like" lattice and a "monomer," the results were not satisfying since they depended essentially on a statistical model. Further, an equally satisfactory explanation of the results could be given in terms of a completely hydrogen-bonded system with bent and/or stretched bonds. The situation was similar with respect to the interpretation of the data on electrolyte solutions [15]. For 1-1 electrolyte solutions, a very satisfactory interpretation of the chemical-shift data could be given in terms of ion-solvent interactions, hydrogen-bond breaking and structural effects on the solvent. It was found, however, that data on higher charge type electrolytes could not be simply interpreted because of the existence of more than a single hydration layer.

In view of the limitations of the chemical-shift measurements, an alternative experimental approach was sought. Because it has become apparent that much of the behavior of water in diverse systems depends not only on its equilibrium behavior but also involves its kinetic properties, i.e., lifetime of states, it was decided to investigate the usefulness of relaxation-time measurements. From studies of the relaxation time for the two isotopic species, ^2H and ^{17}O , in liquid water over a wide temperature range, it was found that there were two processes involved in the relaxation [16,17]. The results were interpreted in terms of an equilibrium leading to the formation of a species which relaxed by an isotropic rotational diffusion process [17].

To gain further insight into the nature of the equilibrium and transport processes in liquid water, two further studies were made in FY 1971. One of these was an examination of the data available on self diffusion and viscous flow in water in terms of the model used for the interpretation of the spin-lattice relaxation. The rotational relaxation, the viscosity, and the diffusion are all presumed to be related through the Debye and Stokes-Einstein equations. It is found that the diffusion data are too discordant and inaccurate to allow interpretation. We have, therefore, constructed and have under test a pulse-field-gradient NMR system that we hope will allow us to make precise measurements of self diffusion coefficients over a large temperature range. It is found, on the other hand, that the viscosity data can be interpreted in terms of the

"equilibrium-relaxation" model used for the spin-lattice relaxation data with, however, significant differences. The activation energy data suggest that at a high temperature, both the rotational process and the flow process involve the same mechanism. On the other hand, analysis of the viscosity data leads to a significantly different value for the equilibrium constant leading to the formation of the relaxing species. Our tentative conclusion with respect to the reconciliation of the two sets of observations is that there is a kinetic process that leads to rotational relaxation but does not involve linear transport of the water molecules.

The second project undertaken during FY 1971 was an experimental study of the spin-lattice relaxation for ^1H in water over a large temperature range. The object of this study was to determine the diffusional contribution to the proton-relaxation process. Although analysis of the data is not complete, the preliminary results indicate that the intermolecular proton-relaxation process is not related to the self-diffusion and viscosity in the manner indicated by the Stokes-Einstein equations.

Two experimental studies on water are planned for the near future. The first is a measurement of the self-diffusion coefficient of water. The second is a study of the frequency dependency of the spin-lattice and spin-spin relaxation times. This latter study is to determine whether there is, as has been reported in the literature, a slow chemical-exchange process in water. In addition to the above, we plan to determine the rotational contribution to the T_1 process in ice. This study should provide a basis for the explanation of the apparently different relaxation mechanisms for the dielectric and diffusional processes in ice and correlation of the relaxation data for water and ice.

Eventually we would hope to extend our studies to more complex systems. One example of such a study would be an examination of the relaxation time behavior of water molecules in the primary hydration shell of an aquo complex correlated with an examination of the motional behavior of the hydration shell of a molten salt. Another area of interest is the study of the effect of nonpolar and polar organic solutes on water structure. Such studies are related to the fundamental question of the nature of structures in cellular water and the influence of such structures on cellular reactions.

C VIBRATION AND DIFFUSION OF HYDROGEN ATOMS IN METAL HYDRIDES BY NEUTRON-SCATTERING MEASUREMENTS (H. E. Flotow, J. M. Rowe, J. J. Rush,** and L. A. DeGraaf**)*

The presence of hydrogen in metals often radically changes their physical and chemical properties. Some of

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these effects can be investigated by neutron-scattering techniques. The large incoherent scattering cross section of the proton makes this method quite powerful for the investigation of the dynamics of hydrogen in transition metals [18]. The spectrum of neutrons inelastically scattered by a hydride represents the exchange of lattice vibrational quanta (phonons) between the lattice and the incident neutrons, and directly reflects the vibration spectrum of the metal hydride. The hydrides which have been studied include: YH_2 , YH_3 , YD_2 , and YD_3 ; UH_3 and UD_3 [19]; and $\text{VH}_{0.2}$, $\text{VH}_{0.4}$, $\text{VH}_{0.8}$, $\text{VH}_{1.2}$, $\text{VH}_{1.5}$, and $\text{VH}_{1.7}$ [20]. Hydrogen vibration peaks in each of these substances have been identified and the results correlated with other data obtained by techniques such as low-temperature calorimetry, infrared measurements, neutron-diffraction studies, and X-ray diffraction. Some hydrides, such as vanadium hydride, can exist in two or more crystal phases. The dynamics of the hydrogen atoms and the changes in their motional behavior that occur at phase transitions in polymorphic hydrides are related to the thermodynamic, electrical, and other physical properties of these substances. One further objective of these experiments is to investigate the diffusion-jump mechanism (and indirectly the sites occupied in the lattice) for hydrogen atoms.

During this year we completed the analysis of quasi-elastic scattering spectra measured previously for the α and β phases of vanadium hydride using an incident beam of cold neutrons ($\lambda = 4.07 \text{ \AA}$, $\text{FWHM} = 0.7 \text{ \AA}$). These spectra for $\text{VH}_{0.20}$, $\text{VH}_{0.40}$, and $\text{VH}_{0.57}$ covered a range of momentum transfers from 0.5 to $2.3 \text{ \AA}^{-1}$, and a temperature range of 23 to 250°C [21]. The analysis of the quasi-elastic peak widths versus momentum transfer was used to determine the hydrogen concentration dependence of the proton diffusion in the body-centered cubic (bcc) β phase. In addition, an activation energy of

$4570 \pm 415 \text{ J/mol}$ was derived from the temperature dependence of the hydrogen diffusion in $\text{VH}_{0.20}$. The neutron spectra for the β phase of $\text{VH}_{0.57}$ indicated an abrupt decrease in the diffusion rate at the $\alpha \rightarrow \beta$ transition. Theoretical calculations of the dependence of the neutron quasi-elastic line broadening on the momentum transfer (κ) for hydrogen diffusion between various tetrahedral and octahedral interstitial sites in the bcc lattice (α phase) were made. However, it was determined that the range of κ covered in the cold-neutron experiment was not great enough for a meaningful comparison of theory and experiment to be made. We have expanded the quasi-elastic scattering work on $\text{VH}_{0.20}$ and $\text{VH}_{0.57}$ from $\kappa = 2$ to $\kappa = 4$ using a crystal monochromator, neutron chopper time-of-flight facility at the National Bureau of Standards, Gaithersburg Site. For these measurements we used an incident neutron wavelength of $2.43 \text{ \AA}$ and studied the scattered spectra over an angular range of 45 to 106° at temperatures between 23 and 215°C . These data are presently being analyzed so that detailed comparison can be made with the theoretical predictions for various diffusion models.

The next phase of this work will include a detailed study of the neutron spectra for three tantalum hydrides: $\text{TaH}_{0.15}$, $\text{TaH}_{0.50}$, and $\text{TaH}_{0.85}$. The tantalum-hydrogen system was selected because it is generally similar to the vanadium-hydrogen system, but the lattice spacings are larger for tantalum than for vanadium. The additional investigation of the tantalum hydrides will be an important test of the theoretical predictions and may provide a more profound understanding of such metal-hydrogen systems.

Neutron studies of the vibration spectra in two crystal phases of palladium hydride are in the planning stage. A sample of very pure palladium metal has been obtained and a design for a suitable sample holder has already been completed.

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"Shape-dependent" Specific Heat of Cerous Magnesium Nitrate

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XII. INORGANIC CHEMISTRY*

The Manhattan Project signaled a renaissance of interest in inorganic chemistry in the United States. For a number of reasons such as classical inorganic problems as rare-earth separations, the synthesis and study of coordination complex compounds, and the determination of oxidation numbers of compounds with unusual oxidation states seemed less exciting in the prewar period than the search for fundamental laws of chemical behavior or the preparation of new compounds of carbon. During World War II, however, it became necessary to produce pure uranium compounds, particularly the hexafluoride, on a very large commercial scale. It also became necessary to separate plutonium, a new element with many stable oxidation states and a most complex aqueous chemistry, from most of the periodic table, and to purify it on an industrial scale to meet the most exacting standards of laboratory reagents in spite of the complications of unprecedented levels of radioactivity. These problems challenged the ingenuity of a number of scientists of diverse technical background, who quickly developed expertise in inorganic chemistry.

This renaissance has persisted in the Argonne Chemistry Division in the form of continuing research on the heavy elements (cf. Chapter I), and on material of unusual origin and interest, such as extraterrestrial substances (cf. Chapter II). It has also led to continuing interest in the techniques developed for these inorganic studies (cf. Chapter V, XIV, and XV), and in inorganic-chemical behavior under unusual conditions (cf. Chapter IX). More directly related to the early research we find work continuing in problems of separation chemistry (cf. Chapter XIII).

In this chapter we have collected the results of some research in progress within the Division, which often can trace its origin to the earliest nuclear-energy interest, but which is pursued today primarily for its contribution to the solution of problems of modern inorganic chemistry.

Fluorine chemistry, always a challenge to the inorganic chemist because fluorine is the extreme electronegative element, has long been associated with nuclear-energy laboratories. The research in fluorine chemistry has led to the development of a rich noble-gas chemistry, and while the two are still intermixed, the field of krypton, xenon, and radon chemistry offers opportunities for exciting novelty and hopefully an increased understanding of chemical-compound formation.

Finally, a number of investigations that are being conducted with less familiar compounds are not easily classified under other fields of study, and these have also been collected and included in this chapter.

A. PREPARATION, PROPERTIES, AND UTILIZATION OF REACTIVE INORGANIC FLUORIDES

Modern industrial research in fluorine chemistry was initially centered around the unique role of uranium hexafluoride in isotope separation technology, and there remains a continuing interest in anything bearing on the synthesis, purification, or more effective handling of this material. At Argonne two programs developed: One involved plutonium hexafluoride, with resulting ramifications into the synthesis and study of a great number of interesting volatile and more or less reactive fluorides; the other explored halogen fluorides as reagents for fluoride-volatility processing and led to the development of techniques for studying nonaqueous reactive solvent systems. About ten years ago, the fundamental research aspects of both programs were combined in the Chemistry Division with a commitment to continuing research with reactive fluorine compounds.

In 1962 xenon tetrafluoride was synthesized at Argonne, and a remarkably large number of scientists within the Chemistry Division contributed to the resulting development of noble-gas chemistry. Argonne was widely recognized as a world center of this research effort, and the effective collaborative support for this program available within the Laboratory was frequently cited as an example of research at national laboratories.

Argonne's continuing strength in fluorine chemistry depends less on the group primarily responsible for such research than on the broad resources of the Laboratory that can be brought to bear on problems which become of interest. These resources include facilities for molecular and nuclear-magnetic-resonance spectroscopy, for X-ray and neutron-diffraction studies, for mass spectrometry, and for thermochemical and electrochemical measurements.

Inasmuch as conventional glass apparatus is not suitable for reactive fluorine chemistry, relatively few laboratories in the world are properly equipped for even preliminary research in this field. Many of those now in operation are headed or staffed by scientists who visited Argonne, usually for a year or two, carried out research in our laboratories, and both contributed to and became familiar with the techniques that have evolved in the Argonne work. These scientists include O'Donnell in Melbourne, Selig and Shamir in Jerusalem, Plurien at Saclay in Paris, Fricc at Ljubljana in Yugoslavia, and the many English scientists with whom we have enjoyed continuing fruitful contact, particularly Peacock and Holloway, who are now at Leicester. (Obviously there are a number of major centers of fluorine chemistry research which have no such history of Argonne association.)

Since most universities find it impractical to establish

*Chapter edited by: E. H. Appelman.

facilities for research on reactive fluorides, the Argonne Chemistry Division will remain an active center for collaboration, particularly with AUA universities. Such collaboration has ranged from the synthesis of a special sample for a university scholar to joint Ph.D. thesis programs with a number of joint publications. Collaboration at the faculty level for a few weeks, a summer, or a semester are even more common. Transmission of our expertise in manipulation of reactive fluorides has also involved industrial collaboration including, of course, consultation with personnel from the fluoride-volatility processing plant at Morris, Illinois.

In the past year the thrust of research in the fluorine-chemistry group showed substantial progress in several areas.

1. Halogen Fluoride and Hydrogen Fluoride Solution Chemistry (H. H. Hyman, L. A. Quarterman, T. Surles, A. J. Perkins,* and A. I. Popov**)

Halogen- and hydrogen-fluoride solutions are of some practical interest and very great theoretical interest. The processing of hydrogen and fluoride-ion transfer, hydrogen bonding, and fluorine bridging, which plays a ubiquitous role in much solution chemistry, can often be understood most clearly from the phenomena taking place in these hard-to-handle systems.

Significant progress has been made in identifying the ionic species present in halogen-fluoride solutions and in establishing acid-base strengths. Chlorine trifluoride has been shown to behave as a weak base in bromine trifluoride, and bromine trifluoride as a slightly stronger base in hydrogen fluoride. These observations connect the generalized concepts of acids and bases to the familiar proton-transfer reactions via directly measurable ionic concentrations. The halogen-fluoride systems have long been recognized as fluoride-ion analogues of proton-transfer acid-base systems. For solvents containing hydrogen, the acid strength, or ability to donate a proton, is measured in logarithmic units: pH in aqueous systems, H_0 or related quantities in nonaqueous solvents. By studying solutions containing anhydrous-hydrogen fluoride (AHF), we can link the fluoride ion transfer scale to the H_0 scale, inasmuch as an H_0 value of -11 has been measured for AHF.

Advances in Raman spectroscopy, using laser light sources, have been particularly helpful in identifying and estimating the concentrations of ionic species in solution. For bromine trifluoride, the square planar anion BrF_4^- has strong Raman bands at 528 and 455 cm^{-1} , the intensities of which are directly proportional to the concentration of the anion. The cation, solvated BrF_2^+ , has a characteristic band

at 625 cm^{-1} . In solutions containing BrF_3 , the relative intensities of these bands will vary, depending on the other molecules present and the relative ease with which they gain or lose fluoride ions.

Infrared spectroscopic studies of these solutions, invaluable in the identification and characterization of specific ions, depend on the use of a cell with a diamond window developed here [1]. Quantitative measurements of infrared absorption bands have not, however, been as satisfactory as measurements of Raman intensities for fixing the concentrations of specific ions.

The behavior and assignments of the Raman bands observed in bromine-trifluoride systems are summarized in Table XII.1.

For the equilibrium

the equilibrium constant

$$K = \frac{(BrF_2^+)(HF_2^-)}{(BrF_3)(HF)}$$

is 2.8×10^3 over the observable range of concentration (~ 10 –90 mol % BrF_3).

The H_0 equivalent value for pure BrF_3 is estimated as -7 on the basis of the concentrations listed in Table XII.2.

For the ClF_3 - BrF_3 system the equilibrium constant for the reaction

$$K = \frac{(ClF_2^+)(BrF_4^-)}{(ClF_3)(BrF_3)}$$

is about 10^4 over a similar range of concentration.

For the ClF_3 - BrF_3 system, no interaction could be observed, and in HF - BrF_3 mixtures fluoride-ion transfer appears not to be the acid-base process taking place; in each of these systems, however, the components are miscible in all proportions.

A few additional systems will be studied in the near future, although a complete systematic analysis of all the halogen-fluoride solutions is not contemplated.

2. Vapor Density of Hydrogen Fluoride (I. Sheft)

The study of the monomer-polymer equilibrium is a classical problem in hydrogen-fluoride chemistry. Having established that significant absorption errors in metal equipment severely limited the accuracy of earlier vapor-density data, we have constructed equipment entirely of Kel-F and have obtained more reliable results. In the low temperature range, however, we have found that even Kel-F equipment has not given absorption corrections low enough or reproducible enough to prevent this factor from limiting the accuracy of the observations. The actual

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TABLE XII.1. Raman Spectrum of Liquid Bromine Trifluoride

Band Location (cm ⁻¹)	Assignment	Change in Intensity with Increasing Temperature	Change in Intensity with Addition of Acid	Change in Intensity with Addition of Base
673	$\nu_1(a_1)BrF_3$	inc		
625	$\nu_1(a_1)BrF_3^+$	dec	inc	dec
581	polymer	dec	dec	dec
531	$\nu_2(b_1)BrF_3$	inc		
528	$\nu_1(a_1)BrF_4^-$	dec	dec	inc
490	possible dimer	inc	dec	dec
455	$\nu_2(b_1)BrF_4^-$	dec	dec	inc
428	polymer	dec	dec	dec
341	$\nu_3(b_1)BrF_3$	inc		
265	$\nu_4(b_2)BrF_3$			
249	$\nu_3(b_1)BrF_4^-$		dec	inc
236	$\nu_5(a_1)BrF_3$			

TABLE XII.2. H_0 Value for BrF_3

Solution	Ratio $(HF_2^-)/HF$	H_0
Pure HF		-11
1M HF_2^- in HF	1/50	-8.4
1M HF in BrF_3	1/10	-7.7 ^a
10M HF in BrF_3	1/30	-8.1 ^a
Pure BrF_3		-7 ^a

^aEstimated.

concentration of monomer can be followed from the intensity of its rotational Raman bands. With the sensitive laser-Raman apparatus now available, we have initiated such a study, which should supplement the vapor-density data and help provide a good quantitative analysis of the monomer-polymer equilibrium. Data are still being collected, and a complete analysis of the equilibrium should be completed in 1972.

Surprisingly enough, although hydrogen fluoride is an important industrial chemical as well as a laboratory reagent of considerable interest, a number of its physical properties, such as its vapor pressure and boiling point, appear to be known only very approximately, presumably because of the impossibility of handling pure material in the apparatus of the conventional physical chemist. We hope to remedy these deficiencies in the near future.

3. Fluorination of Organics with XeF_2 (H. H. Hyman, M. J. Shaw, J. A. Weil, and R. Filler*)

A number of studies on the fluorination of aromatic compounds by XeF_2 were completed this past year.

Inasmuch as fluorine-containing organic molecules of

biological interest are attracting increasing attention in the biochemical and medical world, improved techniques for synthesizing such molecules are of considerable importance. Noble-gas fluorides may now be considered seriously as practical reagents for conventional chemistry.

An analysis of possible mechanisms for the reactions previously reported (2) has been completed. The substituent effects, the catalysis by HF, the products formed, the identification of several radical cations, molecular orbital calculations, a competition study, and the use of HCl and Cl_2 as trapping agents all lead us to suggest that xenon difluoride reacts with aromatic compounds to form a complex containing XeF_2 , HF, and C_6H_5R . This complex may either collapse to give eventually a fluoroaromatic, or it may dissociate to form a radical cation which reacts with starting material to form biphenyls and polyphenyls.

We assume that the use of xenon fluorides for the synthesis of organic molecules will become a technique employed rather routinely by organic chemists interested in the products. Our own efforts will consist primarily of collaborative arrangements aimed at helping such scientists acquire the necessary skills.

A typical experience involved a visiting scientist in a summer program who fluorinated some amino acids. He demonstrated rather effectively the ease with which a reaction can be carried out, and the difficulty encountered in successfully separating the product and interpreting the results when complicated organic molecules are involved.

4. Preparative Chemistry of Reactive Fluorides (J. G. Malm)

The preparation and characterization of reactive inorganic fluorides of the heavy metals and the noble gases are of continuing interest. Besides the many interesting basic

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physical properties that these new compounds exhibit, many of them are the strongest fluorinating agents and the most powerful oxidizing agents that are known. In turn, therefore, they can be used in searches for other new compounds.

In the past year, new methods of preparing noble-gas compounds were investigated. Large-scale preparations, 100 g or more, of pure XeF_2 , XeF_4 , and XeF_6 were made in collaborative efforts with groups measuring the heat capacity and heats of formation of these substances. Samples of the hexafluoride were also employed for structural studies involving molecular and nuclear-magnetic-resonance spectroscopy and X-ray and neutron diffraction. The interpretation of these studies is not yet entirely satisfactory, and the structure and physical properties of XeF_6 remains something of an enigma.

5. Chemistry of Nickel Fluorides (L. Stein)

Only one stable binary compound of nickel and fluorine is known—nickel difluoride, NiF_2 . However, there is some evidence for the existence of unstable higher fluorides of nickel. When the difluoride is heated for several hours in fluorine at 200°C , the color changes from yellow to brown, and the oxidizing power of the solid increases slightly. This may be due to the formation of a small amount of nickel trifluoride or tetrafluoride. Several complex fluorides of nickel(III) and (IV) are known, such as Na_3NiF_6 , K_2NiF_6 , Rb_2NiF_6 , and Cs_2NiF_6 . The nickel is stabilized in the higher-valence states by electron-transfer processes in these crystalline solids; the compounds contain NiF_6^{3-} and NiF_6^{2-} ions, as well as alkali metal ions. Recently it has been shown that solutions of these complex ions can be obtained by anodic oxidation of nickel metal in liquid hydrogen fluoride, when alkali metal ions are present. The electrochemical reactions have been studied to determine the conditions under which nickel metal is oxidized and the effect of various cations on the stability of the complex ions.

Solutions of lithium fluoride, sodium fluoride, cesium fluoride, and ammonium fluoride in hydrogen fluoride have been electrolyzed at 0 – 10°C in cells with nickel electrodes. Complex nickel ions were produced at the anode in each of the solutions, but only at voltages in excess of 4 V. Fluorine was also liberated under these conditions, but when molecular fluorine from a cylinder was bubbled through a saturated solution of nickel difluoride in hydrogen fluoride, no oxidation of the difluoride occurred. A greater oxidizing power, corresponding perhaps to atomic fluorine, is required to raise the oxidation number of nickel.

Several nickel salts were obtained by evaporating the anolyte solutions to dryness in vacuum at room temperature. Solutions containing Cs^+ ions were very stable and yielded chiefly Cs_2NiF_6 ; those containing Na^+ and

NH_4^+ ions were less stable and yielded chiefly Na_3NiF_6 and $(\text{NH}_4)_3\text{NiF}_6$, although Na_2NiF_6 and $(\text{NH}_4)_2\text{NiF}_6$ were also obtained on some occasions. All of the salts contained nickel difluoride and alkali metal or ammonium bifluoride as impurities. The solutions containing Li^+ ions were very unstable; as these solutions were evaporated to dryness, the complex nickel ions decomposed.

B. HYPOFLUOROUS ACID (E. H. Appelman and M. H. Studier)

Hypofluorous acid, HOF, has been synthesized by the reaction of gaseous fluorine with liquid or solid water at temperatures between -50 and $+20^\circ\text{C}$. This is the first time an oxyacid of fluorine has been isolated, although such acids are well known for the heavier halogens. The hypofluorous acid was first identified by time-of-flight mass spectrometry, and its identity was confirmed by the fact that the parent peak at mass 36 shifted to mass 37 when fully deuterated water was substituted for normal water.

Chemists who in the past have studied the reaction of fluorine with water have occasionally observed traces of oxidizing species that they could not identify, but these were usually taken to be impurities. In 1968, Noble and Pimentel photolyzed a mixture of fluorine and water frozen into a solid nitrogen matrix at 14 – 20°K [3]. They observed infrared absorption bands that they attributed to HOF. However, most chemists have assumed that HOF either did not exist at all or at least was too unstable to be studied under ordinary conditions.

Milligram amounts of HOF can readily be prepared by passing a stream of fluorine at low pressure over ice at -20°C . Water is removed by passing the gas stream through a trap cooled to -50°C and then through a trap cooled with dry ice. The HOF is finally caught in a trap cooled with liquid oxygen. Oxygen, OF_2 , and unreacted fluorine are pumped away in high vacuum (see Fig. XII.1).

Fig. XII.1. Preparation of HOF. ANL Neg. No. 121-7648.

HOF at low temperatures is a white solid, melting at about -117°C to a colorless liquid. Its vapor pressure is less than one torr at -79°C and about 5 torr at -64°C .

Hypofluorous acid decomposes to hydrogen fluoride and oxygen. At room temperature its half-life is generally between five and fifteen minutes, although some samples have shown much slower decomposition. It seems that the decomposition may be strongly influenced by impurities.

Because of the compound's instability, efforts to measure its infrared spectrum in the vapor phase have been unsuccessful. However, it has been possible to measure this spectrum in a low-temperature matrix obtained by codepositing the HOF with N_2 at 8°K . This work has been carried out by Howard H. Claassen and Joseph A. Goleb, in collaboration with us. The spectrum suggests that the F and OH in HOF are nearly neutral, the F-O bond being similar to the F-F bond in molecular fluorine and the O-H bond being similar to that in the OH radical. The spectrum also confirms the work of Noble and Pimentel.

Hypofluorous acid reacts rapidly with water to yield HF, H_2O_2 , and molecular oxygen. If oxidizable substances are present in the aqueous solution, they are generally taken to a higher-valence state by the HOF. Thus Ag^+ is oxidized to Ag^{2+} , and in alkaline solution bromate is oxidized to perbromate. This last reaction puts HOF with F_2 and XeF_2 as the only substances known to oxidize bromine to its +7 oxidation state (cf. Sect. C below).

These results suggest that HOF is the intermediate responsible for the oxidizing power of fluorine in aqueous solution. The reaction of fluorine with water probably proceeds through the hydrolysis

followed by the further reactions

and

C. PERBROMATE CHEMISTRY (E. H. Appelman)

Perbromates, compounds of 7-valent bromine, were synthesized at Argonne in 1968 despite numerous rationalizations of their nonexistence. Further elucidation of their properties and manner of formation remains of both theoretical and practical interest to inorganic chemists.

During the past year, a study of the formation of perbromate by oxidation of bromate with aqueous XeF_2 was completed. The results confirm the postulate that an intermediate of unusually high energy must be produced. The need to form such an intermediate may account for the failure of past attempts to prepare perbromates. The acid

fluoride of perbromic acid, perbromyl fluoride (BrO_3F), has been prepared, and we have measured its heat of formation (in cooperation with P. A. G. O'Hare and G. K. Johnson of the Chemical Engineering Division). The results partly explain why BrO_3F is much more reactive than the analogous ClO_3F .

D. AQUEOUS XENON CHEMISTRY (E. H. Appelman)

The investigation of noble-gas chemistry led to the discovery of several xenon compounds that can persist in aqueous solution as powerful oxidants. These compounds are xenon trioxide, XeO_3 , xenon difluoride, XeF_2 , and the 8-valent perxenate ion, HXeO_4^{3-} .

Oxidations with xenon trioxide liberate elemental xenon, but it is unlikely that the reaction proceeds in a single step. More probable is the transient formation of xenon compounds of intermediate oxidation state. By studying the reactions of XeO_3 , we hope to obtain information concerning such intermediates. The reactions of XeO_3 are also of practical interest, inasmuch as the compound has been suggested and occasionally used as an analytical reagent and as an oxidant in synthetic organic chemistry.

Perxenate and aqueous xenon difluoride are especially interesting because of their ability to oxidize water to molecular oxygen. There are relatively few compounds known that can do this, and the manner in which such oxidation takes place is not well understood. Studies of the reactions of perxenate and aqueous XeF_2 should shed light on this process.

During the past year, the Raman spectra of perxenate solutions have been investigated in greater detail in collaboration with H. H. Claassen and Miss Gale Downey, a participant in Argonne's Summer Student Training Project. The equipment used was considerably improved over that employed in a similar study carried out previously. As a result, the earlier conclusion that the principal perxenate ion in strongly alkaline solution is XeO_4^{2-} was found to be incorrect; the principal ion is now thought to be HXeO_4^{3-} .

A preliminary study of the reaction of XeO_3 with hydrogen peroxide has been carried out by Gregg Vandesteeg, an ACM Semester Student. The stoichiometry is variable, indicating that the XeO_3 is reduced to elemental xenon by a series of steps involving the production of unstable intermediates which may spontaneously decompose instead of reacting further with hydrogen peroxide. We intend to investigate this reaction in greater detail, making special efforts to overcome difficulties caused by the presence of impurities. Isotopic exchange studies of the reaction will also be carried out.

The study of the reaction of XeO_3 with formic acid has been completed in collaboration with Miss Regina Shiao and H. Rhodes of the University of Illinois Pharmacy Department. The reaction is complex, and the results are

not easy to interpret, but they appear to support a mechanism similar to that indicated for the reaction between XeO_3 and hydrogen peroxide.

A study of the oxidation of halates to perhalates by aqueous XeF_2 has been completed (cf. Sect. C above). The oxidant in most cases is an intermediate formed by the interaction of XeF_2 with water. The halate is oxidized to a transient intermediate that can either revert to halate or go on to form perhalate.

As soon as practical we would like to study the reaction of XeF_4 with water in more detail, in order to elucidate the mechanism by which this compound disproportionates to Xe(VI) and elemental xenon. We hope also to obtain more definite information on the existence of unstable oxycompounds of Xe(IV) and Xe(II) , which are probably formed as intermediates in the interaction of XeF_4 with water.

E. RADON CHEMISTRY (L. Stein)

Since the discovery of the chemical reactivity of the noble gases, compounds of xenon, krypton, and radon have been prepared. Work on xenon chemistry is now being carried on at many laboratories, but radon chemistry is apparently being studied only at Argonne, primarily because the 3.8-day half-life of the longest-lived radon isotope severely limits the techniques suitable for manipulating and studying compounds of this element.

The noble gases have heretofore been collected and separated by such physical methods as the selective dissolution of krypton and xenon isotopes in Freon-11 and Freon-12, and the adsorption of radon on activated charcoal. We are now looking at chemical methods for collecting radon that involve the synthesis of nonvolatile radon compounds.

Particular applications for such procedures may be found in uranium mines, in which ^{222}Rn and its radioactive daughters constitute a health hazard when present in the air at high concentrations. Radon occurs in these mines because it is a member of the uranium-238 decay chain. The radioactive gas seeps into the air from exposed veins of uranium ore and piles of broken ore, and decays with a half-life of 3.82 days, forming nonvolatile daughters that remain suspended in the air on dust or aerosol particles. These radioactive daughters constitute the primary health hazard; they deposit very readily in lung tissues and can cause lung cancer if they are inhaled at high concentrations over long periods of time. This hazard has been recognized since about 1930, and uranium mines are now extensively ventilated to reduce the concentrations of the radioelements. However, control of the radioelements by ventilation alone has proven to be difficult in many mines, particularly in the working stopes from which the ore is removed.

We have shown that elemental radon reacts with liquid halogen fluorides (ClF , ClF_3 , ClF_5 , BrF_3 , BrF_5 , and IF_7)

and with nickel salts (K_2NiF_6 and K_3NiF_6) in liquid hydrogen fluoride to form solutions of nonvolatile radon fluoride. Several small radon scrubbers with bromine trifluoride as oxidant have been assembled and tested, using synthetic mixtures of ^{222}Rn and air (2.37 to 4.46 mCi/liter, STP). These scrubbers worked very effectively indeed, accomplishing complete removal of the radon. However, the commercial feasibility of employing liquid halogen fluoride scrubbers is somewhat problematical, inasmuch as such compounds react violently with water and pose significant hazards in handling. More recently, solid complexes of halogen fluorides with antimony pentafluoride have been found to be efficient scavengers of radon, and these may be more useful for the control of radon in uranium mining.

The apparatus used in tests with liquid bromine trifluoride is shown in Fig. XII.2. For each test, ^{222}Rn was collected from a 30-mCi radium chloride solution in a metal vacuum line, purified by low-temperature distillation from trap T_1 to trap T_2 , and mixed with dry air. The mixture was then passed successively through two Kel-F test tubes, each containing 4.0 ml of liquid bromine trifluoride at room temperature. The gas was dispersed as very fine bubbles by a stainless steel frit in each tube. After leaving the second tube, the gas flowed through a third tube, which was cooled with liquid nitrogen. Any radon passing through the first two tubes without reacting with the bromine trifluoride was expected to condense in the third tube. At the conclusion of the test, the location of the radon was determined by measuring the γ emission of its daughters ^{214}Pb and ^{214}Bi . The measurements were repeated after several hours, at which time the radon and its short-lived daughters were known to be in radioactive equilibrium.

In three experiments, mixtures of 3.1, 3.2, and 1.9 mCi of radon and 0.69, 0.96, and 0.78 liters of air, respectively, were passed through the system at flow rates of 2.9 to 3.0 ml/min. Each time the radon and its daughters were

Fig. XII.2. Apparatus for Testing Removal of Radon from Air. ANL Neg. No. 121-6848.

found only in the first tube. All of the radioelements were therefore removed from the air stream with very high efficiency in the first unit of the "scrubber."

For tests of solid fluorinating reagents, the tubes containing bromine trifluoride were replaced by a single Kel-F U-tube of 1/4-in. inner diameter. This was filled with a 2- to 4-in.-long section of powdered reagent, and a layer of copper shot was added to each leg to keep the powder in place. The same test procedure was used: a mixture of radon and air was passed through the powder at room temperature and then through the tube cooled with liquid nitrogen, and the distribution of radon and daughters was determined from the γ emission.

Table XII.3 shows the results obtained with a number of solid complexes of halogen fluorides and metal fluorides at flow rates of 5.3 to 11.5 ml/min. Complexes with the strong fluoride ion acceptor (Lewis Acid) SbF_5 removed radon and daughters from air most efficiently. These complexes contain halogen fluoride cations (ClF_2^+ , BrF_2^+ , BrF_4^+ , and IF_4^+) and antimony fluoride anions (SbF_6^- and $\text{Sb}_2\text{F}_{11}^-$). The halogen fluoride cations are believed to be the reactive species in the complexes, and the reactions with radon are believed to occur as follows:

Silver difluoride, cobalt trifluoride, and the complex NOSbF_6 were also tested but failed to react with radon at room temperature.

The halogen fluoride-antimony pentafluoride compounds appear most attractive for use in large air-purification units in uranium mines; although the compounds are sensitive to moisture, they are stable in dry air and can be stored indefinitely in metal or fluorinated plastic containers. Vapor emissions from the compounds are also very low, since the dissociation pressures are below 1 torr at 25°C.

At present, radon daughters are removed from secondary (recirculated) air in uranium mines with fiber filters; the radon itself passes through the filters and continuously generates new daughters. By capturing the radon as well as the daughters in a chemical scrubber, this cycle can be ended, and the total concentration of radioelements in the air can be reduced.

The halogen fluoride-antimony pentafluoride compounds probably can also be used in gas-mask cannisters (in combination with desiccants and halogen-trapping chemicals) and in analytical devices for collecting radon samples from air.

Research with radon proceeds slowly, and much of its presumably rich chemistry remains unexplained. We expect to continue our investigations as available manpower permits.

F. INORGANIC CHEMISTRY OF URANIUM

(H. R. Hoekstra and S. Siegel)

Uranium oxide chemistry is complicated not only by the multivalence of uranium and the amphoteric nature of the element in its highest oxidation state, but also by the existence of the uranyl group and its numerous variants. The complexities of several areas of uranium oxide chemistry have been under investigation during the past year. These include (1) the crystal modifications of UO_3 , (2) the UO_3 hydrates, and (3) ternary oxide systems (i.e., chromium-uranium oxides and rare-earth-uranium oxides).

1. UO_3 Crystal Modifications (cf. Chapter XIV)

The absence of suitable crystalline material has precluded detailed structural studies on any of the six UO_3 crystal modifications except the β phase [4], although structures based on powder data have been published for α [5] and γ UO_3 [6]. The recrystallization of γ UO_3 from a ZnCl_2 melt at 600°C has enabled us to make a single-crystal study of this phase. The basic features of the structure previously derived from powder data have been confirmed, but the revised uranium-oxygen distances are in better accord with the Zachariasen bond length-bond

TABLE XII.3. Removal of Radon from Air with Solid Fluorinating Reagents

Compound	Amount of Radon (mCi)	Volume of Air (l./STP)	Percentage of Radon Removed
KBrF_4	2.8	0.76	28
CsBrF_4	2.2	0.76	7
KClF_4	4.9	0.69	19
RbClF_4	3.4	0.69	16
ClF_2SbF_5	15.0	0.69	100
BrF_2SbF_5	8.0	0.69	100
$\text{BrF}_4\text{Sb}_2\text{F}_{11}$	3.7	0.69	100
$\text{IF}_4(\text{SbF}_6)_3$	7.4	0.69	100
IF_2SbF_5	3.6	0.69	76
BrF_2TaF_5	3.0	0.69	27

length rule [7]. Additional work on α - UO_3 indicates that the generally accepted simple hexagonal unit cell for this phase is incorrect. Dehydration of crystalline $\text{H}_2\text{U}_3\text{O}_{10}$ (previously known as $\text{UO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ or $\text{H}_2\text{U}_2\text{O}_7$) to α - UO_3 , can be accomplished at $\sim 425^\circ\text{C}$ without disintegration of the material into a microcrystalline product. Unfortunately some disorder is always present to handicap structural work, but available data point to the presence of a much larger and more complex cell than is given by the Zachariasen structure [5]. Density and infrared measurements are in accord with the more complex structural picture.

2. UO_3 - H_2O System

UO_3 reacts with water under a variety of conditions to form at least three compounds; up to 8 phases have been reported but only 6 are generally accepted. Although these compounds are usually referred to as hydrates of UO_3 , infrared, magnetic resonance, and X-ray diffraction data indicate that they are more accurately formulated as $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, $\text{UO}_2(\text{OH})_2$, and $\text{U}_2\text{O}_5(\text{OH})_2$. Our study of the UO_3 - H_2O system between 25 and 400°C has produced the following results:

a) The compound previously identified as $\text{UO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ is shown to be $\text{U}_3\text{O}_8(\text{OH})_2$ (or $\text{H}_2\text{U}_3\text{O}_{10}$). This formula, which results from analysis of carefully purified material, is in accord with infrared data and is confirmed by single-crystal X-ray studies (cf. Chapter XIV). The spectrum of $\text{H}_2\text{U}_3\text{O}_{10}$ from 200 to 900 cm^{-1} is virtually identical to spectra of the transition metal triuranates and is indicative of similar U-O bonding configurations in these compounds.

b) Two crystal modifications of $\text{UO}_2(\text{OH})_2$ are well established, and the reaction $\beta\text{UO}_2(\text{OH})_2 \rightarrow \alpha\text{UO}_2(\text{OH})_2$ is known to result from the application of pressure on the β phase [8]. This phenomenon has not been considered in previous infrared studies of $\beta\text{UO}_2(\text{OH})_2$ [9]. The revised spectrum of the β phase is in agreement with its structure as established by X-ray studies.

c) A convenient procedure has been developed for the synthesis of pure $\gamma\text{UO}_2(\text{OH})_2$, which has heretofore been available only as an impurity in α and $\beta\text{UO}_2(\text{OH})_2$. The monoclinic γ phase is precipitated from uranyl nitrate solution by the addition of a weak base, such as $\text{La}(\text{OH})_3$, at 80 – 100°C . Gamma $\text{UO}_2(\text{OH})_2$ has a very limited stability range, converts to $\beta\text{UO}_2(\text{OH})_2$ at 130°C , is pressure-sensitive, and gives an infrared spectrum which indicates a close structural relationship to the β form. Single crystals can be produced, and the X-ray study is planned.

3. UO_3 - Cr_2O_3 System

Although the compounds formed between UO_3 and mono- and divalent metal oxides, i.e., the alkali, alkaline

earth, and transition metal uranates, have been studied in detail, the corresponding U(VI)-M(III) ternary oxide systems have received relatively little attention. The compound Cr_2UO_6 is the first such chromium ternary oxide to be prepared, and it therefore represents a new double-oxide composition for uranium(VI). It is obtained by a hydrothermal reaction of chromium nitrate solution with UO_3 at 315 – 400°C . Powder X-ray diffraction and infrared data indicate that no uranyl group is present in Cr_2UO_6 and that all 6 U-O bonds are equivalent (see Fig. XII.3).

4. UO_3 - RE_2O_3 Systems

Preliminary results on several rare-earth-uranium(VI) oxide systems under hydrothermal conditions indicate that a comparable RE_2UO_6 compound is not formed. Two compounds, tentatively identified as $\text{RE}_2(\text{U}_2\text{O}_7)_3$ and $\text{REU}_6\text{O}_{18}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, have been prepared in the 200 – 400°C temperature range.

G. DYNAMIC CHEMICAL BEHAVIOR OF INORGANIC SYSTEMS

Kinetic studies of oxidation-reduction reactions in aqueous solutions have long been regarded as fundamental in interpreting the inorganic chemistry of systems of interest. The specific behavior of the 5f transition elements in such studies provides important information on such points as the role of orbital symmetry in the determination of reactivity patterns and permits comparison with the d transition series. The information has additional application to such practical problems as the development of analytical and separation procedures.

Fig. XII.3. Structure of Cr_2UO_6 . ANL Neg. No. 121-6961.

1. *Cobalt Complexes* (J. C. Sullivan, R. C. Thompson,*
J. D. White,** H. Taube,** and R. L. Bain†)

The enormous decrease in reactivity brought about by replacing H_2O in $Co(H_2O)_6^{3+}$ by NH_3 is a matter of interest [10]. During the past year, the pentaquomonoamminecobalt(III) species was prepared and identified. Equilibrium measurements and preliminary kinetic studies have been carried out on a remarkable reaction of this ion, the disproportionation $2CoNH_3(H_2O)_5^{3+} + \frac{1}{2}H_2O \rightarrow Co(NH_3)_2(H_2O)_4^{3+} + Co(H_2O)_6^{3+} + H^+ + \frac{1}{2}O_2$.

Some time ago we determined an empirical rate law for the reduction of $Co(III)$ by hydrazoic acid in perchlorate solution. A conflicting formulation was subsequently suggested by other investigators. To resolve this discrepancy, we collaborated in a study of the reaction carried out at the University of Missouri at Columbia, using spectrophotometric techniques over a wide range of initial reactant concentrations [11]. The results of this study supported our original conclusions and were inconsistent with the empirical-rate law presented by Wells and Mays. An independent study by James Espenson at Iowa State University also agreed with our work.

A study of the reactions between azidopentamminerhodium(III) and $Co(III)$ or nitrous acid was undertaken in collaboration with Prof. R. L. Bain, S.I.U. (Edwardsville), and will be continued at that site. Spectrophotometric and mass-spectrometric studies indicate that the reaction products include N_2 , N_2O , and the nitrate and nitro pentamminerhodium(III), as well as aquopentamminerhodium(III) [12].

2. *Np Compounds* (J. C. Sullivan, R. C. Thompson,
and C. S. Burgener††)

The equilibrium quotient for the formation of a dimeric $Np(IV)$ monoperoxo complex from $Np(IV)$ and H_2O_2 was determined to be $3.3 \times 10^4 (M^{-2})$ at 25° in molar perchloric acid [13]. The reaction between $Np(III)$ and O_2 in 0.01M perchloric acid produces 60% $Np(IV)$ and 40% $Np(V)$. The reducing power of the spent reaction mixture is the same as that of the original solution. This is consistent with the interpretation that hydrogen peroxide is produced in the course of the reaction between $Np(III)$ and oxygen. In the reaction between $Np(III)$ and H_2O_2 , the product distribution and initial rate data are consistent with the concept that the major path may be

The empirical form of the rate law for the reaction between $Np(VII)$ and $Tl(I)$ in acid perchlorate media is first order in each of the reactants, and essentially first order in hydrogen ion [14]. No kinetic evidence is obtained for the existence of $Tl(II)$ as an important kinetic intermediate, in contrast to results obtained when $Co(III)$, $Ce(IV)$, and $Ag(II)$ are the oxidants. The gas produced when $Np(VII)$ oxidizes an aqueous solution of perchloric acid contains only oxygen, as determined by a mass-spectrometric scan. Results with ^{18}O -enriched H_2O demonstrate that all the oxygen produced comes from the solvent water of the spent reaction mixture. Continued research on neptunium systems is planned.

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XIII. SEPARATIONS CHEMISTRY*

Historically the separation of plutonium from irradiated fuel elements was the principal practical objective of the chemistry program of the Manhattan project. In a sense, the ability to prepare pure reagents is a necessary prerequisite of most of the research carried out today, and the development of separation techniques within the Chemistry Division has maintained an important role in heavy-element chemistry (Chapter I), geochemistry (Chapter II), and inorganic chemistry in general (Chapter XII).

This chapter includes only the research directed at what is really a modern version of one of the great classical problems of inorganic chemistry, the separation of elements where the principal chemical differences are small, the lanthanide and actinide elements.

A. LIQUID-LIQUID EXTRACTION STUDIES OF ACTINIDES AND LANTHANIDES (D. F. Peppard, G. W. Mason, and S. Lewey)

The extraction of metallic cations, M^{+3} , from an aqueous mineral acid phase into an opposing phase consisting of a monoacidic phosphorus-based extractant, HY, in a carrier diluent has been studied for M(III) lanthanides and actinides and for U(VI) as a function of: (1) type of bonding in HY (C-P or C-O-P bonds), (2) acidity of HY, (3) steric hindrance in HY, and (4) nature of the carrier diluent. In a diluent which is neither a strong donor nor acceptor, the HY extractant is principally dimeric, the dimer having two very strong hydrogen bonds.

In any of the systems studied employing one of the three isomeric bis octyl phosphoric acids, (octyl O)₂PO(OH) (when the octyl group is $n\text{-C}_8\text{H}_{17}$, $\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2$, or $\text{C}_4\text{H}_9\text{C}(\text{CH}_3)_2\text{CH}_2$) or one of the two isomeric octyl phenyl phosphinic acids, (octyl) $(\text{C}_6\text{H}_5)\text{PO}(\text{OH})$ (where the octyl group is $n\text{-C}_8\text{H}_{17}$ or cyclo- C_8H_{15}), the extraction stoichiometry of U(VI) may be represented as

where the subscripts A and O refer respectively to the mutually equilibrated aqueous and organic phases.

In systems in which benzene is the carrier diluent, M(III) actinides and lanthanides are extracted by each of the three isomeric (octyl O)₂PO(OH) extractants according to the stoichiometry

But for the same extractant, in n-heptane diluent, the stoichiometry of extraction of M^{+3} is

The two isomeric (octyl)(C_6H_5)PO(OH) extractants in benzene diluent extract M^{+3} according to the stoichiometry represented by Expression 3.

The important generalizations resulting from mutual comparison of these studies (and certain pertinent previous studies by our group) [1-6] are:

1. The stoichiometry of extraction of U(VI) is independent of:
 - a. Type of bonding within the extractant.
 - b. Steric hindrance within the extractant.
 - c. Acidity of the extractant.
 - d. Nature of the nonbonding diluent. (The stoichiometry is affected if a bonding diluent such as an alcohol is employed.)
2. The K_s value for U(VI), defined by the expression

$$K = K_s F_0^2 / [\text{H}^+]^2_\text{A} \quad (4)$$

where K is the observed extraction coefficient, F_0 is the concentration of extractant in formality units, and $[\text{H}^+]$ is the concentration of hydrogen ions, is nearly independent of the factors listed in 1.a, b, c, and d.

3. In contrast with U(VI), the stoichiometry of extraction of M(III) and the K_s values are functions of the factors listed in 1.a, b, c, and d. With benzene as diluent, the K_s for M(III) in the three isomeric bis octyl phosphoric acid systems is defined by

$$K = K_s F_0^3 / [\text{H}^+]^3_\text{A} \quad (5)$$

but with n-heptane as diluent, the defining expression is

$$K = K_s F_0^{2.5} / [\text{H}^+]^3_\text{A} \quad (6)$$

The two isomeric octyl phenyl phosphinic acids, in benzene diluent, extract M(III) according to Expression 6. For M(III), the K_s is less for:

- a. A phosphinic acid than for the corresponding phosphoric acid.
- b. The more weakly acid extractant, in a mutual comparison of two phosphinic acids or of two phosphoric acids.
- c. A more strongly sterically hindered extractant than for a less strongly hindered.
- d. A benzene diluent system than for a n-heptane diluent system.

Since the variables studied have been shown to exert a strong influence upon both the stoichiometry of extraction and the value of K_s for M(III) but not for U(VI), it is suggested that the M(III) and U(VI) extracted entities differ in their bonding.

*Chapter edited by: D. F. Peppard.

From the results of these studies it seemed that a liquid-liquid extraction system for the separation of Am(VI) from all lanthanides(III) and actinides(III) could be devised. For example, the ratios of K_s values, U(VI) to Am(III), in an HY (benzene) versus aqueous mineral acid system where HY is, respectively, $(n-C_8H_{17}O)_2PO(OH)$ and $(n-C_9H_{17}O)_2PO(OH)$ are 2×10^4 and 5×10^8 . Presumably the ratio of K_s values of Am(VI) to Am(III) should approximate 10^8 for the latter extractant. However, the extractant is not stable in the oxidizing medium required for maintenance of Am(VI) and therefore proved unsuitable for this use.

Consequently, the effect of steric hindrance upon the ratio of K_s values of U(VI) to Am(III) was investigated further, using only phosphoric acids which are stable in oxidizing medium. A high sterically hindered extractant, bis(2,6-dimethyl-4-heptyl) phosphoric acid, $(C_9H_{19}O)_2PO(OH)$, HD(DIBM)P, was found to differentiate strongly in favor of U(VI) with respect to all actinides(III) and lanthanides(III) and with respect to Y(III), Sc(III), and Th(IV). It was therefore, investigated as an extractant of oxidized americium.

Under suitable oxidizing conditions, HD(DIBM)P extracts Am, presumably as Am(VI), with a K of 40 and Am(III) with a K of less than 1×10^{-5} . An efficient mutual separation of Am and Cm has been demonstrated.

Several more liquid-liquid extraction systems have been found in which lanthanides(III) and actinides(III) exhibit the "Tetrad Effect" reported earlier by our group. This effect has been stated: "In systems involving all 15 lanthanides(III), the points on a plot of the logarithm of a suitable numerical measure of a given property of these elements versus Z may be grouped, through the use of four smooth curves without inflections, into four tetrads with the gadolinium point being common to the second and third tetrads and the extended smooth curves intersecting, additionally, in the 60-61 and 67-68 Z regions. In a similar plot for actinides(III), an analogous tetrad effect is apparent with the curium point being common to the second and third tetrads [7]."

B. LIQUID-LIQUID COLUMN CHROMATOGRAPHY

(E. P. Horwitz and C. Bloomquist)

A broad study of liquid-liquid column chromatography (extraction chromatography or LLCC) was undertaken several years ago with the purpose of improving the separation of the transplutonium elements. The basis for

this approach to separation problems was the following: (1) liquid-liquid extraction systems frequently show larger selectivities for metal ions than ion-exchange systems; (2) liquid-liquid chromatography has the potential for very high resolution because the effect of low diffusion coefficients in the stationary phase, which greatly influences zone spreading, can be minimized; and (3) the large number of liquid-liquid systems available would provide great versatility in the selection of specific complexing systems.

The problems of converting a liquid-liquid extraction system to the corresponding chromatographic system are being studied from a fundamental standpoint. We have measured the diffusion coefficients of Eu(III) in dilute nitric acid and di-2-ethylhexylphosphoric acid (HDEHP) as a function of temperature. The data obtained correlate well with the inverse of the viscosity coefficient (i.e., the fluidity) versus temperature indicating that the activation energy for the diffusion process in the binary mixture (Eu(III) and solvent) is the same as the activation energy of viscous shear in the pure solvent. These measurements have also made possible the calculation of the diffusion contribution to zone spreading in both the stationary and mobile phases of a chromatographic system.

The study of column packing structure, thickness of the stationary phase, and structure of the inert support as a function of flow rate has led to large improvements in column efficiency. Liquid-liquid chromatographic columns containing undiluted HDEHP or trioctylmethyl ammonium chloride or nitrate as the stationary phase adsorbed on hydrophobic Celite or Zipax can now be prepared which give 50-100 theoretical plates/cm column length. This achievement has led to the application of LLCC to almost every chemical-separation problem connected with the actinide and transactinide elements.

Specifically, LLCC has been applied with great success to several nuclear studies involving ^{256}Md and ^{256}Fm . Liquid-liquid chromatographic columns containing HDEHP and trioctylmethyl ammonium chloride were used to isolate relatively large quantities ($>10^7$ atoms) of ^{256}Md and ^{256}Fm , prepared by cyclotron bombardments of ^{253}Es and ^4He ions, with a speed and purity never before attained. Decontamination factors of $>10^{10}$ from all fission products and ^{253}Es made possible the measurement of the mass-yield curve for the spontaneous fission of ^{256}Fm by both chemical and physical means. High-speed, high-efficiency liquid-liquid chromatographic columns are also being used extensively in the search for superheavy elements discussed elsewhere (Chapter I.H).

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XIV. STRUCTURAL CHEMISTRY*

Neutron and X-ray crystallography provide the most powerful techniques available for the determination of crystal and molecular structures of materials of chemical, biological, and solid-state interest. This detailed structural information is widely useful for preparation of new materials, for understanding the relations between structure and physical properties, for aid in elucidating chemical reaction mechanisms and to further theoretical understanding of chemical bonding.

Neutron diffraction, because of its special power for hydrogen-atom location, is uniquely useful for studies of hydrogen bonding. The current work of one group therefore is largely centered around molecular-structure studies of hydrogen bonding and the role it plays in determining chemical and physical properties. Recent emphasis has been placed on structural studies of bihalide ions, the binitrate ion, acid hydrates in which the $H_5O_2^+$ ion plays an important role, and some complex acid fluoride anions.

Metal carbides are a most interesting group of compounds which seem destined to play an increasing role in the nuclear industry. Neutron-diffraction studies are an important adjunct to determination of their structures, and are being pursued rather extensively.

Among other compounds of current structural interest are included some rare-earth compounds, with particular reference to magnetic properties, the rare-gas compounds, particularly the xenon compounds with high oxidation and coordination number, and compounds of the actinide elements.

During a rather prolonged shutdown and rehabilitation of the CP-5 reactor, some effort was diverted to X-ray studies, but improved facilities are becoming available and a greater concentration on neutron diffraction can be expected in the future.

The magnetic moment of the neutron interacts with any magnetic moments in the scattering material, making neutron diffraction a unique tool for magnetic-structure determination. The magnetism is a fundamental property associated with quantum electronics and chemical bonds, so basic information is gained. In addition, there is a wide variety of magnetic materials of technological importance, so data of immediate practical value can be obtained. Our principal objective is to study the magnetic structure of selected materials, particularly from the point of view of investigating direct and indirect exchange interactions among the electron spins. The program includes the determination of the crystal structures in order to relate them to the magnetic studies.

Considerable emphasis is being placed on structural studies of uranium and transuranium compounds. The results of these investigations lead to a knowledge of the

valence states and coordination characteristics of these elements. Current studies include structural investigations of triuranates, uranyl hydroxides, uranium trioxides and the nature of the uranyl bond, complexes of NaF with UF_6 , bonding in rare-earth nitrates, and noble-gas compounds.

A. EXPERIMENTAL FACILITIES

1. Neutron Crystallography (S. Peterson and J. Williams)

The main experimental facility of the neutron-crystallography group will be the neutron-diffraction complex installed at the CP-5 reactor in a joint project with the Solid State Physics Division. This facility consists of a large monochromator shield designed to allow one minor and three major beams to be extracted from the H-13 (10-in.-dia) beam hole. One of these beams, monochromated and deflected in a vertical plane, is utilized by a computer-controlled 4-circle neutron diffractometer mounted on top of the large shield.

The 4-circle diffractometer, which is intended to provide single-crystal neutron-intensity measurements for the general run of neutron-structure analyses, is currently being installed and undergoing alignment and testing for routine use. It is interfaced and linked through telephone lines to the Chemistry Division Sigma computer for on-line control and preliminary data processing. This instrument will soon be equipped with a helium cryostat so that the measurements may be made at temperatures ranging down to that of liquid helium.

A second instrument to be shared jointly with Solid State Physics will consist of a heavy-duty neutron diffractometer which can be used interchangeably for neutron-powder or liquid studies, and hopefully, with some modification, for triple-axis work.

A third possible facility using a straight-through "white" beam of neutrons offers the potential of increased efficiency in neutron utilization hence faster data collection. The minor beam alluded to above is intended for this Laue-type experiment.

Improved facilities in this area, as in many others, will depend heavily on future funding allocations.

2. Neutron Magnetic Diffraction (M. Atoji)

The main experimental facility of the neutron-magnetic-diffraction group, an automated multipurpose neutron diffractometer at the CP-5 reactor, has been in operation since 1962 for both magnetic and crystal-structure studies at temperatures from 2°K to 1600°C with a magnetic field of up to 26 kilogauss. Continuing instrumental additions and improvements have been made without interrupting the

*Chapter edited by: M. Atoji, S. Peterson, and S. Siegel.

experimental progress. Recently, a variable-temperature cryomagnetic dewar was added to the system and the data-processing electronics were improved considerably. A set of newly designed vanadium permendur magnet poles was also constructed and is currently in use.

3 X-ray Crystallography and Techniques for Investigating Heavy-element Salts (S. Siegel)

The X-ray diffraction equipment has also been upgraded in the recent past. A computer-controlled automatic diffractometer is now in operation.

Structural studies of heavy-element salts can now be carried out with single crystals in the 50–80-micron size range, and trial efforts indicate that crystals as small as 25 microns can be studied successfully. With X-ray-diffraction techniques it is not always necessary that the composition and the valence state of the heavy element be known. Thus, if cell and symmetry information can be established, then, with the use of the so-called "heavy-atom method," it is quite possible to establish the entire coordination or molecular characteristics of the element in question and its corresponding valence states. We hope to exploit this technique fully, particularly in connection with our actinide studies.

B. HYDROGEN BONDING IN CRYSTALLINE STRUCTURES

1 $(\text{CH}_3)_4\text{NCI}(\text{HCl})$ (S. W. Peterson and J. M. Williams)

The first neutron diffraction study of a bichloride ion has verified the existence of the $[\text{Cl}-\text{H}-\text{Cl}]^-$ ion in the solid state and established that the ion was linear but possesses a highly asymmetric H-bond (Fig. XIV 1). The structure is completely ordered in agreement with earlier heat-capacity studies, but disproves the "symmetric-ion-structure" interpretation made utilizing these measurements. An additional finding of considerable interest is that CH_3 protons appear to be involved in weak C-H-Cl hydrogen bonds. We are planning to study the deuterium analog $(\text{CH}_3)_4\text{NCIDCl}$ early next year.

Fig. XIV 1 The Linear Bichloride Ion as Found in Tetramethyl ammonium Bichloride. ANL Neg. No. 121 6839

2 $\text{CsNO}_3 \cdot \text{HNO}_3$ (J. M. Williams and N. Dowling*)

A full single-crystal X-ray study of $\text{CsNO}_3 \cdot \text{HNO}_3$ has revealed that the lattice is composed of CS^+ and $(\text{O}_3\text{N}-\text{H}-\text{NO}_3)^-$ ions. The latter (binitrate) ion lies in the crystal in such a way that four oxygen atoms from the two nitrate groups form the corners of a distorted tetrahedron with a single proton binding the two nitrate groups.

Further structural studies of the hydrated proton in the solid state will be emphasized next year. Neutron structure studies of $\text{HBr} \cdot 4\text{H}_2\text{O}$, which presumably contain the H_3O_4^+ ions, will be carried out on both of the known phases which exist at low temperatures. Companion studies of the fully deuterated species would appear to be useful in this case as well. The trihydrate of sulfosalicylic acid, which will provide another example of hydrated protons in a quite different environment, will also be investigated.

A little further off we hope to extend the hydrated proton studies to such compounds as $\text{HCl} \cdot 3\text{H}_2\text{O}$, $\text{HCl}_4 \cdot 4\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, investigate hydrated hydroxyl ions in a series of hydroxide hydrates, and extend the bichloride ion studies to dibromide ions and possibly mixed species. Studies of deuterated species will be included when appropriate.

C. CARBIDES

1 Neutron-structure Determination of NaC_2H , Cubic CaC_2 , and Cubic KCN (M. Atoji)

As part of the magnetic and crystal-structure studies of metal carbides, neutron-structure analysis of monosodium acetylide, $\text{Na}^+(\text{C}\equiv\text{CH})^-$, was carried out at room and liquid-helium temperatures. The tetragonal lattice constants are $a = 3.813(2)$ and $c = 8.104(3)$ Å at 293°K, and $a = 3.764(2)$ and $c = 8.062(3)$ Å at 5°K. A large anisotropy in thermal expansion should be noted. The atomic parameters at 293°K are $z(\text{Na}^+) = 0.3520(9)$, $z(\text{C}^-) = 0.6749(7)$, $z(\text{C}) = 0.8261(7)$, and $z(\text{H}) = 0.9540(18)$, all at $(0, 1/2, z)$ and $(1/2, 0, \bar{z})$ in $D_{4h}^1 - P_{4h}^1$ mm. These positional parameters are essentially unchanged by cooling down to 5°K. No magnetic ordering was observed in the diffraction pattern down to 2°K, suggesting no unpaired electron in $\text{C}\equiv\text{CH}$. The molecular axes of $\text{C}\equiv\text{CH}$ align along the c axis. The $\text{Na}^+ \cdots \text{C}$ ionic contacts form a puckered c layer, and the intermolecular $\text{H} \cdots \text{H}$ contacts do likewise. Hence, the crystal force field is partly ionic and partly van der Waals in nature. The $\text{C}\equiv\text{C}$ distance of 1.27 Å is significantly longer than the acetylenic 1.20 Å. All other structural features, including the large anisotropic thermal vibrations, suggest a virtually localized negative charge as represented by $\text{C}\equiv\text{CH}$. The X-ray structure parameters reported previously [1] are considerably different from our neutron values.

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Neutron-diffraction study of the face-centered cubic CaC_2 revealed the characteristics of the hindering potential for rotation of the C_2 group as follows: Just above the transition temperature (450°C), the C_2^{2-} radical takes the $[111]$ random orientations with practically no probability of dynamic reorientation (the Frankel structure); as the temperature is raised, a dynamic tumbling from $[111]$ to $[\bar{1}\bar{1}\bar{1}]$ via $[110]$ sets in gradually; finally, just below the melting point, an essentially spatial hindered rotation will be assumed with prevailing potential barriers effectively around the $[100]$ directions only (the Pauling model). A further refinement of the analysis of the published neutron data of cubic KCN [2,3] indicates a rotational hindering potential practically identical to CaC_2 , resolving the previous contradictory results. An analogous conclusion might well be applicable to all other disordering isostructural crystals, in agreement with some tentative theoretical interpretations [4] in line with heat-capacity measurements but hitherto without direct structural confirmation.

2. Magnetic-spin Structures of $\alpha\text{-Tb}_2\text{C}_3$ and $\alpha\text{-Ho}_2\text{C}_3$ (M. Atoji and Y. Tsunoda)

The carbon atoms in $\alpha\text{-Tb}_2\text{C}_3$ and $\alpha\text{-Ho}_2\text{C}_3$ (both body-centered cubic $\alpha\text{-Pu}_2\text{C}_3$ type) are dimerized to form the C_2 group which is markedly stabilized in the C_2^{2-} state. The valence orbitals of the C_2^{2-} group are considerably aspherical, enhancing the crystal-field anisotropy and also the d-orbit contribution of the metal atom in the conduction-band formation. In addition, the $\alpha\text{-Pu}_2\text{C}_3$ type structure is highly asymmetric, and hence the RKKY interaction and the crystal-field effect should reflect this uniqueness. These aspects are clearly demonstrated by strikingly different ordered magnetic structures found between $\alpha\text{-Tb}_2\text{C}_3$ and $\alpha\text{-Ho}_2\text{C}_3$ as described below (see also Sect. D following).

Neutron-powder-diffraction measurements have shown that, in $\alpha\text{-Tb}_2\text{C}_3$ below 33°K , two out of four body-diagonal Tb arrays become antiferromagnetic chains, but the two remaining Tb arrays exhibit no ordered moment. The nearest Tb atoms between the ordered spin arrays are related ferromagnetically. The moments are most likely directed along the face diagonal which lies in the plane formed by two body diagonals parallel to the ordered spin arrays. The saturation moment per magnetically ordered Tb in this collinear spin structure approximates the free Tb^{3+} value of 9 Bohr magnetons. An equivalent multiaxial antiferrostructure is obtained by combining two collinear magnetic structures with the mutually orthogonal face-diagonal moments. In this biaxial structure, all Tb atoms possess the same saturation-ordered moment of $9/\sqrt{2}$ Bohr magnetons.

In the antiferromagnetic structure of $\alpha\text{-Ho}_2\text{C}_3$ stabilized

below 19°K , two out of four body-diagonal Ho arrays become the ferromagnetic chains and the remaining two arrays show one-dimensional antiferromagnetic alignment. Among three nearest Ho-Ho neighbors bridging between the different body-diagonal arrays are two antiferromagnetic pairs and one ferromagnetic pair. The moment direction is most likely parallel to that of the ferromagnetic pair. The maximum spontaneous moment of 7.3 Bohr magnetons indicates a strong crystal-field suppression, as the free Ho^{3+} ion should have 10 Bohr magnetons. The temperature dependency of the spontaneous magnetization is approximated by the Brillouin function for $S = 1 \pm 1/2$ which departs significantly from the free ion function with $J(g-1) = 2$. In both Tb_2C_3 and Ho_2C_3 , the magnetically ordered phase exhibits a sizable magnetic diffuse scattering having the characteristics of a ferromagnetic short-range order, and this persists down to near 0°K .

D. MAGNETIC-SPIN STRUCTURE OF ERBIUM (M. Atoji)

Properties of magnetic materials and relationship to their chemistry and structure are a continuous field of considerable interest. In these studies the rare-earth metals and compounds are of particular interest since in a series of similar compounds the magnetic properties are a function of the number of inner electrons changing regularly with changing atomic number.

The lanthanides include important fission products, are useful analogs of the less accessible actinides, and have always been of interest to scientists in the nuclear field.

The combination of neutron-diffraction studies with an applied magnetic field is essential for clarifying the mechanism governing the excited and equilibrium magnetic-spin states, and is one of the simplest ways to increase our understanding of the spin correlation in magnetic materials. Among rare-earth metals, a study of this kind has been carried out for holmium [5]. We are planning to pursue the magnetic-excitation study of most other magnetic rare earths and have started gathering comprehensive data on erbium single crystals. The applied field effects are highly complex and a systematic analysis of the magnetic data is in progress. So far it appears that the antiphase domain structure postulated previously for the $20\text{--}52^\circ\text{K}$ [6] phase at zero field must be significantly amended. An additional spin configuration near 28°K suggested by susceptibility measurements is now being clarified, and a secondary spin-density wave was found in the $52\text{--}87^\circ\text{K}$ phase.

E. OTHER STUDIES ON RARE-EARTH COMPOUNDS

1. Ce_2S_3 (M. Atoji)

The analysis of the structure of Ce_2S_3 has been

completed using neutron diffraction. There are a number of isostructural compounds, and this represents the first accurate crystal-structure determination of any of them. The structure parameters are as follows: $a = 8.6084(18)$ at 293°K and $8.5882(16)$ Å at 5°K ; $T_D = 143^\circ\text{K}$; 10^{-3}Ce at $(\frac{3}{8}, 0, \frac{1}{4})$ with the occupancy factor of 0.889; 12S at (u, u, u) with $u = 0.073(1)$. Also, Ce_2S_3 is paramagnetic with the moment equivalent to the free Ce^{3+} ion down to 2°K .

2. $\text{K}_3\text{Pr}_2(\text{NO}_3)_9$ (S. Siegel and W. Carnall)

The complete structure of $\text{K}_3\text{Pr}_2(\text{NO}_3)_9$ has been established. The Pr atom exhibits unusual spectral intensities believed to be related to the site symmetry of the atom. The Pr atom is on a threefold axis and is surrounded by twelve oxygen atoms belonging to six nitrate ions. However, the asymmetry about Pr is high in the sense that each set of three equivalent nitrate ions exhibits entirely distinct bonding characteristics.

F. THE STRUCTURE OF URANYL COMPOUNDS

(S. Siegel and H. Hoekstra)

Uranium compounds are being investigated with particular emphasis on the structure of the uranyl bond.

The trioxides of uranium are unique in that they represent compositions in which uranium bonding can exist without other cation influences. A high-pressure modification was studied a few years ago [7]. The structure is orthorhombic and each uranium atom is bonded to seven oxygen atoms leading to shared $[\text{UO}_7]$ configurations. Two short bonds of 1.80 and 1.85 Å are nearly equal and collinear and are identified as modified uranyl bonds. The other five oxygens form secondary bonds in a puckered pentagonal arrangement coordinated about the uranyl groups.

The structure of gamma- UO_3 , the more commonly available commercial powder (Mallinckrodt UO_3) has been derived from powder data [8] and we have now reinvestigated this substance using single crystals. The cell is orthorhombic and exhibits two octahedral arrays with uranium at the centers and each with its own distinct primary and secondary bonds (Fig. XIV.2). In one case, the $\text{U}(2)-\text{O}(1)$ bonds of 1.88 Å are considered to be modified uranyl bonds, since the $\text{O}(1)$ atoms are shared via weak secondary bonds (2.32 Å) with $\text{U}(1)$ atoms. For the second configuration, the $\text{U}(1)-\text{O}(3)$ bonds of 1.79 Å appear to be pure uranyl bonds, for the next nearest cation neighbor is another $\text{U}(1)$ at 3.06 Å. The value of 1.79 Å is about 0.1 Å longer than expected for a pure double bond, but in

Fig. XIV.2. The Structure of $\gamma\text{-UO}_3$. ANL Neg. No. 121-5288.

accord with the infrared results of 1.76 Å [9]. This may be an indication of weak bonding interactions, even at distances in excess of 3 Å in the crystal. The alpha-form of UO_3 is currently under study. The reported small hexagonal cell is not consistent with our neutron-diffraction data. Disordered single crystals of alpha- UO_3 produced from $\text{H}_2\text{U}_3\text{O}_{10}$ lead to a very large pseudo-orthorhombic cell [10].

$\text{H}_2\text{U}_3\text{O}_{10}$ has been shown to be the best formulation of a compound originally described as $\text{UO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, but now determined by us to be $\text{UO}_3 \cdot \frac{1}{3}\text{H}_2\text{O}$. Both infrared and X-ray studies now confirm the formulation as a triuranate [11].

The infrared spectrum of $\text{H}_2\text{U}_3\text{O}_{10}$ shows a remarkable similarity to the spectra of a number of transition metal triuranates. The compound has indeed been found to contain triuranate groups composed of shared bipyramid-octahedron-bipyramid configurations (Fig. XIV.3). The apex (uranyl) oxygen atoms of each bipyramid form part of an octahedral array of oxygen atoms with a point $0\frac{1}{2}0$ of the triclinic unit cell as a "center." The hydrogen atoms can be shown to be associated with this octahedral array of oxygen atoms.

Fig. XIV.3. Perspective View of $\text{H}_2\text{U}_3\text{O}_{10}$. ANL Neg. No. 121-7639

The pseudo-orthorhombic cell of alpha- UO_3 can be obtained from the $\text{H}_2\text{U}_3\text{O}_{10}$ structure. In addition, preliminary studies of $\text{CuU}_3\text{O}_{10}$ indicate a structural configuration quite similar to that found in $\text{H}_2\text{U}_3\text{O}_{10}$ with the copper atoms probably located in the hole defined by the octahedral array of oxygen atoms. This structure will be quite different from that which we have found for CuUO_4 [12], where distinct U-O octahedra only are developed, and the oxygens form the characteristic square planar configuration about copper. However, in CuUO_4 , the uranyl oxygens form two long off-axis ligands about the copper to create a distorted octahedron.

X-ray-diffraction studies of uranium oxides and uranium oxide double salts as well as uranium trioxide hydrates are continuing. The structure of Cr_2UO_6 has been obtained from powder data [13]. The infrared spectra suggest the equivalency of all U-O bonds so that the uranyl bond cannot be identified. The X-ray studies show all U-O bonds to be equivalent (2.08 Å) within experimental error, leading to single bonds. This is an unusual coordination for U(VI).

G. COMPLEXES OF NaF WITH UF_6 (S. Siegel and J. G. Malm)

Complexes of NaF with UF_6 have been studied and employed on a rather large scale in connection with purification processes developed for UF_6 which depend on absorption-desorption cycles. Both NaUF_7 and Na_2UF_8 have been isolated and characterized as pure compounds. Their complete structures, however, have not yet been elucidated.

H. CRYSTALLOGRAPHIC STUDIES ON NOBLE-GAS COMPOUNDS

1. $(\text{NO})_2\text{XeF}_8$ (S. W. Peterson, B. A. Coyle,* J. M. Williams, and J. H. Holloway**)

The structure of $2\text{NOF} \cdot \text{XeF}_6$ has been determined by a detailed X-ray study and shown to consist of discrete NO^+ cations and XeF_6^{2-} anions (Fig. XIV.4). The XeF_6^{2-} configuration is that of a slightly distorted Archimedean antiprism. The distortion largely involves elongation of XeF bonds on the antiprism side to which the NO^+ ions make close approaches indicating weak $\text{F} \cdots \text{NO}^+$ interactions. Of especial significance is the lack of distortion in the F-Xe-F bond angles. Such a distortion, to accommodate the xenon-atom lone pair, would appear to be required by the Gillespie-Nyholm localized electron-pair model.

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Fig. XIV.4. The Archimedean Antiprism Arrangement of Fluorine Atoms about Xenon in the XeF_6 Group of $(\text{NO})_2\text{XeF}_6$. ANL Neg. No. 121-6829.

2. XeF_6 (S. W. Peterson and S. Siegel)

This remains perhaps the most interesting noble-gas compound, from the point of view of its complex phase relationship and polymeric structure, debate over the symmetry of the monomer, and the uncertainties in interpretation of the molecular spectra. Structural analysis of several phases has been reported [14], but ambiguities are present and some contradictory observations have not been resolved.

In collaboration with P. Agron* the X-ray and neutron data for the monoclinic phases are undergoing further refinement. While progress has been slow, a good final solution appears feasible.

Crystals of the cubic phase have again been grown and their transformation into the monoclinic phase demonstrated, in contrast to the observations reported by Burbank and Jones.

3. NO_2XeF_7 (S. W. Peterson and B. A. Coyle)

One related project, determination of the structure of the XeF_6 addition product, NO_2XeF_7 , is currently stalled

because untwinned crystals have not been obtained. Because of the fundamental interest in this structure, a further attempt to obtain good crystals will be made.

4. $(\text{CsCl})_2\text{XeO}_3$ (S. W. Peterson, B. A. Coyle, J. M. Williams, S. Siegel, and E. Sherry)

Although many xenon compounds containing Xe-F bonds are known, none yet has been conclusively shown to contain Xe-Cl bonds. The compound $(\text{CsCl})_2\text{XeO}_3$ and related $(\text{RbCl})_2\text{XeO}_3$, both prepared in this laboratory, are believed, on the basis of infrared evidence, to contain such linkages. X-ray-crystallographic studies have been initiated in order to determine the complete structures and bonding.

Two crystalline modifications, tetragonal and triclinic, were found for each compound. They have not, however, been shown to have the original composition, and indeed the triclinic forms are probably decomposition or reaction products. The unit cells and space groups were determined and the tetragonal Cs and Rb crystals were found to be isomorphous. Complete sets of intensity data were then collected for both tetragonal species, and structure analyses were attempted. Tentative Cs and Xe atom positions have been found, and intensive efforts are underway to refine the structure and locate the light atoms.

1. COHERENT NEUTRON SCATTERING AMPLITUDES OF Br AND ^{127}I (M. Atoji)

Neutron diffraction data of KBr and KI yielded the thermal neutron coherent scattering amplitudes in 10^{12} cm, $b(\text{Br}) = 0.670 \pm 0.004$, $b(^{127}\text{I}) = 0.525 \pm 0.004$, taking $b(\text{K}) = 0.370 \pm 0.001$ as standard.

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XV. MOLECULAR SPECTROSCOPY*

Few techniques have been more important than infrared and Raman spectroscopy in understanding the nature and predicting the behavior of chemical molecules. At Argonne one group has largely applied them to reactive fluorides (cf. Chapter XII): the volatile, symmetrical, and industrially important hexafluorides; the halogen fluorides, powerful reagents for fluorination; the interesting noble-gas fluorides; oxide fluorides; and a host of more or less related compounds of special interest. Another has concentrated on complex inorganic compounds with special emphasis on behavior under applied pressure. The use of molecular spectroscopy is ubiquitous in studies aimed at understanding the properties of both inorganic and organic compounds of interest (cf. Chapters I and VIII). The diverse instrumentation available, and the existence of equipment adapted for handling reactive materials and of skilled personnel to instruct novices and assist in its use, have made this laboratory a major resource for many university scientists. It is hoped that this situation can continue.

Successive improvements in instrumentation and techniques have multiplied the power of the spectroscopy method. The advent of powerful krypton and argon lasers have made acquisition of Raman data far more simple than in the past. New computing techniques have made practicable the application of observed molecular spectroscopic data in order to test hypotheses concerning the arrangement of atoms in molecules and the fundamental features of chemical bond formation.

A. STRUCTURAL STUDIES AND MOLECULAR POTENTIAL FUNCTIONS OF HALIDES AND OXIDE HALIDES (H. H. Claassen, J. Goleb, C. Williams, H. Kim,** P. Tsao,† J. Tyson,†† and C. C. Cobb‡)

In Sect. XIIA we have described the Division interest in reactive fluorides. As molecular spectroscopic techniques developed in power, the application to this field was inevitable and indispensable. Of particular interest has been the attempt to understand the behavior of inorganic fluorides and oxides with rather simple fundamental rules based on the well-defined electronegative character of these elements and the relative predicability of the nature of the compounds.

The description of molecules in terms of localized electron pairs, systematized by Gillespie and Nyholm [1], has proven to be very successful in predicting the structure of inorganic molecules such as fluorides and oxide fluorides. Since this approach views repulsions between

pairs of ligand atoms, or between a ligand atom and a lone pair, as important in determining the equilibrium structure of a molecule, an obvious extension of the idea is to evaluate the repulsive forces at the equilibrium configuration by means of Urey-Bradley potential constants. The same forces that determine the equilibrium shape of a molecule, i.e., directional bonding orbitals and interligand repulsions, also determine the vibrational frequencies of the molecule. Work of this type is being done in a number of laboratories. The particular contribution here has been the derivation of new potential-energy matrices that express, for a number of different molecular symmetries, the energy of angular distortion of molecules in terms of degree of overlap of directional bonding orbitals.

1. Noble-gas Fluorides and Oxide Fluorides

The compounds XeF_4 , XeOF_4 , XeF_2 , XeO_3F_2 , and XeO_4 are unusually favorable cases since they provide meaningful repulsion constants, not only between pairs of fluorine atoms, but between fluorine and oxygen atoms, between pairs of oxygen atoms, and between fluorine atoms and lone pairs.

A number of such investigations have come to fruition this year. It was shown, for example, that with potential constants evaluated from known frequencies of XeF_4 and XeOF_4 , the frequencies of XeF_2 and XeO_3F_2 can be predicted with fair accuracy. Extension of this work to other oxide fluorides would indeed be very interesting, but lack of personnel will probably make this impossible in the near future.

2. Pentafluorides

The pentafluorides PF_5 , AsF_5 , and VF_5 as vapors have been studied in detail, and their normal coordinates and force constants determined in terms of the potential function described above. Other group V pentafluorides, SbF_5 , TaF_5 , and NbF_5 , are currently being studied by matrix-isolation techniques, required because their vapors are polymeric. Obtaining matrix-isolated monomers has proven to be very tedious. Even at very low pressures, the vapors still contain polymers and it appears that both high temperatures and very low pressures will have to be used to obtain pure monomers, a difficult feat because of their reactivity with container materials. This work is being continued.

3. Some Pseudo-octahedral Oxide Fluorides

Raman and infrared spectra of IOF_5 , OsOF_5 , and ReOF_5 vapors have been obtained and complete assignments made. Evaluation of potential energy functions and force constants for these molecules is in progress.

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**B. SPECTROSCOPIC INVESTIGATIONS OF
INORGANIC AND COORDINATION COMPOUNDS
UNDER VARYING PRESSURES** (J. R. Ferraro,
L. J. Basile, and A. Quattrochi)

Experimental techniques developed at ANL permit spectroscopic investigations ($28,000-50\text{ cm}^{-1}$) of inorganic and coordination compounds under high external pressures (to 80 kbar). These techniques suggest the possibility of investigating some hitherto inaccessible phenomena of both fundamental interest and some practical importance. Five general types of problems have been investigated so far.

(1) Infrared-active phonon modes in ionic and pseudo-ionic crystals (of the type AB) have been observed under high pressures. Such studies are important for developing fundamental concepts of lattice dynamics. The experimentally determined parameter $d\nu/dp$ leads rather directly to an experimental value for the Grüneisen constant (γ). This can then be compared with the (γ) obtained from equations of state based on certain theoretical models [2]. The Grüneisen parameter (γ) relates the vibrational frequency and the elastic properties of a solid.

$$\gamma(T,V) = V\alpha\beta_T/C_V$$

T is the temperature, V is the volume, α is the thermal coefficient of volume expansion, β_T is the isothermal compressibility, and C_V is the specific heat at constant volume.

$$\gamma \text{ may also be expressed as } -\frac{d \ln \gamma}{d \ln V}$$

and

$$(1/\gamma_0\beta_T)(d\gamma/dp)_T$$

where γ is the observed vibrational frequency, γ_0 the value at low ambient pressure (p), and it is the change in this frequency with applied high pressure as measured either in the infrared or Raman spectrum that we now observe.

(2) Solution studies of the vibrational modes of ionic materials in nonaqueous solvents at high pressure are important for developing new concepts involving solution dynamics, an area which has been little explored.

(3) At high pressures, measurement of the visible absorption bands of 5-coordinate complexes of the type $[MLX]Y$, MLX_2 , ML_3X_2 (where $M = \text{Ni(II)}, \text{Pt(II)}, \text{Pd(II)}$, $X = \text{halogen or pseudohalogen}$, L is a tetradentate, tridentate or monodentate ligand, and $Y = \text{polyatomic anion}$) are significant in that they provide an experimental technique for studying the nature and the importance of Jahn-Teller effects in these molecules [3].

(4) Differences in behavior of various modes of vibration under pressure have been observed for coordination com-

pounds and have led to a better interpretation of their infrared and Raman spectra.

(5) Studies of the glassy state under pressure are of direct practical importance. Glass components are widely used in submarines, and indeed all-glass vessels are being considered by the Navy for underwater exploration. Preliminary experiments have allowed us some insight into the fundamental factors affecting the nature of structural order and disorder in silicate glasses.

In the past year, much of the work on 5-coordinate complexes was accomplished. We expect to continue this effort on divalent Ni , Co , Pt , and Pd complexes including particularly the MA_2L type, where M is one of the metals, A is bisdithioacetyl acetone, and L is triphenyl phosphorus, arsenic, antimony or bismuth (Q_3P , Q_3As , etc.).

Most of our additional effort has been centered on the behavior of glasses. Until recently, structural information from spectroscopy in glasses has been limited mostly to studies at ambient pressure in the visible and relatively accessible middle IR region. We have initiated studies at higher pressures and lower frequencies, and begun to add Raman studies, also over a wide pressure range.

Indeed even for crystalline materials high-pressure Raman studies have been particularly limited, a quartz, for example, being a rare exception [3].

Tischer and Drickamer [4] have observed several glasses incorporating transition-metal ions as tracers under pressure in the visible region. Some glasses containing unfilled f-shell cations have been studied at ambient pressure. Such studies have provided information concerning the nature of the stereochemistry surrounding the central ion and distortion and local compressibility in the vicinity of the central ion in the glass structure.

We believe studies over a range of pressures will add greatly to the information derived from observations of the optical spectra of glasses containing rare-earth oxides and aid in the development of new formulations with improved properties.

It has been established that an increase in coordination number (C.N.) in glasses is associated with a significant increase in the Young's moduli. The incorporation of rare-earth oxides in glasses (Morey-Eastman Kodak Type) has created glass with extremely high Young's moduli. This has been attributed to the compacting of the octahedra of large, highly charged, highly polarizable cations and the O^{2-} ions. Under high pressures, these glasses may be induced to increase their coordination number and show still higher Young's moduli.

It is of interest to note that, under pressure, glasses become more closely related to the solid state than to the liquid state. Thus, an extrapolation to the solid state may be appropriate. Our experiences with pressure measurements of alkali metal halides have shown that where phase transitions occur (cubic-phase - C.N. = 6 $\rightarrow$ CsCl phase - C.N. = 8), the high-pressure phase with a C.N. = 8 is always a stronger material.

Some preliminary studies on SiO_2 polymorphs have suggested that some glasses become more ordered under pressure. The topic of order-disorder in glasses seems to us to merit considerable further attention.

One phenomenon observed in some glasses is still little understood: negative thermal expansion and negative Grüneisen parameters.

It has been proposed, for example, that the addition of M_2O to silicate glasses causes a negative thermal expansion due to an impedance of the low-frequency transverse vibration of the oxygen atoms in the Si-O-Si links. The relationship between specific modes of vibration and γ should be further investigated.

To further develop the Grüneisen relationship with ν , it is intended to initiate extensive Raman measurements ($4000\text{--}50\text{ cm}^{-1}$) of new and old glasses at ambient and higher pressures. Since our Raman cell will provide hydrostatic pressures, we will have the possibility, in glasses of lower symmetry, of obtaining γ 's from the infrared measurement under directionally oriented nonhydrostatic pressure and γ 's from the Raman measurement (uniformly existing hydrostatic pressures). A comparison between the two γ 's is of considerable interest. In high-symmetry materials (for example α -quartz) unique modes (relatively infrared forbidden) may be studied by the Raman technique.

Conducting complete vibrational studies (Raman and IR) of glasses as a function of pressure for the first time will permit an attempt to extend solid-state theory to glasses. We intend to make use of group-theory methods to determine the space-group selection rules of the individual

components of a glass and extrapolate an interpretation of the vibrational spectrum of the glass from this. We hope such studies will eventually bridge the gap between glasses and the much better understood spectra of crystalline solids.

C. RAMAN SPECTRA OF TECHNETIUM HEPTOXIDE (S. Fried and H. Selig*)

The Raman spectra of technetium heptoxide were determined on samples of the gaseous, liquid, and solid phases of this compound. The purpose of the experiment was to demonstrate both the similarities and differences between this compound and its homologue, Re_2O_7 . It is noteworthy that the liquid and vapor (Tc_2O_7) must have similar structures, and that these structures correspond closely to the structures of Re_2O_7 (vapor and liquid).

The spectrum for solid Tc_2O_7 shows some similarity to that of Re_2O_7 . However, where Re_2O_7 shows more than ten high-frequency Raman modes, Tc_2O_7 (s) has only seven. This is consistent with the higher symmetry for Tc_2O_7 units in the crystal lattice of the solid.

D. REACTION OF RHENIUM AND TECHNETIUM METALS WITH LITHIUM PERCHLORATE (D. Cohen, S. Fried, and H. Selig)

Rhenium metal and technetium metal were found to dissolve in molten LiClO_4 . The Raman spectra of the corresponding melts show that the perhenate and the pertechnetate ions were formed.

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XVI. ATOMIC SPECTROSCOPY*

Atomic spectroscopy at Argonne is focused on the energy levels of the actinides, and to a lesser extent the lanthanide elements. Two rather complementary groups are involved, one dealing with emission spectroscopy and using principally elemental sources, the other employing absorption spectroscopy and concentrating on the actinide ions in compounds.

In the near future, a number of other elements and compounds may become of interest in the nuclear-energy field as thermonuclear reactions become more important. We are initiating a program which hopefully will contribute to development in this field as well.

We have also employed our special facilities to study problems of both intellectual interest and practical importance outside the nuclear-energy category in individual circumstances that have presented appropriate targets. And, of course, these facilities continue to be made available to a number of groups outside the laboratory who share similar interests.

A. EMISSION SPECTROSCOPY (F. S. Tomkins, M. Fred, A. Giacchetti, and W. R. S. Garton**)

The main objective of the atomic-spectroscopy group continues to be the comprehensive experimental and theoretical investigation of the spectra of the actinide and related heavy and rare-earth elements. The atomic properties of these complex atoms are of increasing importance in astrophysics, and in the study of the plasma physics of proposed gas-core nuclear reactors.

Because the Argonne 30-ft Paschen-Runge spectrograph is uniquely suited to the study of these complex spectra, as well as because of our limited manpower, most of the experimental programs of the group are of a cooperative nature. Joint programs are carried on with the Lawrence Radiation Laboratory at Berkeley and Livermore, the National Bureau of Standards, the Johns Hopkins University, Purdue University, and in Europe the Laboratoire Aimé-Cotton at Orsay, France, Imperial College, London, and the Zeeman Laboratorium, Amsterdam, The Netherlands.

1. Lanthanide and Actinide Studies (F. Tomkins, M. Fred, E. Meinders,† H. M. Crosswhite,† and J. Blaise††)

During the past year, improved Zeeman-effect exposures of plutonium and dysprosium have been made for the

program with the Laboratoire Aimé-Cotton, and spark-excited doubly ionized spectra of various lanthanides for the program with the Johns Hopkins University and the Zeeman Laboratorium. It is now evident that the experimental cooperation with the Laboratoire Aimé-Cotton will henceforth be on a more reciprocal basis, with the successful completion of several Fourier-transform spectrometers in that laboratory. These have provided high-resolution spectra in the infrared region, beyond the photographic limit accessible to the Argonne 30-ft spectrograph. Spectra have been obtained, using ANL-fabricated light sources containing thorium, protactinium, and plutonium, yielding tens of thousands of new spectrum lines with superior wavenumber resolution, because of the favorable wavenumber-wavelength relationship in the infrared. This is a rich region for actinide spectra because of the presence of a number of low-lying electron configurations, and the new measurements have provided valuable additions to the known energy levels. The Argonne spectrograph is still the best of its kind for the photographic region, but the availability of the French infrared spectrometers makes the combination globally unique.

During the 1969–1970 stay of one of us (A. Giacchetti) at the Laboratoire Aimé-Cotton, the thorium and protactinium infrared spectra were obtained, and many new levels in the arc and spark spectra of both elements were identified as a result. Plutonium wavelengths have been obtained for 10,000 new lines.

The systematic set of Hartree-Fock calculations for the actinide elements is essentially complete, and is being used in the theoretical interpretation of their spectra.

Metal-vapor absorption spectra of uranium and tungsten have been recorded, using high-temperature-furnace and flash-heating techniques, in the region between 2000 and 1100 Å. The uranium data are being reduced and promise to add several hundred new levels to the present classification of UI spectra.

2. Some Special Problems in the Spectrum of Barium of Astrophysical Interest (F. S. Tomkins and E. M. Reeves‡)

The depression of the first ionization limit in the absorption spectrum of Ba I, by irradiation of the vapor with high-intensity light of wavelengths including and shorter than that corresponding to the limit, was investigated. The Argonne 30-ft spectrograph and metal-vapor absorption techniques developed here were used. Systematic variation of light levels and frequencies, with simultaneous monitoring of the concentrations of Ba II species, has given a good understanding of the

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mechanism involved. The effect has counterparts in solar and stellar spectra, and is thus of interest in astrophysics.

The 50-kilogauss superconducting magnet has been delivered and has been used to obtain spectacular photographs of Zeeman spectra of Ba. These will be very valuable for the interpretation of the quadratic Zeeman effect in the high series members. We expect this powerful tool to greatly expand the value of Zeeman-effect studies in assigning spectral lines to appropriate energy levels, particularly for metal vapors. The application of our research to astrophysical problems is an intellectually exciting addition to our traditional role in dealing primarily with the elements of interest to the nuclear-energy world.

B. ABSORPTION SPECTROSCOPY OF THE ACTINIDE ELEMENTS (P. R. Fields, W. T. Carnall, J. Morrison,* K. Rajnak,** R. Sarup,† and E. Sherry)

This program is concerned with experimental measurement of absorption spectra of actinide (and lanthanide) ions, theoretical interpretation of the observed spectra, and application to prediction of actinide thermodynamic properties. Theoretical analysis relates observed energies and intensities of the electronic transitions to a model based on interactions involving the *f*-electrons. Evaluation of the parameters of this model enables calculation of energies and intensities for all transitions within the lowest-lying configuration. The greater shielding of the 4*f* electrons from the environment results in certain simplifications in the theoretical treatment of lanthanide spectra. Hence, refinements of the theoretical interpretation to include higher-order interactions are first compared to lanthanide spectra before the more complex spectra of the actinides are attacked. Changes in interaction parameters across the actinide and lanthanide series and as a function of different ionic environments provides us with insight into the coordination chemistry of these elements as well as a basis for predicting spectroscopic properties of heavier actinide ions not yet measured. They also provide a reference for evaluating the results of *ab initio* (e.g., Hartree-Fock) calculations. The spectra due to higher-lying configurations have been related to predictions of structural types and of thermodynamic properties such as ionization potentials.

In the near future we will extend our calculations of corrections to Hartree-Fock Slater integrals for both lanthanide and actinide ions. Experimental studies of the spectra of the following systems are in progress: $\text{Cm}^{3+}(\text{aq})$, ErF_3 and $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, Sm^{3+} in several crystal matrices, and BkCl_3 .

Eventually we expect to measure low-temperature crystal spectra of curium and the transcurium elements. As

improved interaction parameters are obtained for actinide ions, we will investigate their application to the calculation of thermodynamic properties.

1. Plutonium Trichloride (W. T. Carnall, P. R. Fields, and R. Pappalardo††)

An experimental and theoretical analysis of the spectrum of PuCl_3 observed at 4, 77, and 298°K was completed. These measurements made it possible to identify a number of new levels and to extend the theoretical interpretation of the system. The interaction parameters obtained, when considered with results for other actinide ions previously investigated by us and with studies currently in progress, provide a much improved basis for extrapolating spectroscopic properties to the transcurium elements.

2. Gadolinium Spectra (R. Sarup, P. R. Fields, and W. T. Carnall)

The absorption spectra of GdF_3 and $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ were analyzed in detail at low temperature and high resolution. The results fully confirmed our earlier tentative identification of transitions occurring near 2000 Å. The high precision of the experimental data enabled refining of the theoretical analysis and allowed examination of higher-order magnetic interactions. These interactions are expected to be considerably larger and consequently to play a more critical role in the analysis of actinide ion spectra than for lanthanide spectra.

3. Pr^{3+} Spectra (J. Morrison, W. T. Carnall, and P. R. Fields)

Crystal-field calculations on PrCl_3 ($4f^2$) which involved diagonalization of the complete electrostatic, magnetic, and crystal-field matrices were successfully concluded. The interaction parameters obtained previously in first-order analyses were confirmed, and a basis for more complete calculation for actinide ions such as U^{4+} was provided.

Preliminary results were obtained for calculated corrections to the Hartree-Fock Slater integrals due to electrostatic configuration interaction in Pr^{3+} ($4f^2$). These corrections appear to be approaching those obtained using a previously fitted parametric model; this suggests that the method and the assumptions underlying the parametric approach are valid. Since the corresponding correction term for each actinide is much harder to determine by parametric means, the ability to use theory for calculating the second-order electrostatic interaction correction terms would greatly facilitate the analysis of actinide spectra, and would allow investigation of other processes characteristic of 5*f* electron systems.

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†Consultant, College of the Holy Cross, Worcester, Massachusetts.

4. *The Spectra of Bk³⁺ and Bk⁴⁺. A Guidepost to Electronic Structure in the Transcurium Elements* (P. R. Fields, W. T. Carnall, R. Barnes, and R. Sjolblom)

The recent availability of several hundred micrograms of Bk, the first member of the heavy half of the actinide series, has now made possible spectrophotometric studies which revealed important isolated absorption bands in both Bk³⁺ and Bk⁴⁺ (Fig. XVI.1). The observed energies of these bands provided the first experimental basis for correcting and extending calculations derived from the structure established in the lighter actinides. Thus Bk spectra serve as an important key to a further understanding of the electronic structure of the heavy-actinide elements, Cf, Es, Fm, and No.

Using a maximum of 450 μ g of Bk in deuterated solvents, spectra were observed in microspectrophotometer cells specially designed to fully utilize the limited sample available. The spectrum of Bk⁴⁺ (5f⁷) was particularly revealing because of its relative simplicity. As in the case of isoelectronic Cm³⁺ (5f⁷), observation of the transition to the first excited electronic level provided a basis for evaluating the relative importance of electrostatic and magnetic interaction in determining the energy-level scheme. Estimates of the magnetic interactions extrapolated from light-actinide spectra were consistent with the experimental observation, but electrostatic interactions were determined to be $\sim 20\%$ less than expected. Revised estimates of the structure parameters in Cf³⁺ and Es³⁺ are in better agreement with preliminary measurements on the spectra of these two elements. The structure parameters derived from systematic studies of lighter actinides, as corrected by the Bk data, provide the most accurate basis presently available for interpreting or predicting electronic structure of the heavier-actinide ions.

C. *CHEMISTRY AND SPECTROSCOPY OF HIGH-TEMPERATURE SYSTEMS* (D. M. Gruen, A. Zielen, R. L. McBeth, and D. H. W. Carstens*)

Spectroscopic studies impinge on many fields of high-temperature research. Thus, spectroscopic measurements are used in the identification of high-temperature molecules, the determination of their thermodynamic properties and the assignment of electronic, vibrational, and rotational energy levels. In molten-salt systems, spectroscopic studies lead to the identification of solute species, the characterization of the oxidation states of metal ions, redox reactions and complex ion formation. Spectroscopic methods provide powerful tools for investigating chemical interactions between gases and solids to form volatile compounds and for elucidating the reaction kinetics of gas phase atom-molecule, ion-atom, and ion-molecule reactions.

Needless to say, the spectroscopic properties of substances at high temperatures are of the utmost importance in nuclear-energy research.

There is the continuing development of high-temperature fission reactors. On the horizon, however, a new era of spectroscopic work is opening with the recognition of many challenging problems arising from the initiation of serious feasibility studies for thermonuclear fusion reactors. The operation of such reactors will of course be crucially dependent on the satisfactory performance of a wide variety of materials at very high temperatures.

1. *Refractory Metals and Gaseous Metal Hydrides* (D. H. W. Carstens and D. M. Gruen)

An intensive research program is underway directed at the formation, identification, and characterization of

Fig. XVI.1. Absorption Spectra of Bk³⁺ and Bk⁴⁺ in 0.4 M D₂SO₄. ANL Neg. No. 121-6259.

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gaseous metal hydride molecules formed by the interaction of hydrogen and its isotopes with refractory metals such as Ti, V, Zr, Nb, and Mo. Stability correlations for diatomic hydride molecules of more than two dozen metallic elements suggest that hydrides of the above-named elements may also form stable gaseous species. Such molecules produced by reactive sputtering in a fusion reactor would have to be considered in vacuum wall erosion and plasma-contamination processes.

Various approaches to the formation of diatomic hydride molecules are under investigation in our laboratory. Once formed, the molecules will be frozen out in noble-gas matrices using the technique of matrix isolation. Because beams of refractory metal atoms are involved in the preparation of the hydride molecules, the metal atoms form an unavoidable component of the matrix deposits. Therefore, the atomic spectra must be characterized first to distinguish them from the hydride molecular spectra.

During FY 1971 techniques for matrix-isolating refractory-metal atoms have been developed in our laboratory using an electron-beam sublimator coupled to a closed-cycle helium refrigerator. This apparatus has the advantage of eliminating reactive gas impurities and allows one to apply the matrix-isolation technique to substantially more refractory elements and more complex spectra than heretofore. The Ti metal atom spectrum (Fig. XVI.2) consists of eight major band systems, each system in turn being

composed of several partially resolved bands. Upon excitation with UV light, an intense, highly structured luminescence spectrum is observed. The spectra have been interpreted by combining the known gaseous atom spectral assignments with intensity data for ground- to excited-state transitions. The transition energies were found to have been shifted to higher energies in an argon matrix but to lower energies in a xenon matrix.

During FY 1971, refractory metal atoms other than Ti will be isolated in noble-gas matrices and their spectra measured at low temperatures. The theoretical procedures developed for the interpretation of Ti atom spectra will be applied to a number of other complex metal atom spectra in order to test the generality of this approach.

An apparatus is being designed and built for reacting crossed beams of refractory metal atoms with thermally hot beams of molecular hydrogen. Simultaneously, the diatomic metal hydride reaction products will be matrix-isolated and their spectra measured in the UV, visible, and IR regions.

Eventually we expect to supplement work on matrix-isolated metal hydride molecules with gas-phase studies on crossed beams to characterize primary reaction products, determine ionization energies, and measure lifetimes of excited states. It is also planned to construct a King furnace to study the metal hydride molecules under equilibrium conditions.

Fig. XVI.2. The Absorption Spectrum (a) and Luminescence Spectrum (b) of Titanium Atoms Isolated in an Argon Matrix near 4° K ($M/R = 3.6 \times 10^5$). The vertical lines superimposed on the spectrum represent the energies and intensities of all transitions reported for gaseous titanium atoms from the ground manifold a^3F . The lines below the spectrum indicate the energies of all spin- and symmetry-allowed transitions from this manifold. The upper cm^{-1} scale refers to the experimental spectra, the lower to the gaseous transitions. See text for a discussion of the shift in the lower scale. ANL Neg. No. 121-6487 Rev. 1.

With reference to the practical problems of thermonuclear reactors, interest in the hydrides of refractory metals involves not only the properties of the compounds, but perhaps even more importantly the processes by which they may be formed.

In general, the complex set of processes initiated by the interaction of the plasma with the walls of the container includes the chemical sputtering by hydrogen. It is anticipated that both experimental and conceptual contributions to dealing with this problem will be forthcoming from this program. In fact, as the development of thermonuclear reactors proceeds, it seems certain that this sputtering process will require intensive study on a scale well beyond that which can reasonably be supported out of a basic research budget, and appropriate proposals for an expanded program involving both computational and experimental studies have been initiated.

2. Rare-earth Halides (J. R. Clifton* and D. M. Gruen)

Among the spectroscopic problems of theoretical interest, those involving transitions of the f electron are sufficiently complex to offer an important challenge to our understanding and accessible enough to permit extensive experimental effort. As has been noted repeatedly in this report, the behaviors of rare-earth and actinide elements are linked and studies involving systematic behavior are frequently encountered at Argonne and other national laboratories supported by the AEC.

Our most recent contribution in this field involves matrix isolation of some interesting compounds and the study of significant aspects of their spectra. Fluorescence spectra of PrI_3 molecules isolated in Ar and Xe matrices have been interpreted by use of an intermediate-coupling model which considers electronic repulsion, spin-orbit, and "crystal-field" interactions. The "crystal field" is assumed to arise from iodide ions located at the points of an equilateral triangle giving the PrI_3 molecule D_{3h} symmetry. Results of least-squares-refinement calculations give values for the splitting parameters as follows: $A_2^0(r^2) = -282 \text{ cm}^{-1}$; $A_4^0(r^4) = 36 \text{ cm}^{-1}$; $A_6^0(r^6) = 27 \text{ cm}^{-1}$; $A_6^6(r^6) = 232 \text{ cm}^{-1}$. The effect on the parametric values of going from ninefold coordination (Pr^{3+} in LaCl_3 crystals) to threefold coordination (PrI_3 molecules) was calculated using the point-charge model and found to affect the A_2^0 parameter most strongly, in agreement with the experimental results.

3. Sulfur in Molten-salt Systems (R. L. McBeth, A. Zielen, and D. M. Gruen)

There is a significant and continuing interest in sulfur and sulfur compounds as possible components of batteries operating at moderately elevated temperatures.

The fact that elemental sulfur dissolves in molten salts was first established in this laboratory some time ago [J. Chem. Phys. 29, 461 (1958)]. Current work on this system is aimed both at the quantitative determination of the solubility of sulfur in LiCl-KCl eutectic as a function of temperature and at the elucidation of the sulfur species in solution. A further goal of the work is to study the interaction of neutral sulfur species with sulfide ions in melts and to characterize possible polysulfide species. Toward these ends, experiments have been performed to measure the light absorption of solutions of sulfur in LiCl-KCl eutectic, varying both the eutectic temperature and the pressure of sulfur vapor over the melt. In other experiments, sulfide ion has been generated in LiCl-KCl eutectic, using a nickel sulfide electrode. Early results indicate a two-electron Nernst slope and give an upper limit for the solubility of Li_2S at 400°C of $0.04M$.

D. CIRCULAR DICHROISM SPECTRA (L. I. Katzin)

Absorption spectroscopy reveals energy levels within a system, and so is an invaluable tool in characterizing and understanding a material. Inorganic transition cations have levels which are degenerate under symmetric environments, but split in revealing patterns under decreased symmetry following chemical combination. When the new system is dissymmetric, either intrinsically or because a component is dissymmetric, the spectral transitions show circular dichroism. Because of a variety of factors, this can lead to resolution of transitions in a manner not possible from ordinary absorption spectra. In particular, operation of new selection rules which depend on internal symmetry relations may give unique information on the structural organization of the species in solution, not available from the direct absorption spectrum.

In our prior studies, circular dichroism spectra have shown when complexes of a transition or rare-earth element cation are formed, when one complex is transformed into a second, etc. In some interesting special cases, the geometry of a complex, as determined by which of several possible active sites on a molecule form a chelate complex with the metal ion, has been established and information was obtained on the general question of structural conditions that affect complex stability.

These studies have been continued this year through investigation of the mixed complexes of Ni(II) with acetylacetonate (not optically active) and L-amino acids (optically active). Circular dichroism spectra have served to demonstrate the formation of a mixed complex, containing one each of acetylacetonate and of amino acid, both ligands chelating to the Ni(II) . From group-theoretical considerations of the selection rules, it has been possible to deduce that the ligands are arranged equatorially around the central metal ion. It has further been indicated, from similar criteria, that the normal bis-amino acid complexes of Ni(II)

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form as equatorial complexes also, but that in alkaline solution (using the proline complex as an example) the bischelate transforms into a *cis* form instead of the normal equatorial *trans* form. A possible mechanism for the alteration has been indicated.

Further, in collaboration with Prof. I. Eliezer of Tel Aviv University, a survey has been made of the literature on the

chelate complexes of Co(III) which are optically active because of intrinsic dissymmetry. It has been possible to systematize the spectral data, and to demonstrate that the circular dichroism spectrum reflects the particular functional-group bound, as well as the crystal field symmetry around the Co(III).

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XVII. THEORETICAL CHEMISTRY*

The last year or two have brought advances in theoretical chemistry. Techniques for utilizing fast digital computers have been devised at Argonne which permit the high accuracy needed for the increasing application of basic equations to the calculations of observable chemical behavior.

The field of chemistry is blessed with an incredible wealth and complexity of experimentally observable phenomena. To understand these phenomena and utilize them most effectively, one must discover empirical regularities and devise useful models. An unattainable ideal would be a small number of basic principles from which all observable results could be calculated by straightforward means. For chemical phenomena many chemists believe that such principles are known and are embodied in the currently accepted ideas of quantum mechanics, electromagnetic theory, statistical mechanics, and thermodynamics. More specifically, the Schrodinger equation provides a key to the microscopic structure and properties of chemical reactions, and major new insights into chemical bonding, chemical reaction, and other chemical phenomena could be achieved if we could obtain more precise and detailed solutions. At present we are able to solve the Schrodinger equation only for relatively simple (but by no means uninteresting) chemical systems with the accuracy needed to provide reliable data on the properties of such systems.

In particular there are effects needed to correlate the motion of the electrons which make a complex and significant contribution to the binding energy of even diatomic molecules. The intelligent use of large, fast digital computers offers some hope of eventually dealing with this problem.

Not too long ago, the calculation of an orbital picture would take hundreds of hours of computer time, even for a simple diatomic molecule. Now, with better programs and bigger, fast computers, it takes only a few minutes to compute the electronic structure of a small molecule in a given quantum-energy state. This qualitative change has taken place during the last ten years.

We are able to get certain other properties out of the orbital picture satisfactorily. One property is the geometry of a molecule: the angles between its chemical bonds and the lengths of those bonds. Another is the vibration frequency of the atomic nuclei in a molecule. By extending the orbital model for diatomic molecules, we are also beginning to get satisfactory accuracy in calculating the dissociation energy of the chemical bond. Computations of this type, however, require several hours on the IBM System/360 Model 75 at Argonne.

In the last year, progress has been demonstrated at Argonne using one of the most accurate general approxima-

tions yet proven practical (also developed at Argonne). The "optimum-valence-configuration" (OVC) method is a version of the multiconfiguration self-consistent-field (MC-SCF) approximation which has been most useful. Calculations have been completed on the fluorine and HF molecules which reproduce the potential between the atoms within the accuracy with which it is known experimentally, accurately enough indeed to decide between two divergent empirical results obtained in recent measurements and settle a controversial debate over the dissociation energy of these molecules. Simpler calculations, when coupled with experimental consideration, have thrown considerable light on short-lived intermediate species such as the OF, SF, and SeF molecules and their ions which cannot be examined experimentally in conventional experiments.

We feel that we are now coming to the point where a chemist or physicist can really turn to the computer for an answer to a chemical question. We have done some thinking about how to make our BISON** system into an instrument that will be responsive to the nonspecialist chemist who does not understand complicated computer programs. Most specialists stop programming as soon as they learn how to get an answer out of the computer efficiently. In developing BISON, however, we kept going and tried to put into the system as much of our research experience as possible—so that the general user would not have to learn all of our sophisticated input codes and special computational artistry.

The basic structure of the instrument we call BISON consists of three functional sections. The first is an INTERVIEW module, in which the chemist defines his problem by conversing with the system. The second is a batch-processing phase under the control of a PROCEDURE EXECUTIVE module. The third is a MOLECULAR DISPLAY module, which helps the chemist study his results.

Such mathematical modeling enables us to see things here which, in some ways, the experimentalists will never see in the laboratory (which of course raises philosophical questions about whether they're really there, and so on).

We can slow down the time scale in the formation of a molecule, or speed it up for some process that would take too long otherwise. We can expand the spatial scale to look at details of a chemical reaction, actually watching the bond break and go over to form another bond on the product side of the reaction. This ability to look at a chemical process slowly and adiabatically (when allowed) is

**BISON is the name given by A. C. Wahl to this general computer approach to studying and teaching chemical interaction. He explains, "I have always liked the American buffalo and always wanted to name something after it. The term has absolutely no other meaning."

*Chapter edited by Arnold C. Wahl

one of the main advantages of MOLECULAR DISPLAY. We can show a molecule forming in terms of contours of electron density, or in terms of varying shades which provide a more artistic representation of density. The density contours, of course, are more quantitative; the chemist can make measurements from them, and students can use them in exercises.

Also, the MOLECULAR DISPLAY module can be interactive. At an IBM 2250 display unit we can see how chemical processes take place. For example, we can watch a molecule undergo excitation and ionization in terms of its changing electron density.

Among the most intriguing things to a chemist is the chemical bond. With MOLECULAR DISPLAY, chemical bonding can be analyzed in a variety of ways. The chemist can compute properties of a bond, and he can subtract the charge density of the constituent atoms to see where the density is increased or decreased by the bonding.

This year we have completed a number of interaction projects. Calculations on alkali metal interactions have been applied to the thermodynamic and transport properties of alkali metal vapors, a problem of considerable interest in reactor technology. Progress was also made in describing the entire region of interaction of noble-gas atoms which particularly include the intermediate region around the van der Waals minimum. The interaction potential computed for two atoms of helium not only agreed well with previously accepted semiempirical values, but actually was used by an atomic beam group at The University of Chicago to predict the scattering cross section for helium on helium in an atomic beam experiment which may lead the way to an even more refined semiempirical potential.

Even more exciting in recent months have been the extension of these techniques to the study of an actual chemical reaction, the calculation of the complete energy surface in a three-body system as one atom approaches a diatomic molecule and the new diatomic combination is formed while the third atom leaves the combination.

We have chosen by way of illustration our results on the evaluation of van der Waals forces, the reaction of lithium with hydrogen, deuterium, and tritium, and the transport properties of alkali dimer gases.

A more philosophical note on the role of mathematical logic and physical reality is included as a final contribution to this chapter.

A THE A PRIORI EVALUATION OF VAN DER WAALS FORCES (A. C. Wahl, P. Pertoncini, and G. Das)

In general, there are two ways of evaluating forces between atoms and molecules, by computation and by experiment. In the area of the weak, long-range effects known as van der Waals forces, it is extremely difficult to uniquely and precisely characterize these important interactions by semiempirical parameterization of experiment.

In addition, since these forces are of extremely small magnitude, their calculation by first principles has remained a challenge since the dawn of quantum mechanics.

Progress can now be reported in making theoretical calculations describing the entire region of interaction of closed-shell atoms which particularly include the intermediate region around the van der Waals minimum. The closed-shell atoms are those of the noble-gas family, and an early goal has been to obtain an accurate potential curve [1] for He_2 over the entire range of internuclear distances by a single consistent and feasible computational technique and model. In Fig. XVII.1, the interaction potential we have computed for He_2 is presented and compared with other approaches. The results can be seen to agree well with accepted semiempirical values for the potential, as well as with an accepted a priori long-range form of the potential.

An interesting set of experiments has now provided additional support for the results of these calculations. The most refined calculation of the depth of the well shown in Fig. XVII.1 at about 5.6 bohrs yields a value corresponding to about 115°K. Within this well-depth region, the computed interaction potential has been used by an atomic-beam group (Lee and his collaborators at The University of Chicago) to predict the scattering cross section for He on He in an atomic-beam experiment. Their experiments have demonstrated significantly better agreement with cross sections calculated from the ab initio interaction potentials than with those calculated from any of the previously existing semiempirical potentials.

The techniques we have used in this work are an extension of a scheme which has been applied successfully to obtain chemically accurate potential curves for a variety of diatomic systems [e.g., H_2 [2], F_2 [3], NaLi [4], and the long-range interaction in HeH [5]]. In the calculations

Fig. XVII.1 Comparison of Helium Potential Curves

for these systems, we have used an approximation to a full multiconfiguration self-consistent field (MC-SCF) method [1-8].

This MC-SCF model as we have employed it is quite general, and due to its simplicity is applicable to other closed-shell interactions, and with clear changes to appropriate closed-open and open-open shell long-range forces, thus extending its usefulness beyond the He group gases. In fact, recent success has been achieved by similar techniques for Li_2 [9], LiHe [10], and the long-range interaction of Li with the H_2 molecule as described in the next section.

B. A PRIORI CALCULATIONS ON THE CHEMICAL REACTIONS
 $\text{Li} + \text{H}_2 \rightleftharpoons \text{LiH} + \text{H}$, $\text{Li} + \text{T}_2 \rightleftharpoons \text{LiT} + \text{T}$,
 AND $\text{Li} + \text{D}_2 \rightleftharpoons \text{LiD} + \text{D}$ (A. Karo,* A. C. Wahl, and G. Das)

This chemical reaction, of interest in the CRT program due to the processes for recovering tritium from a solution of LiT and lithium, is being studied by a priori techniques in a collaborative effort between ANL and LRL. In this study we approximately solve the Schrodinger equation as a lithium atom approaches a hydrogen** molecule from various angles and reacts, with the products then moving away from each other. The hydrogen molecule is allowed to vibrate during this collision process. The solution to the Schrodinger equation for this reaction (consider the system to be a "supermolecule") yields the wavefunction and the energy surface for the reacting system. When the energy surface is completed (we now have 100 points done out of a projected 300), it will be used in a molecular-dynamics study. Namely, lithium atoms will be "fired" at a vibrating hydrogen* molecule from various angles with various relative velocities. From this study reaction cross section can be predicted. From the wavefunction we can "see" reactions take place (Figs. XVII.2-XVII.4), and when viewed along with the energetics we can already speculate that the reaction will only occur if the hydrogen molecule is very highly excited vibrationally. Namely, energy must be put into this mode and not into translation unless the collision can vibrationally excite the H_2 .

This study also represents one of the first such a priori accurate studies of a full reactive surface, and collaborative experimental molecular beam work is planned in the Chemistry Division.

C. THERMODYNAMIC AND TRANSPORT PROPERTIES OF ALKALI DIMER GASES
 (A. C. Wahl and P. Bertocini)

In order to calculate the virial equation of state and the transport properties of alkali vapors (both of interest in reactor design) it is necessary to have the pair-wise

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**Take hydrogen to mean H, D, or T. The energy surface calculated is the same for all three. It is in the molecular-dynamics stage that atomic mass enters.

Fig. XVII.2. Lithium Atom (Li) Has Approached H_2 Molecule Where Bond Has Already Been Stretched to 2.2 bohrs but Reaction Has Not Yet Occurred.†

Fig. XVII.3. H_2 Bond Has Now Been Stretched to 2.5 bohrs and Reaction Has Now Occurred. Note how diffuse outer-electron density of lithium has moved in to form incipient LiH bond.†

Fig. XVII.4. Rightmost Hydrogen Atom Now Moves Away to Form LiH Molecule and Free H Atom.†

†Lines are contours of equal electron density. Outermost contour has a value of 6.1×10^{-3} electrons/(bohr)³, and each successive inner contour increases by a factor of 2.

interaction potential between ground-state alkali atoms. In theoretical chemistry we have evaluated such interaction potentials for Li_2 , $NaLi$, and Na_2 . Although there was experimental information for the $^1\Sigma$ potential, the $^3\Sigma$ is usually "guessed" and no experimental information was available for $NaLi$. We provided accurate potentials for these systems and are planning to proceed upward in the periodic table to NaK and K_2 . Recently, our a priori prediction of the properties of $NaLi$ were experimentally confirmed to within 10%.

D. THE RELATIONSHIP BETWEEN EPISTEMOLOGY, MATHEMATICAL LOGIC, AND PHYSICS (P. A. Benioff)

The whole program begins with the premise that the basic aspects of physical reality are determined, in essence, by the basic properties of the process by which one acquires knowledge. This view is different from the conventional one which holds that the basic aspects of physical reality are essentially independent of the knowledge acquisition process (KAP). If our premise is correct, then a deeper understanding of the KAP and, in particular, of its dynamics should yield a better understanding of physical reality and may even yield new physics.

Seen in this light, the goal of the KAP is the construction of a physical theory which "agrees with experiment." Clearly one must at the outset have a good idea of what it means for a physical theory to agree with experiment.

To this end, a precise definition of this concept for a large class of physical theories has been given and discussed and shown to have many properties which intuitively it should have [11,12]. The class of physical theories considered consists of those which in essence correspond to a map U with domain in the set of possible infinite sequences of measurements and range in the set of all probability measures defined on Σ^ω , which is a standard σ -field of subsets of N^ω , the set of all infinite sequences of natural numbers. It is a minor restriction to assume that for each infinite sequence Q of measurements, the outcome sequence ψ_Q obtained by actually doing Q , lies in N^ω .

The reason that infinite sequences rather than finite sequences of measurements must be considered is that, in any statistical theory, the comparison between an empirical mean and a theoretical expectation value can be given a precise meaning in terms of infinite sequences only [11].

The proposed definition of agreement between theory and experiment is the following statement: "For all infinite sequences Q of measurements in the domain of U , all properties of outcome sequences which are τ -definable from the probability measure $U(Q)$ and are true $U(Q)$ almost everywhere in N^ω are true for ψ_Q , the outcome sequence obtained by actually doing Q ."

By a property of outcome sequences being τ definable from $U(Q)$ we mean that the property is expressible by

some formula $q(\phi, U(Q))$ in the language of a formal axiom system (or theory) τ . Each property of sequences defines a subset E of N^ω in Σ^ω of outcome sequences, namely, the set of all sequences which have the property in question. Equivalently, for some formula $q(\phi, U(Q))$, E is the set of all sequences ϕ for which $q(\phi, U(Q))$ is true.

In Ref. 1, τ was taken to be the axiom system of an extended arithmetic. However, it was seen that this was not strong enough. In Ref. 2, τ was taken to be Zermelo-Frankel set theory. It was shown that this very strong τ includes the properties which intuitively should be considered. In particular, it includes all comparisons between limit empirical means and general expectation values given by the theory U . Such comparisons were not included in the weaker τ of Ref. 1.

A satisfying consequence of the proposed definition of agreement between theory and experiment is that one can prove that if U agrees with experiment, then for each Q in the domain of U such that $U(Q)$ is a product probability measure, ψ_Q is a τ -random sequence. Informally this says that every sequence Q which consists of an infinite sequence of repetitions of the same measurement, where the measurements are independent of one another, will generate a random output sequence. Clearly this is required by most sequences of repeated measurements in the laboratory.

A very important question left unanswered in Refs. 1 and 2 is whether or not Quantum Mechanics is a theory of the type U . In particular, the problem centers on how to describe infinite sequences of single measurements using the mathematical apparatus of Quantum Mechanics.

This problem was solved recently by the use of operator-valued measures. In particular it was shown [13] that to each process Q which consists of a finite or infinite sequence of observable measurements separated by transformations (such as space-time translations, rotations, etc.) there is uniquely associated a probability-operator measure O^Q which gives all the statistical properties of the process. That is, for each set E in Σ^Q , a σ -field of subsets of S , the set of all possible outcomes of Q , the probability of carrying out process Q on a system in state ρ and obtaining an outcome sequence on E is given by $\text{Tr}(\rho O_E^Q)$. Here O_E^Q is a positive self-adjoint operator with $0 < O_E^Q < O_S^Q = 1$.

There are some interesting consequences [13] of this association of probability-operator measures to processes. One is that for many E in Σ^Q , there are two ways of measuring the probability $\text{Tr}(\rho O_E^Q)$. One way, method 1), consists of an infinite sequence of repetitions of 'prepare system in state ρ —carry out Q on ρ to give outcome sequence—discard system.' This generates an infinite sequence, α , of outcome sequences from which one generates an infinite sequence $\Theta \alpha$ of 0's and 1's by the prescription $(\Theta \alpha)(j) = 1$ if and only if $\alpha(j)$ is in E [$\alpha(j)$ is not in E] for each j . Finally, the limit mean, $\bar{M} \Theta \alpha$, gives the desired probability. Method 2) consists of an

infinite repetition of measurements of O_E^Q on ρ to give the infinite sequence β . $\bar{M}\beta$ gives the desired probability.

An interesting aspect of this equivalence is that the physical operation of method 2) (the infinite repetition of measuring O_E^Q on ρ) is equivalent to the physical operation of method 1) (the infinite repetition of carrying out Q on ρ), plus the mathematical operation of generating $\Theta\alpha$

from α . The limit mean operation is the same for both methods. Thus one can replace physical plus mathematical operations by purely physical operations. It is noted [13] that this is an extension to sequences of a general property of operators in Quantum Mechanics, which, although well known, is not usually thought of in this way.

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XVIII CENTRAL REAL-TIME COMPUTER FACILITIES* (P P Day, J J Hines, and A J Zielen)

The Chemistry Division's central Sigma 5 computer facility is currently providing sophisticated real-time service to 11 concurrently running, remotely located (up to one mile distant) experiments, and supporting an open-shop batch-processing facility for moderate-sized computational problems. The real-time service consists of some or all of the following: program loading and control from the remote laboratory, direct data transmission to the computer for immediate computation and/or storage, graphic display of processed data during the course of an experiment, automated control of the experimental process, and immediate final analysis of the experiment at its termination. Using teletypewriters and graphic-display equipment located in his laboratory, the experimentalist can control his experiment and view analysis of its progress using programs that are specifically designed to meet his changing requirements.

The successful operation of this facility over the past two years has clearly demonstrated the practicality and many advantages of providing on-line data acquisition and automatic experiment control with a central computer operating as a utility (computational service on demand for a variable number of users). The system is practical in that it costs no more than a much less flexible (useful) service which would be provided if a small computer were dedicated to each experiment. Among the many advantages are the ease of program modification and debugging, the ease of rapid implementation of new experiments, the availability of sophisticated hardware, and the availability of immediate final analysis of experiments at their conclusion. The Operating System (master control program) for our central computer, which was designed and written by Chemistry Division personnel, has proved very effective in providing a multiprogramming environment for our ever-changing work load (on a multisecond time scale). This environment meets all the requirements of our experi-

mentalists: insured program and data integrity, performance of very complex computations in real time, rapid implementation of new experiments, efficient sharing of sophisticated input-output media (magnetic tape, disk storage, digital plotting, etc.), and easy user-program modification.

Table XVIII 1 provides a list of the research and analytical facilities currently connected to the system and identifies the staff scientist responsible for each operation. The level of sophistication and flexibility reached in supporting some of these experimental facilities (e.g. pulsed NMR, Chapter VIII C) has surpassed that available at the implementation date at any other laboratory. Current effort is being expended in bringing four additional experiments on-line and in upgrading the level of service provided to some experiments in the current group. There are about 15 additional experimental situations in the Division whose research effectiveness (extension of current physical limits and/or increased output) would be greatly enhanced if provided real-time service by our computer utility. We are thus planning to expand the system to provide real-time service to about 30 experiments in the next couple of years.

An ancillary, but very important, benefit of our central computer operation is the 24-hr/day-7 day/week support of an open-shop batch-processing facility: individuals may use the computer themselves to debug and run programs, obtaining immediate results. Unfortunately, the usual facility available to the scientist who does his own programming is the large batch-processing one where a job is submitted, and where several hours later the requester often finds that his job failed to run correctly because of some simple mistake in coding or a control card error. This type of operation can be tolerated, but it is not the best use of the working scientist's time. While some argue that he should have his programming done by a professional

TABLE XVIII 1 On-line Experiments

Implementation Date			
1	12/69	J. Unik	Nuclear Fission and Heavy element Studies
2	1/70	A. Friedman	Inelastic Alpha scattering Distribution from Actinide Elements
3	3/70	D. Rokop	(Instrument 1) - Analytical Mass Spectrometry
4	4/70	D. Rokop	(Instrument 2) - Analytical Mass Spectrometry
5	6/70	D. Osborne	Precision Heat-capacity Measurements
6	8/70	W. Ramler	Line Operation
7	12/70	J. Katz	Infrared Absorption Spectrometry
8	1/71	J. Katz	Pulsed NMR Studies on HA-100
9	6/71	P. Fields	Study of Neutron deficient Heavy element Nuclei
10	7/71	S. Wexler	Molecular Beam Chemistry
11	7/71	S. Peterson	Neutron Diffractometer

*Chapter edited by P. Day

programmer, generally by the time the communications gap is bridged and the problem is defined in terms the programmer can understand, the scientist could have done the job himself and in so doing oftentimes obtained a better insight into the nature of his problem and its best solution. A highly interactive facility is much to be preferred for this type of scientist who is willing and able to function as his own part-time programmer. An open-shop such as we

provide is just such a facility. By being able to see the progress of his job either on a plotter or printer, the casual (but extremely sophisticated from a theoretical point of view) user can work quite efficiently by learning of and correcting his oversights immediately. This very useful service is provided by the Sigma 5's Operating System without inhibiting or interfering with the on-line experiments, and is essentially a free service.

XIX. ANALYTICAL CHEMISTRY*

The analyst plays a significant role in much of the chemistry reported in this volume, but in relatively few areas at Argonne is the analytical procedure an end in itself. In several situations, however, procedures have been developed here which provide unusual or even unique analytical capability.

In several cases we have applied these to social problems of some importance not directly related to the nuclear effort which has shaped most of the other divisional programs.

While as might be expected, Argonne has complete capability in analytical procedures utilizing radioactivity, and nuclear processes in general, we have developed a number of mass-spectrometric procedures to offer perhaps the most effective collection of such instruments available in any known laboratory.

It is not surprising, therefore, that most of the applications to problems of environmental concern which have been incorporated into our research program involve the use of the mass spectrometer. In this chapter we include a brief look at our instrumental capability and some recent developments in this area and a slightly more detailed look at a few applications of interest.

A. MASS-SPECTROMETRY TECHNIQUES

The Chemistry Division Mass Spectrometry Group has constructed a number of research mass spectrometers over the years, the most unique being the 100-in. double-focusing instrument in Building 203. Two instruments for precision isotope ratio determination, one for general-purpose gas analysis, and four for isotopic analysis of solids are also available. All these instruments have been automated in the past three years and equal or surpass the performance in sensitivity, precision, and versatility of any comparable spectrometers of which we are aware. They are used in collaborative research with groups both throughout the Laboratory and in universities and other research organizations.

There are also available a number of commercial instruments, often modified at Argonne to handle special samples or operate more effectively in some particular mode. These include a spark-source mass spectrometer, time-of-flight mass spectrometer, and a high-resolution AEI-MS-9 spectrometer designed to handle complex molecules.

1. Precision Mass Measurements (C. M. Stevens and P. E. Moreland)

The Argonne 100-in.-radius mass spectrometer was specially designed to measure atomic masses with an order

of magnitude higher precision than values existing at the time. In the last three years, the masses of H, D, ^{35}Cl , and ^{37}Cl have been measured with the Argonne machine to a precision between one to ten $\times 10^{-8}$ of the mass. These results have now been confirmed by new measurements of L. Smith at Princeton University using a mass-synchrotron method of measuring the masses. Only a limited number of atomic masses have been measured to accuracies of less than 1 kV; for most of the atomic table, the accuracy is >10 kV. The Argonne instrument is one of three or four instruments in the world with proven capability of measuring atomic masses to a precision of less than 1 kV.

2. Spark-source Mass Spectrometer (J. Lerner and G. Lamich)

The spark-source mass spectrometer has great promise as an analytical instrument because of its high sensitivity (of the order of parts-per-billion) for virtually all elements. The most significant problem to date has been a lack of reproducibility and precision; variations by a factor of one or more orders of magnitude have been common. The principal sources of error are lack of homogeneity in the electrodes, variation in the ion-beam composition during sparking, and a loss of accuracy in converting photoplate darkening to relative ion concentrations.

In order to prepare electrodes from nonconducting materials, a technique of mixing and grinding with ultra-pure graphite and subsequent compression has been developed that yields uniform and reasonably sturdy electrodes. A similar technique for squeezing metallic powder or granules into suitable homogeneous electrodes has also been established.

Reproducibility has been improved markedly by the insertion of a variable-ratio scaler between the spark pulse-generator and the ion-beam chopper amplifier, thus permitting accurate control of the short exposures while yet sampling a relatively large volume. The speed and accuracy of photoplate interpretation have also been vastly improved by the modification of an obsolete microdensitometer to give quantitative density readings and by the writing of a computer program to calculate ppm directly from the raw data. A digital peak-reading voltmeter currently under construction will contain provision for operation of a paper tape punch, so that data can be processed without intervening manual card-punching.

B. ENVIRONMENTAL STUDIES

As any newspaper reader will readily note, interest in the nature of the environment has mounted rapidly in 1970. Argonne scientists have been interested for some time, but it has not always been easy to find adequate

*Chapter edited by: C. M. Stevens, M. H. Studier, and M. A. Wahlgren.

support for the programs that have suggested themselves as both appropriate to the Laboratory capabilities and immediately useful to the supporting agency.

Some suitable areas have emerged, however, of which the carbon monoxide problem has been most prominent and the Lake Michigan environment the most tempting general problem area.

*1. Isotopic Abundances of Atmospheric Carbon Monoxide** (C. M. Stevens, L. Krout, D. Walling, and A. Venters)

In recent years several investigations have revealed that carbon monoxide may have a more active and complicated role in nature than had generally been known [1-5]. Very little is understood about the overall cycle of atmospheric CO, nor about its major sources, sinks, and residence time. The abundance of the stable isotopes of CO might be a way of distinguishing CO from different origins and thus identifying the origins of atmospheric CO. Both carbon and oxygen have quite variable isotopic compositions in nature [6-8]. At almost every stage of any natural process involving these elements, there are isotopic fractionation effects. Further the combination of isotopic variations for two elements having different cycles might be of special diagnostic value.

A program of measuring the isotopic composition of CO in the atmosphere and from natural sources has been going on at Argonne since 1969. The atmospheric studies consist of two separate studies: (1) the determination of the global-average isotopic composition of all CO emitted by internal-combustion engines, and (2) the determination of the isotopic pattern of CO in the least polluted atmosphere in different latitudes and at different seasons and times of day.

The air samples are collected in rural locations upwind of cities and highways and then processed in a gas-extraction system which produces a pure sample of CO₂ from the oxidation of the CO, after removal of all atmospheric CO₂. The CO₂ samples are then isotopically analyzed for both carbon and oxygen by high-precision mass spectrometry.

a. World-average Engine CO

Petroleum carbon has a variable isotopic abundance which is reflected in the CO of engine emissions. The isotopic composition of world average engine emissions was determined by analyzing samples of air from major cities of both the U.S. and Europe and using automobile registrations as the relative weight factors. The average

¹³C/¹²C ratio is found to be -28.1 per mil versus PDB carbonate, and the average ¹⁸O/¹⁶O ratio is +23.5 per mil versus Standard Mean Ocean Water, which is close to the value for atmospheric oxygen, Fig. XIX.1.

b. Atmospheric CO

Figure XIX.1 shows the isotopic patterns of atmospheric CO for minimum pollution conditions at locations near Argonne (approximately 40-50 mi upwind from Chicago and at several distant locations in the northern hemisphere). Figure XIX.2 shows the seasonal variation of the concentration, and oxygen and carbon isotopic abundance for surface atmospheric CO from August 1970 to the present time. Samples before July 1970 were analyzed for only concentration and carbon-isotopic abundance and are indicated as solid (night) or open (day) squares for Illinois rural locations and plus signs with squares for urban locations.

Fig. XIX.1. The Isotopic Composition of Carbon and Oxygen in Carbon Monoxide in Nonurban Air. ANL Neg. No. 121-8449.

*This work supported by Coordinating Research Council-Department of Health, Education, and Welfare, Contract CAPA 4-68 (1-69), and U. S. Atomic Energy Commission.

Fig. XIX.2. Seasonal Variations in Atmospheric Carbon Monoxide: (a) Concentration, (b) $\delta(^{18}\text{O}/^{16}\text{O})$, (c) $\delta(^{13}\text{C}/^{12}\text{C})$. The collection sites and times are indicated above. ANL Neg. No. 121-8450.

Atmospheric CO in Illinois has the lowest concentration (0.13 ppm) and the greatest difference isotopically from world average engine CO in the summer when automobile traffic density is the highest—18% higher than in winter. The $^{18}\text{O}/^{16}\text{O}$ ratio for this northern-hemisphere summer-

time CO is within 1 to 2 per mil of CO in air collected on the west coast of Australia in May and is 19 per mil different from engine CO. These results indicate the principal source of atmospheric CO in the northern hemisphere in the summertime is 10 to 30 times greater than engine

emissions or 2 to 6×10^8 tons per month. If this CO were produced by surface emissions such as the oceans, lakes, trees, etc., the rate would have to be greater than one std cc/hr/m². This is 1 to 2 orders of magnitude too much to be accounted for by known surface sources in the surface biosphere. Junge et al [9] estimated the supersaturation of CO in ocean waters to produce 0.06 std cc/hr/m². We have found that freshwater lakes and rivers emit CO at a rate equal to or less than this rate depending on the degree of pollution. Some species of trees and plants show somewhat similar rates. The supersaturation of CO in rainwater found by Swinnerton et al [1] and verified by us is a clue to the existence of an atmospheric source. The source of the CO in rainwater or of any other possible atmospheric sources is not understood.

The abrupt increase in the $^{18}\text{O}/^{16}\text{O}$ ratio in September and October for Illinois samples with a simultaneous large increase in concentration is most likely related to the end of terrestrial plant life in the autumn. It has been suggested by Katz [10,11] that CO emissions may possibly accompany the degradation of chlorophyll in plants and trees. This seasonal burst of CO produces an estimated amount of 10^9 tons of CO over 1-1/2 months. November shows a decrease in concentration corresponding to either an increase in average windspeed, dispersion of the CO throughout the northern hemisphere, or the effects of the scavenging process.

The conclusion (based on evidence from isotopic compositions) that natural emissions of CO are many times the amount of engine CO implies that the residence time is shorter than had been estimated previously by Weinstock [12] and Junge et al [9]. Using our estimates of natural production rates in the northern-hemisphere summertime of 2 to 6×10^8 tons/month, the corresponding residence time is 0.5 to 1.5 months. Average residence time may be difficult to estimate because of seasonal variations, short-term effects of atmospheric circulation, and geographic variations of sources. Two of the three processes which have been suggested as mechanisms for CO sinks would have marked seasonal changes: the soil bacterial consumption reported by Inman et al [3], and the photochemical reactions involving OH radical in the atmosphere by Weinstock [12].

2 Sulfur Isotope Study of Environmental Water and Air (B. D. Holt, A. G. Engelkemeir, and A. Venters)

The mass-spectrometric measurement of variations in the ratio of stable isotopes of sulfur, $^{32}\text{S}/^{34}\text{S}$, in samples of natural water systems, rain, and air have been reported recently by other laboratories. Brookhaven National Laboratory has been using this method to trace sulfur in the atmosphere to sources of pollution [The Atmospheric

Diagnostic Program at Brookhaven National Laboratory], Cortecchi and Longinelli of Laboratorio di Geologia Nucleare, Pisa, Italy, have made recent applications of the method to the study of rainwater. Horwitz et al of the Federal Water Pollution Control Administration have compared the sulfur-isotope ratio method to other methods for tagging oil spills in surface-water systems.

We have made $^{32}\text{S}/^{34}\text{S}$ ratio measurements on many of the easily accessible environmental media (streams, wells, lakes, sewage-plant effluents, rain, and air) within a metropolitan suburban area to look for patterns of isotopic variation that could be useful to pollution studies.

About 340 samples of BaSO_4 , derived from environmental specimens, were converted by a rapid, simplified, pyrolysis method [13] to SO_2 for mass-spectrometric determination of $^{32}\text{S}/^{34}\text{S}$.

It was determined that Salt Creek, a small stream draining a terrain of glacial deposits in a western suburban area of Chicago, was characterized by a negative enrichment of sulfur-34, with respect to Canyon Diablo meteoritic troilite, of about -7 parts per mil (%). Neighboring streams were also negative, whereas Lake Michigan and shipping canals draining the Lake into the Illinois River were positively enriched by about +6%. Three major perturbants of the enrichment of Salt Creek were (1) rain (about +5%), (2) earth disturbances such as gravel mining and road construction, and (3) effluents from sewage-treatment plants which were supplied by water from municipal wells. Shallow wells contributed to negative sulfur-34 enrichment of the receiving stream and deep wells to positive enrichment. The largest tributary had apparently been reversed from naturally negative enrichment to strongly positive enrichment by the influx of sewage-plant-effluent water originating from deep municipal wells.

Sulfur-34 enrichments in rainwater sulfates varied in an orderly fashion in sequential samples from single storms, but varied randomly in sequential composite samples from separate storms. Enrichments both in rain and in atmospheric air were small compared to that of sea water.

The high-precision equipment and improved laboratory techniques remain available for extension of the stable-isotope examination of environmental water systems to a large area of the Midwest, including Lake Michigan and major underground water supplies. Experimental data derived from such an investigation are expected to be valuable to the assessment of the quality of important water supplies in areas of urban and industrial expansion. The large difference in sulfur-34 enrichment found between deep wells and shallow wells of municipal supplies suggests that stable isotope measurements may be useful in identifying underground water supplies and in detecting changes that occur due to pollution or to mixing of supplies. However, with no funding specifically allocated to this project, no further work is presently anticipated.

3. Lake Michigan Environmental Studies* (M. Wahlgren)

A collaborative effort with J. Robbins of the Great Lakes Research Division at The University of Michigan is being carried out to study the behavior of various trace elements near the mouth of the Grand River (Michigan). Five and one-half weeks during the current field season were spent aboard the research vessels *Mysis* and *Inland Seas* in the Grand River area of Lake Michigan.

To date, the effort has been concentrated in 3 related but distinct projects: a) sediment sampling with the Benthos Corer and the Ponar grab sampler, b) locating and obtaining useful specimens of deep lake biota from the lower trophic levels (oligochaete worms, the crustacea amphipods and shrimp, and the small fish sculpin and stickleback), and c) trace-element behavior at the river-lake interface and near-shore region.

To obtain biota and water samples suitable for trace-element analysis, extensive modification of existing limnological equipment and techniques has been necessary. A large number of sediment and water, and a lesser number of biological samples will be analyzed to determine concentrations of a number of trace elements of radiological, biological (nutritive and toxic), and geochemical interest.

Preliminary analysis of 35 tributary and lake-water samples using the spark-source mass spectrometer (see next section) to determine 20 selected trace elements indicates a general grouping into 3 more or less distinct patterns. Isopleths derived from *in situ* measurements of temperature, conductivity, dissolved oxygen, pH, and "chloride ion" activity in certain interfacial regions also show deviation from the correlation expected if dilution by lake water were the only significant change occurring.

The primary analytical method which will be used for analysis of the samples is neutron activation analysis. The sampling techniques and data from the current samples will be the basis for a concerted study next field season on radionuclide and trace-element cycling and/or concentration in the food chain. The program will be expanded to include a study of the contribution of atmospheric aerosols to the Southern Lake Michigan Basin.

4 Trace Elements in the Lake Michigan Environment (J. Lerner and G. Lamich)

The spark-source mass spectrometer has been used sporadically to analyze samples from Lake Michigan and tributary river waters, as much to test the technique as to obtain useful results. The method is rapid and sensitive; the average standard deviation for some two dozen trace elements has been reduced to 15–25%, and the results

agree quite well with analyses by other methods. The same techniques and precision should apply to analysis of water and airborne particulate matter or other samples obtained in the course of pollution or environmental-control studies.

C MASS SPECTROMETRY APPLIED TO DRUG

TRAFFIC CONTROL** (M. H. Studier, L. I. Katzin,
A. L. Harkness, and L. P. Moore)

Time-of-flight mass spectrometry is a rapid, extremely sensitive and powerful technique for characterizing minute amounts of organic molecules, particularly when used in conjunction with various types of chromatography. Its application to the drug-traffic-control problem can be in a number of different directions—characterization of drug raw materials, intermediates, pure drugs, commonly used adulterants, "street samples," etc., and conceivably even to the locating of sites of drug manufacture by analysis of samples taken from the neighborhood of the suspected activity.

Fragmentation patterns have been determined for characterization purposes for drugs and common diluents such as morphine, morphine monoacetate, heroin, methadone, methapyrilene, quinine, procaine, mannitol, lactose, and potato starch. Several "street" samples collected by drug-control officers were characterized based on the fragmentation pattern data thus obtained.

It was determined that the ultimate limit of sensitivity for heroin of the time-of-flight technique is between 10^{-8} and 10^{-9} g or less than 10^{-11} moles.

D MISCELLANEOUS APPLICATIONS OF TIME-OF-FLIGHT MASS SPECTROMETRY (M. H. Studier)

Time-of-flight mass spectrometry, combined with a variety of other techniques, continues to have a wide range of applications. The extreme detection sensitivity of the instrument and its high versatility makes it possible to handle problems of both basic and applied nature that would be very difficult or impossible to solve successfully by other means.

During this year, the following studies were made:

1. In collaboration with E. H. Appelman, hypofluorous acid, HOF, was detected by the TOF technique as a reaction product of fluorine with water (cf. Chapter XII). The reaction was carried out in a Kel-F line connected to the TOF mass spectrometer. With this system a procedure for producing macroquantities of HOF was developed and put to use.

2. In cooperation with H. Claassen and J. Goleb (cf. Chapter XV), antimony pentafluoride was shown to be dimeric even at very low pressures.

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3. Preliminary studies of application to studies of air pollution were made. It was found that the components of automobile exhaust could be identified in a 10-ml sample of air taken in Chicago. On a "smoggy" day, off-gases from refineries a number of miles away were detected at ANL.

4. In cooperation with the Chicago Crime Laboratory, a narcotic was identified and a sample associated with a murder case was analyzed (cf. Sect. C above).

As a general-purpose instrument, collaboration efforts such as those noted above can be expected as a regular contribution to the divisional program.

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