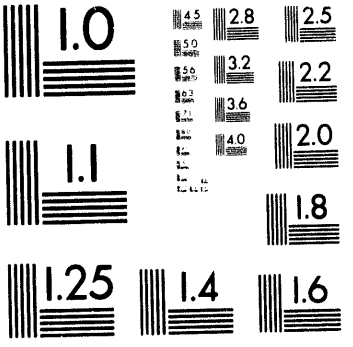

1.0
4.5
2.8
2.5
5.0
5.6
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

1 of 3

ORNL-6756
Distribution Category
UC-4

CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

for Period Ending April 30, 1993

M. L. Poutsma, Division Director
L. M. Ferris, Section Head - Organic, Inorganic, Transuranium, and Catalytic Chemistry
R. E. Mesmer, Section Head - Aqueous Chemistry, Geochemistry, Separations Chemistry, and Polymer Science

Date of Issue: August 1993

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under Contract No. DE-AC05-84OR21400

MASTER

Reports previously issued in this series are as follows:

ORNL-2386	Period Ending June 20, 1957
ORNL-2584	Period Ending June 20, 1958
ORNL-2782	Period Ending June 20, 1959
ORNL-2983	Period Ending June 20, 1960
ORNL-3176	Period Ending June 20, 1961
ORNL-3320	Period Ending June 20, 1962
ORNL-3488	Period Ending June 20, 1963
ORNL-3679	Period Ending June 20, 1964
ORNL-3832	Period Ending May 20, 1965
ORNL-3994	Period Ending May 20, 1966
ORNL-4164	Period Ending May 20, 1967
ORNL-4306	Period Ending May 20, 1968
ORNL-4437	Period Ending May 20, 1969
ORNL-4581	Period Ending May 20, 1970
ORNL-4706	Period Ending May 20, 1971
ORNL-4791	Period Ending May 20, 1972
ORNL-4891	Period Ending May 20, 1973
ORNL-4976	Period Ending May 20, 1974
ORNL-5111	Period Ending Nov. 1, 1975
ORNL-5297	Period Ending Mar. 31, 1977
ORNL-5485	Period Ending Aug. 31, 1978
ORNL-5665	Period Ending Feb. 29, 1980
ORNL-5817	Period Ending July 31, 1981
ORNL-5954	Period Ending Jan. 31, 1983
ORNL-6037	Period Ending Jan. 31, 1984
ORNL-6152	Period Ending Jan 31, 1985
ORNL-6261	Period Ending Jan. 31, 1986
ORNL-6385	Period Ending Mar. 31, 1987
ORNL-6481	Period Ending Mar. 31, 1988
ORNL-6668	Period Ending Mar. 1, 1991

1. INTRODUCTION AND DIVISIONAL OVERVIEW 1

2. COAL CHEMISTRY 9

INVESTIGATIONS OF MECHANISMS UNDERLYING THERMAL AND CATALYZED TRANSFORMATIONS OF COAL 9

Studies of Catalyzed Reactions in Dispersed Solids: Acid Catalysts 9

Model Compound Studies of Catalytic Hydropyrolysis . . 11

Studies of Retrogressive Reaction Pathways Under Restricted Diffusion 12

Influence of Cross-linking on the Thermolysis of Diphenylalkanes 14

Thermolysis Pathways for Surface-Immobilized Phenethyl Phenyl Ether 17

APPLICATIONS OF SOLID STATE NMR TO STUDIES OF COAL: ^{19}F MAS NMR OF ORGANOFLUORINE SUBSTANCES AND OF FLUORINATED LIGNITE 20

^{13}C and ^{19}F Relaxation Measurements in Monofluorinated Substances 20

^{19}F MAS NMR Spectral Characteristics 23

^{19}F MAS NMR of DAST Fluorinated APC #8 North Dakota Lignite. 25

3. AQUEOUS CHEMISTRY AT HIGH TEMPERATURES AND PRESSURES 29

CHEMICAL EQUILIBRIA AND THERMODYNAMICS OF REACTIONS 29

Metal Chloride Complexation 29

Magnesium Hydrolysis 30

Uranyl Hydrolysis and Complexation 31

Ion Association by the Conductance Method 32

A Model for Prediction of Reaction and Standard State Thermodynamic Quantities 33

THERMODYNAMICS OF ELECTROLYTES 34

Enthalpies of Dilution of Sulfates 34

Isopiestic Studies of Phosphates 35

Thermodynamic Model for $CaCl_2$(aq) 36

Low Temperature Isopiestic Studies 37

VOLATILITY OF AQUEOUS ELECTROLYTES 37

HCl(aq) and NaCl(aq) to 350°C (Geothermal Division, OEE and RE) 37

Volatility of NH_4Cl(aq) and Transport in Steam Generators 39

TECHNICAL SUPPORT FOR SUPERCRITICAL WATER OXIDATION (SCWO) PROCESSES (CRADA - MODEC) 41

4. GEOCHEMISTRY 43

GEOCHEMISTRY OF CRUSTAL PROCESSES TO HIGH TEMPERATURES AND PRESSURES. 43

Hydrothermal Geochemistry 43

Stable Isotope Systematics of Fluid-Rock Interactions 45

Thermodynamics of Rock-Forming Crystalline Solutions and Silicate Melts 46

CRUSTAL STABILITY OF HYDROCARBONS AND C-O-H-N FLUIDS 47

Activity-Composition Relationships of C-O-H-N Gases . 49

Thermal Stability of Acetic Acid 49

FUNDAMENTAL RESEARCH IN THE GEOCHEMISTRY OF GEOTHERMAL SYSTEMS. 50

Geochemistry of Aluminum in Natural Waters 51

Oxygen and Hydrogen Isotope Systematics in Brines . . 51

STABLE ISOTOPE SYSTEMATICS DURING BURIAL DIAGENESIS IN THE ALBERTA BASIN: AN ION MICROPROBE STUDY 52

ADVANCED CONCEPTS 53

5. CHEMISTRY OF ADVANCED INORGANIC MATERIALS 57

PREPARATION AND CHARACTERIZATION OF ELECTROCATALYTIC SURFACES 57

XPS Characterization of Anodic Layers Grown on Ir- and Rh-Implanted Titanium 57

RESEARCH ON NOVEL INORGANIC COMPOUNDS, NONOXIDIC CERAMICS, AND HIGH T_c SUPERCONDUCTORS 62

Elongated Crystals of ZrO_2 by Flux Evaporation 62

Synthesis of Acicular Crystals of Sodium-Tungsten Bronzes; Candidates for Pseudomorphic Reactions . . . 63

Carbon-Nitrogen Pyrolyzates: Attempted Preparation of Carbon Nitride 65

Nitrogen and/or Boron-Containing Polymers as Precursors of Ceramic Materials 65

Plasma-Enhanced Chemical Vapor Deposition of Boron Nitride Using Polymeric Cyanoborane as Source 65

Preparation of Tin Nitride via an Amide-Imide Intermediate 66

Deposition of Crystalline Binary Nitride Films of Tin, Copper, and Nickel by Reactive Sputtering 66

Paracyanogen Reexamined 68

Maskless Laser Writing of Microscopic Metal Lines . . 69

Study of High T_c Superconductors 70

6. STRUCTURE AND DYNAMICS OF ADVANCED POLYMERIC MATERIALS . . . 73

ADVANCED THERMAL ANALYSIS 74

The Advanced THermal Analysis System (ATHAS) Data Bank. 74

New Instrumental Thermal Analysis Techniques 74

The Mesophases of the Tetra-*n*-alkylammonium Halides . 75

Thermal Analysis of Miscellaneous Materials 75

STRUCTURE AND THERMAL PROPERTIES OF POLYMER FIBERS 76

Fourier Filter for Separating Crystalline and Amorphous Scattering 76

The Separation of Oriented and Isotropic Amorphous Phases in PET Fibers 77

Full-pattern Refinement of High-modulus PE Fibers . . 77

SAXS from PET and PE Fibers 77

AMORPHOUS AND SEMICRYSTALLINE POLYMERS 78

X-ray Diffraction Studies of Symmetric Tetra-*n*-alkylammonium Halides (TAAH) 78

Crystal Folding in Poly(ethylene oxide) 79

The Phase Diagram of Poly(oxybenzoate)-co-poly(oxynaphthoate) 80

SCANNING PROBE MICROSCOPY 80

Comparision of STM and AFM Imaging 80

Atomic Structure in Selenium 81

Surface Morphology of PET and PE Fibers by AFM 81

COMPUTER SIMULATION OF POLYMER STRUCTURE AND DYNAMICS . . . 82

Simulation of Scanning Microscopy Probe Tip-Sample Interaction 82

Modeling the Fermi Resonance Interaction in Polyethylene 83

BLENDS OF MACROMOLECULES WITH NANOPHASE SEPARATION 85

Experiments and Analysis 85

Theory 85

ATOMISTIC SIMULATIONS OF MATERIALS: A NEURAL NETWORK APPROACH 87

7. CHEMISTRY OF TRANSURANIUM ELEMENTS AND COMPOUNDS 89

Studies of Actinide Materials under High Pressure . . 90

High-Pressure Spectroscopy Studies 94

Spectroscopic Investigations of Structural and Electronic Properties 96

Theoretical Chemistry 97

Photoelectron Spectrometry 99

Vaporization of Actinide Oxides 101

The High-Temperature Chemistry of Technetium Vapors . 103

Studies of Np Alloy Systems 104

Studies of Thermal Decomposition Mechanisms of Oxalates 106

Laser-Mass Spectrometry 107

8. CHEMICAL AND STRUCTURAL PRINCIPLES IN SOLVENT EXTRACTION . . 109

BINDING OF ALKALI METAL CATIONS BY CROWN ETHERS AND IONIZABLE LARIAT ETHERS 109

Motivation, Approach, and Target Compounds 109

Synthesis of Crown Ethers 113

Structural Studies of Crown Ethers and Complexes . . . 114

Solution Thermodynamic Studies on Lariat Ethers . . . 116

MULTIEQUILIBRIUM MODELING IN SOLVENT EXTRACTION 118

CROWN ETHERS AS SELECTIVE EXTRACTANTS FOR TRANSITION METAL CATIONS 119

Extraction Studies 119

Calorimetric Investigations 120

Thia Crown Ethers as Extractants for Cu(II) 122

SYNERGISTIC EXTRACTION PHENOMENA IN RESIN SYSTEMS 123

9. SURFACE SCIENCE RELATED TO HETEROGENEOUS CATALYSIS 125

REACTIONS OF ORGANIC AND ORGANOSULFUR MOLECULES ON MODEL CATALYTIC SURFACES 125

Patterns of Reactivity for Ni(110) With Organosulfur Compounds 125

Reactions of Polyfunctional Thiols 126

Selectivity of Ethane and Ethylene Formation 127

Effects of C-X Bond Energies on Reaction Pathways . . 128

Adsorption and Reaction of Methanethiol, CH_3SH, on W(001) and Ru(0001) 130

STRUCTURAL STUDIES OF SURFACES BY SXPS AND ION SCATTERING . 131

Chemisorption Studied by Core Level Spectroscopy From the Substrate 131

Chemisorption and Bi-Metallic Surfaces Studied by Ion Scattering 134

WORK FUNCTION DEPENDENCE IN RELAXATION OF MULTI-CHARGED IONS. 137

IMPROVED SURFACE ANALYSIS SYSTEM 138

10. PHOTOLYTIC TRANSFORMATIONS OF HAZARDOUS ORGANICS 141

HETEROGENEOUS PHOTOCHEMISTRY 141

Photolysis of Substituted Naphthalenes at an SiO_2/Air Interface 142

Photodecomposition of Acenaphthylene on the Surface of SiO_2. 143

AQUEOUS PHOTOCHEMISTRY 144

Photolysis of Naphthalene and Acenaphthylene in Water 145

11. DNA SEQUENCING AND MAPPING 147

STABLE ISOTOPE LABELS 147

Triethylstannylpropanoic Acid Labels 147

Lanthanide Ion Labels 149

LUMINESCENT LANTHANIDE IONS AS LABELS FOR DNA 151

ELECTROCHEMICALLY ACTIVE FERROCENE DERIVATIVES AS LABELS FOR DNA. 153

CHEMICAL MODIFICATION OF SURFACES FOR THE IMMOBILIZATION OF DNA 155

12. SPECIAL TOPICS 159

MICROEMULSION FUELS 159

Novel Fuel Systems 159

Alcohol Partition in Water-in-Oil Systems 160

Micelles of Low-Equivalent-Weight Amphiphiles 161

SEMICONDUCTOR-CATALYZED PHOTOOXIDATION OF ORGANIC CONTAMINANTS SEPARATED BY MEMBRANE-ASSISTED SOLVENT EXTRACTION . . 162

IN SITU SCANNING PROBE MICROSCOPY OF ACTIVELY CORRODING SURFACES 165

STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAM . . 166

New Options for Crystalline Waste Forms; The Crystallochemistry of Lanthanide and Actinide Titanates 166

SINGLE CRYSTAL NEUTRON DIFFRACTION INSTRUMENT 168

TOPOLOGY OF CRYSTALLOGRAPHIC SPACE GROUPS AND CRYSTAL-STRUCTURE ELECTRON-DENSITY FUNCTIONS 169

BACTERIA MONITORING BASED ON AUTOMATED OPTICAL MICROSCOPY . 171

PUBLICATIONS, PRESENTATIONS, AND PATENTS 175

FUNDING SUMMARY FY 1992 240

ORGANIZATION CHART. 241

1. INTRODUCTION AND DIVISIONAL OVERVIEW

The Chemistry Division carries out basic and applied research in the chemical sciences on projects that are important to the Department of Energy's missions in fundamental sciences, energy technologies, advanced materials, and waste management/environmental restoration. It also conducts complementary research for other sponsors in areas where it has developed special expertise. The scope of the research includes physical chemistry, inorganic and organometallic chemistry, organic chemistry, geochemistry, surface science, and polymer science. This report contains descriptions of recent progress. Selected highlights are compiled below; more details can be found in the section of the report indicated by the number in parentheses.

1. Further examples were obtained of the use of surface-immobilized model compounds to give mechanistic insights into heterogeneous aspects of coal processing. Effects of restricted mass transport and hydrogen donors on retrogressive pathways were revealed by pyrolysis studies of diphenylalkanes that were either rigidly cross-linked or co-immobilized with hydrogen-donor or nondonor molecules. Temperature-programmed reduction of immobilized diphenylmethane under high-pressure hydrogen demonstrated the ability of a dispersed sulfided molybdenum catalyst to effect hydrocracking in a solid-solid system. (2)

2. Methodology was developed to obtain solid-state magic-angle-spinning NMR spectra for ^{19}F in organofluorides. Application to a lignite that had been treated with the selective fluorinating agent, diethylaminosulfur trifluoride, provided new evidence for primary alcohol functionality in this low-rank coal. (2)

3. Much improved quantitation of Mg^{2+} hydrolysis to form $Mg(OH)^{+}$ as a function of ionic strength and temperature to 250°C was achieved; the observed heat capacity change was remarkably small. Further unraveling of the multiple hydrolysis and oligomerization steps involv-

ing UO^{2+}(aq) was made possible by combining potentiometric and Raman spectroscopic data. (3)

4. New data on enthalpies of dilution of $(NH_4)_2SO_4$(aq), {NH_4HSO_4 + H_2SO_4}(aq), and H_2SO_4(aq) to high temperatures were obtained and are being modeled. Whereas describing the excess thermodynamic properties of $(NH_4)_2SO_4$(aq) becomes more complex with increasing temperature, the H_2SO_4 system is actually more complex at lower temperatures because of its sensitive dependence on the ionization of HSO_4^-. (3)

5. A new capability to determine the liquid-vapor partitioning of sparingly volatile salts in high-temperture aqueous systems under corrosive conditions was brought on line. Data and simultaneously developed correlating models for HCl, NaCl, and NH_4Cl to 350°C are applicable to control of corrosion and solids deposition in electric power plant turbines and geothermal energy production facilities. (3)

6. New information on hydrolysis and acetate complexing of Al^{3+} and on the acid dissociation constants and thermal stabilities of other natural carboxylates, such as formate and oxalate, provides new insights into the transport of aluminum in brines that is associated with development of secondary porosity in sedimentary basins. (4)

7. Implementation of a unique high temperature-pressure vibrating tube densimeter for gas mixtures in the CO_2-CH_4-N_2 system to 200°C and 1000 bars revealed surprisingly large deviations from ideal mixing for systems containing CO_2 at lower temperatures. (4)

8. Effects of dissolved salts on the equilibrium distribution of H/D and $^{16}O/^{18}O$ isotopes between brines and vapor were quantified for several salts as a function of concentration and temperature. Including these corrections is significant when drawing geological conclusions from natural isotope distributions. (4)

9. Electrochemical performance and photoacoustic and XPS spectroscopies confirmed the importance of the M^{4+} state in the anodically-oxidized overlayer ($M_xTi_{1-x}O_2$) on M-implanted Ti electrodes to achieve efficient electrocatalysis of the chlorine evolution reaction. Whereas M = Ru and Ir meet this condition, Rh does not. (5)

10. Conditions were established to prepare sodium tungsten bronzes, Na_xWO_3, with consistently needle-like morphology in high yield for $0.15 \leq x \leq 0.28$, although the crystal structures at the two composition extremes are different. Such materials are candidates for pseudomorphic conversions to carbide or nitride reinforcing agents for ceramic composites. (5)

11. Plasma chemistry allowed preparation of various useful coatings (e.g., BN via a polymeric cyanoborane precursor) and bulk materials (e.g., paracyanogen via the sputtering of a carbon electrode in a nitrogen plasma). Films of the thermally labile compounds Sn_3N_4, Cu_3N, and Ni_3N were formed similarly by sputtering the metals in a nitrogen plasma and were used for maskless laser writing of metallic lines. (5)

12. Refinement of x-ray diffraction data from polymer fibers was further developed to allow the first quantitation of a three-domain model: crystalline, oriented amorphous, and random amorphous regions. This model is being compared with the crystalline-rigid amorphous-mobile amorphous model suggested from previous thermal analysis data. (6)

13. Lamellar and isolated fibrils in base-etched spun PET fibers were visualized by atomic force miscroscopy (AFM). Molecular dynamic simulations of the interaction between the AFM tip and the polymer surface revealed important roles of structural deformation and surface impurities that must be considered in image interpretation. (6)

14. A novel approach that combines neural networks, genetic algorithms, and graph theoretical structure methods to relate the

chemical structure of materials to their mechanical, physical, and chemical properties is being developed in a CRADA with Hoechst-Celanese Corporation.

15. Ultra-high-pressure behavior of the transplutonium metals had revealed the interatomic distances necessary for the occurrence of f-electron overlap. This background was used to assess other potential electronic interactions that may be responsible for the volume collapses which accompany pressure-induced structural transitions in actinide compounds. (7)

16. Several new high-temperature species of Tc, a long-lived radioactive fission product, were identified in laboratory vaporization studies. Such information contributes to understanding the vapor transport of Tc during thermal nuclear-waste processing concepts. (7)

17. Selected binary actinide alloys were characterized by differential thermal analysis and x-ray diffraction. Such studies give enthalpies for allotropic and fusion transitions, contribute to developing alloy phase diagrams, and provide insights into bonding interactions between f-electron (itinerant or localized) metals and between f- and d-electron metals. (7)

18. X-ray structural data for 14-crown-4 ethers, with varying degrees of flexibility imposed by peripheral substituents, and of their Li^+ complexes helped to clarify the role of preorganization of macrocyclic ligands in selective complexing of cations. High-resolution solution NMR data on lariat 14-crown-4 ethers correlate well with the x-ray structures. (8)

19. Two-phase extraction selectivity for Li^+ over Na^+ by lipophilic 14-crown-4 ethers that also contain an ionizable carboxylate attached by a "lariat" side-arm is reversed by the presence of an additional O atom in the tether. Interestingly, there is not a simple correlation

with calorimetric data for binding these cations in homogeneous methanol solution. (8)

20. Calorimetric characterization of complex formation between cyclohexano-15-crown-5 ether and several divalent transition metal salts in wet propylene carbonate confirmed the enthalpic basis for the unusual extraction selectivity for Mn(II) and Zn(II), which was observed earlier and postulated to result from the relatively weak ligand field provided by this O-based macrocyclic ligand. (8)

21. Previous studies of reactivity of organosulfur compounds on the Ni(110) surface were extended to the polyfunctional $HSCH_2CH_2XH$ (X = S,O). For X = S, ethylene is evolved selectively. For X = O which contains a stronger C-X bond, different surface chemistry leads to successive surface thiolate formation, surface ethoxide formation, and evolution of the O in a series of organic products. (9)

22. Synchrotron-based soft x-ray-excited S 2p photoemission revealed distinct differences in adsorption sites and elementary steps for reactions of methanethiol on W(001) and Ru(0001) surfaces. Structural information on multiple sorption sites for S, C, O, and Ni on a W(001) substrate was obtained by surface-specific W 4f core level photoemission and by ion-scattering spectroscopy. (9)

23. Results from Li^+ ion scattering from a $Mo_{0.75}Re_{0.25}(001)$ surface revealed a first-layer enrichment in Mo, a second-layer enrichment in Re, and a first-second interlayer contraction that are fully consistent with recent state-of-the-art LEED results; the two methods are based on entirely different physics. (9)

24. Representative polycyclic aromatic hydrocarbons (PAHs) are readily oxidized photochemically when adsorbed on the highly polar but non-semiconducting surface of dry silica gel, but multiple mechanisms have been detected. For naphthalene, electron transfer from its excited singlet state to O_2 produces superoxide, O_2^-; in contrast, for acenaph-

thalene, energy transfer produces singlet O_2 as the key intermediate. (10)

25. New information on photochemical reaction pathways and lifetimes of PAHs in very dilute aqueous solution is relevant to understanding their environmental fates. For acenaphthalene, a unique mix of photooxidation and photodimerization behavior was uncovered. (10)

26. In research on DNA sequencing methodology aimed at using the long-lived resolvable f-f luminescence from a set of complexed Ln^{3+} cations as base-specific reporters, progress was made toward design of complexing ligands that contain a light-absorbing antenna function to excite the luminescence by intramolecular energy transfer. (11)

27. Microemulsion fuel technology continues to show promise as a means to incorporate NO_x emission control compounds into fuel formulations for large stationary diesel engines. (12)

28. Proof-of-principle experiments demonstrated the potential for a novel two-stage process for removal of organic contaminants from aqueous mixed-waste streams: membrane separation into an organic medium coupled with semiconductor oxide-mediated photo-mineralization. (12)

29. Progress was made on developing a concept for automated characterization of bacteria and other biological agents in air or water media by combining immunologically specific collection, automated video microscopy, and image analysis. (12)

In addition to these research accomplishments, progress continues to be made in the environment, safety, health, and quality arena. A division-specific Chemical Hygiene Plan constitutes a working mechanism for compliance with the OSHA Laboratory Standard. More formalized procedures have been instituted for prior review of experimental

activities, site-specific training of staff and guests, and self-assessment.

Summaries of publications and presentations, staffing, organization, and funding are provided at the end of this report. In addition to the permanent staff, a growing number of guests (postdoctoral fellows, professors on sabbatical leave, graduate students, and undergraduate students in special training programs) and subcontracted technical support personnel contribute to the work of the division.

2. COAL CHEMISTRY

The objective of this program is to conduct fundamental research that advances our understanding of the organic chemical structure and reactivity of coal. Reaction mechanisms that underpin thermal and catalyzed reactions of coal are explored through the use of model compounds that represent organic structural features present in the coal macromolecule. Silica-immobilized compounds are being employed to study the impact of restricted mass transport on free-radical reaction pathways. Current investigations focus on retrogressive reaction pathways for silica-immobilized diphenylalkanes and phenethyl phenyl ethers, which are surrogates for aliphatic and ether bridges prevalent in low rank coals and lignites. Retrogressive reactions are often promoted by restricted diffusion, and this behavior has been found to be exacerbated by cross-linking. The role of solid-state interactions in catalysis of coal conversion is under investigation with silica-immobilized model compounds employed as probes. Current studies focus on solid-state, acid-cracking reactions with 15 nm dispersed aluminosilicate catalysts, and hydrocracking reactions applicable to coal hydropyrolysis employing a dispersed, sulfided molybdenum catalyst. Solid-state NMR methods are being developed to obtain structure/reactivity information in chemically modified coals. NMR techniques under investigation include high resolution solid-state ^{19}F-NMR, and ^{13}C-NMR methods that exploit the ^{13}C-^{19}F dipolar interaction in ^{19}F-labeled organic molecules, polymers, and coals to elicit localized structural information. Fluorination chemistry is being investigated with current emphasis on oxygen replacement chemistry (e.g. alcohols into alkyl fluorides) in low rank coals using diethylaminosulfur trifluoride and sulfur tetrafluoride. Information derived from these investigations will contribute to the base of scientific knowledge necessary for the development of novel concepts for the conversion of coal to chemicals or fuels in an environmentally acceptable manner.

INVESTIGATIONS OF MECHANISMS UNDERLYING THERMAL AND CATALYZED TRANSFORMATIONS OF COAL

Studies of Catalyzed Reactions in Dispersed Solids: Acid Catalysts

A. C. Buchanan, III, P. F. Britt, K. B. Thomas

Our previous studies revealed that a small particle size (15 nm), nonporous aluminosilicate (SiO_2-1% Al_2O_3) could induce acid-catalyzed cracking reactions for a variety of silica-immobilized coal model compounds in the solid state. Intimate contact between the solid

catalyst and substrate particles was clearly implicated. In order to further assess the nature and importance of such interactions, a variety of reactions were performed using catalysts of varying constitution and particle size. These tests were conducted with silica-immobilized 1,3-diphenylpropane (≈DPP) and 1,4-diphenylbutane (≈DPB) substrates whose acid-catalyzed reactions have been well-characterized. Results for 60 min reactions (catalyst: substrate = 1.0 by wt) are shown in the table below.

Table 2.1. Influence of Catalyst on ≈DPP and ≈DPB Reactivity at 345°C

Catalyst (avg. particle size)	Surface Area (m^2/g)	≈DPP Conv. (%)	≈DPB Conv. (%)
None	---	2	0.7
Fumed Silica (12 nm)	200	not measured	0.40
Silica Gel (100 μ)	300	0.74	0.61
Silica-1% alumina (15 nm)	170	18.9	14.9
Silica-1% alumina (30 nm)	80	14.2	11.0
Montmorillonite (< 1 μ)	220-270	19.6	18.3

As found previously for ≈DPP at higher temperatures (375°C), dilution of ≈DPB with a 12 nm fumed silica results in a decreased conversion as a result of the dilution and generates only free-radical-derived products. In the presence of a large particle size (100 μ), porous silica gel catalyst, both ≈DPP and ≈DPB again show a decrease in conversion. However, in this case, the silica gel exhibits some acid functionality (perhaps as a consequence of its 0.05% alumina content), and about 10% of the products in each case are acid-derived. Dilution of ≈DPP and ≈DPB with the silica-1% alumina catalyst produces, instead, a dramatic increase in conversion and a product set that is essentially completely acid-derived. The sensitivity of the acid-catalyzed reaction to the available catalyst surface area is evident by the measurable decrease (ca. 25%) in the efficiency of the acid-catalyzed reaction for ≈DPP and ≈DPB when the silica-alumina particle size is increased from 15 to 30

nm. If the ≈DPB reaction is run, instead, with twice the amount of 30 nm catalyst (and, hence, twice the catalyst surface area), a conversion of 14.2% is obtained, comparable to the 14.9% conversion obtained for the 15 nm catalyst.

Clay minerals have been implicated as key catalysts in the thermal maturation of lignin into coal, and the role of montmorillonite as a solid-state catalyst in artificial coalification studies has been demonstrated. Clays such as montmorillonite are also known to be active solid acid catalysts for a variety of organic reactions. Consistent with these results, we have found that montmorillonite effectively catalyzes the acid-induced reactions for both ≈DPP and ≈DPB in the solid state. This study has provided further evidence for the crucial importance of direct contacts between the active sites on small catalyst particles with the physically intermixed substrate particles in this solid-state reaction chemistry.

Model Compound Studies of Catalytic Hydropyrolysis

A. C. Buchanan, III, P. F. Britt, K. B. Thomas, C. E. Snape[1]

Hydropyrolysis continues to be investigated as an alternative to coal liquefaction. However, appropriate model compounds for studying fundamental hydropyrolysis phenomena, such as catalytic interactions, at 400-600°C in pressurized fixed-bed flow reactors have not been available. Preliminary studies suggested that the silica-immobilized model compounds developed in our research group could meet these requirements.

We have focused on studies of the hydrocracking of silica-immobilized diphenylmethane (≈$PhCH_2Ph$, or ≈DPM), and investigated the effect of a dispersed, sulfided molybdenum catalyst on the process. Temperature programmed reduction (TPR; 5°C min^{-1}) in a flow reactor at pressures of 150 bar of hydrogen or nitrogen was employed, and products were swept into a mass spectrometer for detection. Silica-immobilized benzene (≈PhH) was examined first to determine the stability of the SiO-C bond that links the model compounds to the surface of the silica. Significant cleavage of this linkage is not observed until 520-550°C under hydrogen pressure indicating that silica-immobilized model compounds are stable enough to be used as probes in many hydropyrolysis studies.

For ≈DPM under nitrogen, the peak evolution temperatures for benzene and toluene formation are both ca. 520°C, and considerable char formation is observed. Under hydrogen pressure and without catalyst, roughly equal amounts of benzene and toluene evolve (more than in the nitrogen case), as described by Equation 2.1, and the white color of the residue indicates that the char yield is small.

$$2\ \approx PhCH_2Ph + 2H_2 \rightarrow \approx PhH + PhCH_3 + \approx PhCH_3 + PhH \qquad (2.1)$$

The peak evolution temperatures for C-C bond cleavage to form toluene (470°C) and benzene (500°C) under hydrogen are lower than in the nitrogen case demonstrating a promoting effect of hydrogen pressure on the hydrocracking process. The interesting observation of a lower peak evolution temperature for toluene relative to benzene formation in the presence of hydrogen is currently unexplained.

In the presence of the sulfided Mo catalyst, the peak evolution temperatures for benzene and toluene are 430 and 410°C, respectively, and are shifted to significantly lower temperatures than those observed without catalyst. Hydrogenolysis of diphenylmethane in the liquid phase has been reported to occur at a similar temperature of 425°C in the presence of a sulfided Mo catalyst to produce the same product distribution. Hence, we find that a dispersed Mo catalyst can similarly reduce the activation energies for the primary hydrogenolysis of the C-C linkages for the solid, silica-immobilized diphenylmethane despite the restrictions on mobility. This study provides further evidence that solid-state interactions between catalyst and coal particles may be important under related coal processing conditions.

---

1. University of Strathclyde, Glasgow, UK.

Studies of Retrogressive Reaction Pathways Under Restricted Diffusion

A. C. Buchanan, III, P. F. Britt, K. B.Thomas

Previous studies of the thermolysis of silica-immobilized bibenzyl (≈$PhCH_2CH_2Ph$, or ≈BB) revealed that, in contrast to fluid-phase behavior, restricted diffusion imposed by surface attachment resulted principally in retrogressive reaction chemistry for this model of

related weak linkages in coal. The key retrogressive reactions promoted were: (1) rearrangement to the more thermally stable ≈Ph(Ph)$CHCH_3$, which is the dominant reaction for ≈BB; and, (2) cyclization/dehydrogenation to ≈dihydrophenanthrene and ≈phenanthrene. We have begun an investigation designed to probe the sensitivity of these retrogressive reaction pathways for ≈BB to the structure of neighboring molecules in a diffusionally restricted environment.

Samples were prepared that contained low surface coverages of immobilized bibenzyl in the presence of a second immobilized component that is either thermally inert (≈naphthalene, or ≈NAP), contains potentially reactive benzylic C-H bonds (≈diphenylmethane, or ≈DPM), or is a hydroaromatic capable of acting as a radical capping agent (≈tetralin, or ≈TET). Preliminary results at 400°C, shown in Table 2.2 below, indicate that both the ≈BB thermolysis rate and product distribution are very sensitive to the chemical structure of neighboring molecules surrounding immobilized free-radical intermediates. In contrast, the rate for initial homolysis of the weak central C-C bond to form ≈$PhCH_2$• and $PhCH_2$• is relatively insensitive to the structure of neighboring molecules on the surface. The measured homolysis rate constants are also comparable to previously reported values for fluid-phase bibenzyl in tetralin.

Table 2.2. Thermolysis of ≈$PhCH_2CH_2Ph$ at 400°C With Spacer Molecules

Surface Composition	Coverage (mmol g^{-1})	Rate x 10^4 (% s^{-1})	k_{homol} x 10^6 (s^{-1})	Rearr. Prod. (mol %)
≈BB	0.57	68	8.4	51
≈BB / ≈DPM	0.089/ 0.38	42	9.1	34
≈BB / ≈TET	0.10 / 0.34	21	8.3	30
≈BB / ≈NAP	0.073/ 0.33	12	6.7	8

As indicated in the Table, the decrease in the overall decomposition rate for ≈BB in the spacer series ≈DPM, ≈TET, and ≈NAP correlates strongly with the striking decrease in selectivity for the rearrangement product. We have presented evidence previously that this retrogressive

rearrangement path is a free-radical chain route, shown in Eqs. 2.2 - 2.3, promoted by restricted diffusion on the surface.

$$\approx PhCH\bullet CH_2Ph \rightleftarrows \approx Ph(Ph)CHCH_2\bullet \qquad (2.2)$$

$$\approx Ph(Ph)CHCH_2\bullet + \approx PhCH_2CH_2Ph \rightarrow \approx Ph(Ph)CHCH_3 + \approx PhCH\bullet CH_2Ph \qquad (2.3)$$

Interestingly, the hydroaromatic tetralin appears to be only slightly more effective at inhibiting this retrogressive pathway than is diphenylmethane. Furthermore, the aromatic non hydrogen donor, naphthalene, is the most effective spacer molecule at inhibiting the rearrangement path. These preliminary results are intriguing, and the impact of the spacer molecules on the rearrangement path may lie in their effect on the rate-limiting hydrogen transfer step (Eq. 2.3). The naphthalene spacer may effectively retard the rearrangement process by acting as a barrier for this key hydrogen transfer step. The influence of these spacers on the ≈BB reaction, including the cyclization/dehydrogenation channel, continues to be investigated.

Influence of Cross-linking on the Thermolysis of Diphenylalkanes

P. F. Britt, A. C. Buchanan, III, E. A. Malcolm[1]

The goal of this work is to investigate the effects of crosslinking on the rates and reaction mechanisms in the thermally induced free radical decomposition of 1,3-diphenylpropane (DPP) and 1,4-diphenylbutane (DPB) at temperatures relevant to coal processing (350-400°C). The cross-linked diphenylalkanes were prepared by condensation of a diphenol, *p,p'*-$HOC_6H_4(CH_2)_nC_6H_4OH$, with a silica surface. Since the surface-attachment reaction is not quantitative, mono- and diattached species are present on the surface. As shown in Table 2.3, the fraction of diattached DPP (≈DPP≈) increased with decreasing surface coverage, but only 80% diattachment could be obtained. The di-para linkage to the surface, employed above, was not the principal factor limiting the attachment efficiency since a cross-linked meta,para-isomer of DPP (0.091 mmol g^{-1}) had a similar attachment efficiency. Pyrolysis of

≈DPP≈ (0.465 mmol g^{-1}) at 375°C and low conversion (<5%) produces approximately equal amounts of surface-immobilized toluene and styrene as the major products, and minor amounts (5%) of secondary products which include two products not previously detected in the pyrolysis of ≈DPP or DPP. As the degree of diattachment increases, the alkane to alkene ratio increases and retrogressive reactions, to form more refractory products, dramatically increase. A comparison of the mole % secondary products from the pyrolysis of ≈DPP≈ and ≈DPP at similar coverages and conversions (<6%) reveals that as cross-linking increases, retrogressive reactions increase over 190-fold at the lowest surface coverage, Table 2.3.

Table 2.3. Rate of Conversion as a Function of Surface Coverage

≈DPP≈			≈DPP		≈DPP≈/≈DPP
Coverage (mmol g^{-1})	% Diattached	Rate (% h^{-1})	Coverage (mmol g^{-1})	Rate (% h^{-1})	Secondary Products
0.465	24 ± 4	3.9	0.57	7.7	3.9
0.181	60 ± 4	0.45	0.14	0.40	20
0.105	82 ± 5	0.063	0.10	0.26	>190
0.091*	78 ± 10	0.036	-	-	-

* *meta-*, *para-* isomer of ≈DPP≈

Hence, as a consequence of restricted mass transport, products and radical intermediates remain in close proximity for the duration of the reaction leading to an increase in retrogressive reactions as well as the formation of new reaction products which were not seen in the pyrolysis of DPP or ≈DPP at similar conversions.

We anticipated that the rate of decomposition of ≈DPP≈ would be sensitive to the extent of cross-linking, since the geometric constraints placed on the chain-carrying benzyl radical and the neighboring DPP molecules would influence the key hydrogen abstraction reactions. However, there is only a modest reduction in the rate with increasing diattachment compared to ≈DPP at similar surface coverages. As shown in Table 2.3, a 100-fold decrease in rate was observed for a 5-fold

decrease in surface coverage and a 3-fold increase in the degree of diattachment. The observed rate depression is probably a lower limit since complete diattachment was not possible and gas phase *p*-$HOPhCH_2\bullet$, from the decomposition of the mono-attached DPP, is an effective chain carrying radical. Moreover, the rate of initiation could be accelerated by strain introduced into the aliphatic chain by cross-linking, which could also explain the increase in the selectivity for formation of $\approx PhCH_2CH_3$ at low surface coverages.

The pyrolysis of a cross-linked DPB (≈DPB≈) was examined at coverages of 0.113 and 0.10 mmol g^{-1} with 90 and 88% of the material diattached. The rate of decomposition of ≈DPB≈ at 400°C was 3-6 fold slower than that for ≈DPB at a similar coverage, 0.117 mmol g^{-1}, indicating again that cross-linking hinders the free radical chain decomposition. Pyrolysis of ≈DPB≈ produced products which are consistent with those found in the pyrolysis of DPB and ≈DPB, and an analogous free radical chain mechanism can be invoked. The selectivity of product formation is determined by the relative rates of hydrogen abstraction and β-scission of $\approx PhCH\bullet CH_2CH_2CH_2Ph\approx$ and $\approx PhCH_2CH\bullet CH_2CH_2Ph\approx$. In the pyrolysis of ≈DPB (0.117 mmol g^{-1}), a product selectivity factor, S, was 2.0 indicating the thermodynamically more stable benzylic radical, $\approx PhCH\bullet CH_2CH_2CH_2Ph$, is favored. For ≈DPB≈ at 0.113 and 0.10 mmol g^{-1}, the corresponding value of S was 0.67 ± 0.03 and 0.70 ± 0.03, respectively, and independent of conversion. Thus, restricted mass transport resulting from cross-linking alters the reaction selectivity to form products preferentially from the thermodynamically less stable aliphatic radical, $\approx PhCH_2CH\bullet CH_2CH_2Ph\approx$. In addition to the altered product selectivity, the alkane to alkene ratio increases with conversion and the allylbenzene has been isomerized to β-methylstyrene. This indicates that in this constrained environment, the products are interacting with the free radical intermediates leading to enhanced reductions, isomerizations, and retrogressive reactions.

The cross-linked diphenylalkanes were also used as solid state probes to study the effectiveness of hydrogen donor solvents in limiting retrogressive reactions in a constrained heterogeneous environment. In the pyrolysis of ≈DPP≈ (0.181 mmol g^{-1}), secondary products are enhanced 20-fold compared to ≈DPP at a similar coverage and conversion. Pyroly-

sis of ≈DPP≈ in the presence of excess tetralin, as a model liquefaction solvent, reduces the secondary products only by a factor of two while diphenylmethane had no effect. Surprisingly, the external hydrogen donors did not significantly inhibit the retrogressive reactions. Pyrolysis of DPB with tetralin behaves similarly in homogeneous and heterogeneous, i.e. cross-linked, environments. These studies indicate that the cross-linked diphenylalkanes appear to be good solid state probes for exploring the impact of hydrogen donor solvents on thermal free radical decomposition reactions in a heterogeneous environment. These results also indicate that simple homogeneous model compound studies are not always good indicators of the effectiveness of a liquefaction solvent at hindering retrogressive reactions in the depolymerization of the macromolecular network structure of coal.

---

1. Oak Ridge Research Institute, Oak Ridge, TN.

Thermolysis Pathways For Surface-Immobilized Phenethyl Phenyl Ether

P. F. Britt, A. C. Buchanan, III, E. A. Malcolm[1]

It has been proposed that oxygen functional groups (-OH, -OR, -COOH) are responsible for retrogressive reactions and, thus, low liquefaction yields in low rank coal. However, there is limited mechanistic information on the chemical reactions that lead to cross-linking. Therefore, we initiated an investigation into the thermal decomposition of ether bridges which are prevalent in low rank coal to determine their impact on retrogressive reactions. The thermolysis of a series of substituted phenethyl phenyl ethers, $PhCH_2CH_2OPh$, was studied in the gas and liquid phases at 375°C as a model of ether linkages in lignite and lignin.[2] A new reaction pathway was uncovered which could provide a pathway for cross-linking reactions. We have now studied the impact of restricted diffusion on the free radical decomposition of surface-immobilized phenethyl phenyl ether.

Thermolysis of $\approx PhCH_2CH_2OPh$ produces four major products (PhOH + $\approx PhCH{=}CH_2$ and PhCHO + $\approx PhCH_3$) by a free radical chain mechanism similar to that proposed for the decomposition of phenethyl phenyl ether, PPE, in the liquid phase. The key steps in the reaction mechanism are shown below.

$$\approx PhCH_2CH_2OPH + PhO\bullet \rightarrow \approx PhCH\bullet CH_2OPH + PhOH \quad (2.4a)$$

$$\approx PhCH_2CH_2OPH + PhO\bullet \rightarrow \approx PhCH_2CH\bullet OPH + PhOH \quad (2.4b)$$

$$\approx PhCH\bullet CH_2OPH \rightarrow \approx PhCH{=}CH_2 + PhO\bullet \quad (2.5)$$

$$\approx PhCH_2CH\bullet OPh \rightleftarrows \approx PhCH_2C(Ph)HO\bullet \rightarrow \approx PhCH_2\bullet + PhCHO \quad (2.6)$$

$$\approx PhCH_2CH_2OPh + \approx PhCH_2\bullet \rightarrow \approx PhCH\bullet CH_2OPh + \approx PhCH_3 \quad (2.7a)$$

$$\approx PhCH_2CH_2OPh + \approx PhCH_2\bullet \rightarrow \approx PhCH_2CH\bullet OPh + \approx PhCH_3 \quad (2.7b)$$

The product selectivity, measured by the $PhCH{=}CH_2$ / PhCHO yield, is determined by the rate of the hydrogen abstraction reactions and the 1,2-phenyl shift, since the β-scission reactions are fast compared to the other processes. At high coverage (0.54 mol g^{-1}), the product selectivity is 5 indicating that the rate of hydrogen abstraction and the 1,2-phenyl shift are competitive. However, at low surface coverage (0.057 mmol g^{-1}), the selectivity is 27, in contrast to the thermolysis of liquid PPE where the product selectivity was independent of concentration. Additionally, the 10-fold reduction in surface coverage produced a slight increase in the rate, see Table 2.4, and two isomers of $\approx PhCH_2CH_2OPh$ were formed that account for over 20 mole % of the products formed. These results suggest that, at low coverages, interaction of ≈PPE with the silica surface is altering the selectivity and rate of reaction.

In order to mimic the PPE-silica interactions, thermolysis of liquid PPE was studied at 375°C in the presence of glass chips and silica, Cab-O-Sil. Surprisingly, the additives had no effect on the product selectivity or rate. In the gas phase, glass chips caused an increase in the product selectivity by a factor of two, but had no effect on the rate. These results suggest that the silica surface could perturb the reaction. The covalent linkage to the surface might enhance the interaction between the silica and the substrate and, thus, enhance the perturbation in selectivity. Therefore, thermolysis of a low

coverage of ≈PPE-3 was studied in the presence of inert spacer molecules, biphenyl and 2-naphthyl, which will minimize the interaction of the organic substrate with the silica surface under conditions of restricted mobility. It was predicted that the inert spacer molecules would change the product selectivity back to that found for ≈PPE-3 at high coverages. As shown in Table 2.4, the spacers have only a modest impact on the selectivity,

Table 2.4. Product Selectivity in the Thermolysis of ≈PPE-3 at 375°C

Surface Composition	Coverage (mmol g^{-1})	Rate (% h^{-1})	Selectivity
≈PPE-3	0.54	8.3	5 ± 1
≈PPE-3	0.057	9.7	27 ± 2
≈PPE-3 / ≈BP	0.050 / 0.536	3.6	21 ± 2
≈PPE-3 / ≈Naph	0.072 / 0.45	3.4	20 ± 5
≈PPE-3 / ≈DPM	0.059 / 0.48	6.6	12 ± 1.8

although they did reduce the rate by a factor of two. Since the PPE product selectivity is not altered in the liquid phase by dilution with biphenyl, covalent attachment of the reagents and the local environment must be placing constraints on the reactive intermediates which lead to the altered product distribution. The spacer molecules should not perturb the branching selectivity in hydrogen abstraction reactions 2.4 and 2.7. Hence, the spacers must be hindering the 1,2-phenyl shift compared with high coverage samples of ≈PPE alone. In the presence of a spacer that can shuttle hydrogens across the surface, diphenylmethane (≈DPM), the rate is enhanced and the selectivity is altered compared to that for the inert spacers. This could be a consequence of the steric effects of the neighboring molecules or the participation of ≈PhCH•Ph in the hydrogen transfer reactions. In the thermolysis of liquid PPE with tetralin, the selectivity increased from 3 to 7.

The product selectivity was also altered by changing the orientation of the molecule to the silica surface. A meta-isomer of ≈PPE-1

(0.44 mmol g^{-1}) was synthesized from *m*-$HOC_6H_4OCH_2CH_2C_6H_5$ to determine if the orientation of the phenyl radical, from the decomposition of ≈PhCHO, under conditions of restricted diffusion could enhance or hinder retrogressive reactions, e.g. aryl-aryl coupling. It was predicted that the meta attachment might increase retrogressive reactions compared to the para-isomer since the reactive intermediates would be positioned toward a neighboring molecule. Surprisingly, thermolysis of the *m*-≈PPE-1 at 375°C produced no significant amounts (< 0.01 mole %) of retrogressive products while for the para-isomer, 10 % of the ≈PhCHO decomposed to produce crosslinked products. From the studies of ≈PPE-3 and ≈PPE-1, it is evident that the local environment surrounding the reactive molecules and intermediates can make a significant impact on the favored reaction pathways and, thus, the reaction products.

---

1. Oak Ridge Research Institute, Oak Ridge, TN.
2. Britt, P. F.; Buchanan, III, A.C.; Hitzman, V. M., Proceedings, 1991 International Conference on Coal Science, Butterworth-Heinemann, Ltd., 1991, 207.

APPLICATIONS OF SOLID STATE NMR TO STUDIES OF COAL: ^{19}F MAS NMR OF ORGANOFLUORINE SUBSTANCES AND OF FLUORINATED LIGNITE

^{13}C and ^{19}F Relaxation Measurements in Monofluorinated Substances

E. W. Hagaman, M. C. Woody

Our ^{1}H-^{13}C-^{19}F triple resonance NMR experiments on low molecular weight organic fluorides have implicated both the proton and fluorine spin systems as contributors to the fast ^{13}C T_2's of carbon resonances that are strongly dipolar coupled to ^{19}F nuclei in the same molecule. Previously, we identified ^{13}C-^{19}F dipolar dephasing as the ^{13}C T_2 relaxation pathway. We have now developed the capability to perform high resolution proton dipolar decoupled solid state ^{19}F NMR experiments. We have measured the ^{19}F T_2's directly, as a function of the strength of proton dipolar decoupling, to delineate the interactions between the proton and fluorine spin systems. The ^{19}F T_2 lengthens as the strength of the proton decoupling field, H_{1H}, increases and attains a plateau

value independent of H_{1H} for values of this field in excess of 55 kHz. The plateau T_2 reflects ^{19}F-^{19}F intermolecular interaction strength.

In a conventional CP/MAS ^{13}C NMR experiment performed on an organofluoride, the ^{13}C magnetization evolves during the detection period under the influence of the ^{13}C-^{19}F dipolar interaction. If interacting ^{13}C-^{19}F spins are isolated spin pairs, the ^{19}F nuclei do not provide a ^{13}C relaxation pathway. However, in non-polymeric monofluorinated organic substances, the strength of the ^{19}F magnetic moment is sufficient to establish efficient *inter*molecular dipolar coupling in the ^{19}F spin system, a fact demonstrated by direct measurement of ^{13}C and ^{19}F T_2's in 16-α-fluoro-α-estradiol-3-methyl ether, 1, and 3-fluoro-p-anisic acid, 2. The ^{13}C T_2's were measured with ^1H dipolar decoupling and then remeasured with concurrent ^1H and ^{19}F dipolar decoupling. ^{19}F T_2's were measured with and without ^1H dipolar decoupling.

The ^{19}F T_2's measured in the absence of proton decoupling are on the order of 10's of microseconds for 1 and 2 and increase in length to 100's of μs in the presence of H_{1H}. The ^{19}F T_2's measured in the presence of H_{1H} pertain to the ^{19}F spin system in experiments that measure the ^{13}C T_2's with H_{1H} on and H_{1F} off. In the absence of ^{19}F decoupling, ^{13}C T_2's are short, ca 1 ms, and equal to or longer than the ^{19}F T_2 measured under the same conditions. Concurrent ^1H and ^{19}F dipolar decoupling result in a 20 to 30-fold increase in ^{13}C T_2 for the fluorinated carbons in 1 and 2.

The ^{19}F T_2's of 1 and 2, measured as a function of H_{1H} amplitude, illustrate the following points: (1) ^{19}F T_2 increases monotonically with H_{1H} and attains a plateau value that is independent of H_{1H}. The plateau value is reached at a lower H_{1H} amplitude for 2 than for 1; (2) at $H_{1H} = 0$ the T_2 for 1 is shorter than for 2; (3) The plateau T_2 is longer for 1 than for 2. The first two points relate to the strength of the ^1H-^1H dipolar interaction. The proton distribution in 2 consists of methine hydrogens and those of the methyl group, in close spatial proximity, but with a motionally narrowed ^1H-^1H dipolar interaction. The maximum ^1H-^1H dipolar interaction in 2 is less than in 1 which has strong ^1H-^1H dipolar coupling between the geminal hydrogens of the methylene moieties. Hence, the H_{1H}-independent ^{19}F T_2 in 2 is reached using an H_{1H} amplitude of 40 kHz while 1 requires $H_{1H} > 50$ kHz. At H_{1H} =

0, the stronger proton dipolar interactions in **1**, relative to **2**, produce faster ^{1}H magnetization diffusion. This, in turn, promotes more efficient ^{1}H-^{19}F dipolar dephasing, i.e., shorter ^{19}F T_2. Point 3 is relevant to the ^{19}F spin diffusion process. In the region where the ^{19}F T_2 is independent of H_{1H} amplitude, the relaxation rate depends on parameters of the ^{19}F spin system, *inter alia*, ^{19}F-^{19}F internuclear distance. Based on the relative size and geometry of the molecules, the intermolecular array of ^{19}F nuclei in **2** is assumed denser than **1**, yielding stronger homonuclear dipolar interactions and shorter T_2 for **2**.

The ^{1}H and ^{19}F spin systems of rigid monofluorinated organic substances exhibit rapid homonuclear magnetization diffusion, the former on the microsecond and the latter on the millisecond time scales. The pulse sequence used for the ^{13}C T_2 measurement with just H_{1H} on for the evolution period constitutes, by virtue of omission of H_{1F}, a ^{13}C-^{19}F dipolar dephasing experiment when applied to the ^{1}H-^{13}C-^{19}F three spin system of these molecules. The ^{13}C T_2's, measured with H_{1F} off, largely reflect the ^{13}C-^{19}F dipolar dephasing time, T_{DD}, for these substances. T_{DD} itself, corrected for the ^{13}C T_2 decay that occurs in the presence of both H_{1H} and H_{1F}, is given by $(T_{DD})^{-1} = (T_a)^{-1} - (T_b)^{-1}$, where T_a and T_b represent the T_2 measured with H_{1F} off and on , respectively. T_{DD} is 0.93 and 1.05 ms for **1** and **2**, respectively. The difference between T_{DD} and ^{13}C T_2 for the fluorocarbon resonances of **1** and **2** is less than the estimated error of the T_2 measurements.

The dephasing rate for the transverse ^{13}C magnetization is proportional to the strength of the ^{13}C-^{19}F dipolar interaction and therefore to $(r)^{-3}$. With efficient ^{19}F magnetization diffusion, i.e., with H_{1F} off during the evolution period of the measurement, ^{13}C T_2's should be similar for directly bonded ^{13}C-^{19}F pairs and otherwise independent of larger scale molecular structure. The T_2's for the fluorocarbon resonance of **1** and **2**, 1.0 +/- 0.1 ms, confirm this expectation.

A ^{13}C-^{19}F dipolar dephased ^{13}C spectrum of **1** was compared to the ^{1}H,^{19}F doubly dipolar decoupled spectrum. The evolution time for the dephased spectrum, 3.0 ms, is ca $3(T_2)$ for the C(16) fluorocarbon resonance (one bond removed from fluorine) and one T_2 for C(15) and C(17) (two bonds removed). The C(16) resonance is dephased fully in this spectrum and the resonances of C(15) and C(17) are greatly dimin-

ished. The result demonstrates the qualitative use of dipolar dephasing for the recognition of three carbon subsets in lightly fluorinated organic substances: (1) carbon directly bonded to fluorine ($r_{CF} \approx 0.14$ nm), (2) carbons two bonds removed from fluorine ($r_{CF} \approx 0.24$ nm), and (3), all other carbons (by difference). The structure-insensitive r_{CF} in subsets (1) and (2) uniquely label the resonances of these carbons with distinguishable T_2 ranges.

^{13}C T_2's measured in the presence of concurrent ^1H and ^{19}F dipolar decoupling fields are equivalent to ^1H dipolar decoupled ^{13}C T_2's (bench mark values) measured on the corresponding nonfluorinated analog of the molecule, *except* for the carbons one and two bonds removed from the fluorine. The T_2's for these carbons are a fraction of their bench mark value, typically 30-70%, even in the presence of the largest H_{1H} experimentally attained in this study, 70 kHz. The result indicates incomplete decoupling of the ^1H and ^{19}F spin systems and is nominally in conflict with the H_{1H} independence of the ^{19}F T_2's at high H_{1H} discussed above.

^{19}F MAS NMR Spectral Characteristics

E. W. Hagaman, M. C. Woody

In this section the spectra of several model compounds are discussed that are relevant to the analysis of ^{19}F MAS NMR coal spectra.

Chemical Shifts. The range of ^{19}F chemical shifts in organic substances for common functional groups is about 300 ppm. Usual chemical shift ranges for functional groups that can be generated by oxygen replacement chemistry are, relative to $\delta(CFCl_3) = 0$ ppm: alkyl fluorides; primary (-210 to -230), secondary (-170 to -190), tertiary (-125 to-160). Alkyl difluorides: primary (-110 to -130), secondary (-90 to -120). Trifluoromethyl (-55 to -80); and acyl fluoride (+20 to+50). There is marginal overlap in these ranges. The ^{19}F chemical shifts of many common inorganic fluorides appear in the chemical shift range of the organic fluorides and difluorides. Although not comprehensively surveyed, the ^{19}F resonances of a series of metal fluorides lie in the range -80 to -220 ppm.

Linewidth. The ^{19}F resonance linewidth of non-spinning, proton dipolar decoupled solid organic fluorides is due to ^{19}F chemical shift

anisotropy and to ^{19}F homonuclear dipolar interactions. The extent to which each of these interactions contributes to the linewidth is structure dependent, as described below. Fluorine chemical shift anisotropy (CSA) is a measure of the deviation from spherical symmetry of the electron density at the fluorine nucleus. The shielding of the nucleus by the electrons is described by a second rank tensor, σ. The elements of σ depend on the orientation of the molecular axis with respect to the external field, H_o. For the principal axis system, the shift tensor can be expressed with the diagonal shielding elements; σ_{11}, σ_{22}, and σ_{33}. CSA, $\Delta\sigma$, is defined as $\sigma_{33} - 1/2(\sigma_{11} - \sigma_{22})$. The principal elements of the ^{19}F chemical shift tensor for several perfluorinated aromatic substances (C_6F_6, $C_{10}F_8$, $(C_6F_5)_2$) have been measured by other investigators; the anisotropy in these substances ranges between 126 and 159 ppm (12-15 kHz at 2.35 T). CSA in monofluoroaromatic substances e.g., 3-fluoroanisic acid, **2**, can be estimated by inspection of the non-spinning spectrum. The chemical shift measured in the MAS spectrum is related to the principal tensor elements by $(\sigma_{11} + \sigma_{22} + \sigma_{33})/3 = -140$ ppm (13.2 kHz). The fair agreement between the MAS chemical shift, -135 ppm, and 1/3 of the tensor elements, -140 ppm, suggests that to a first approximation the CSA interaction defines the powder lineshape. The dipolar contribution is minimized in monofluoroorganic substances by relatively large ^{19}F-^{19}F internuclear distances.

The CSA in the tertiary alkyl fluoride triamcinolne acetonide, **3**, is small, 13 ppm (1200 kHz). For rigid organic molecules, this is the smallest CSA that has been measured in our laboratory. The large CSA for the aryl fluoride **2** results in prominent first and second sideband pairs in the MAS spectrum and a centerband that contains just 60% of the total resonance area. At the same MAS speed (6050 +/- 50 Hz) the alkyl fluoride resonance centerband contains 97% of the resonance area. The order of magnitude difference in the CSA between **2** and **3** and the resulting differences in sideband intensity distributions are a caution signal with respect to the interpretation of centerband areas in "slow" MAS spectra. Spectra can be acquired with very high MAS probes that can reduce sideband areas to a few percent of the centerband so that center-band areas are an accurate reflection of species concentration. The "slow" MAS spectra are very useful qualitatively in that it is possible

to estimate the magnitude of the CSA interaction by the centerband/-sideband area ratio. Although the static spectrum provides a direct measure of the anisotropy, these spectra are useful only in pure compounds where the lineshape reflects a single interaction. The analysis of static spectra becomes very difficult if multiple overlapping ^{19}F resonances are present. The spinning range selected for this work uses the line narrowing advantages of MAS while permitting a qualitative measure of CSA even in highly congested ^{19}F spectra.

The magnitude of the ^{19}F CSA in acyl fluorides, as in methyl 4-fluorocarbonyl- benzoate, 4, is similar to that in aryl fluorides. This conclusion is based on the 66% centerband area of the acyl fluoride resonance at MAS = 6080 Hz. Aryl fluoride measurements at the same MAS speed reveal centerband area of 60% (vide supra).

In contrast to the CSA-dominated static powder lineshape of monofluoroorganics, that of molecules containing a difluoromethylene moiety is both CSA and dipolar in character since the two fluorine nuclei bonded to the same carbon have a strong pairwise ^{19}F-^{19}F dipolar interaction. The presence of both broadening influences complicates a simple estimate of CSA from the static spectrum. The $\Delta\sigma$ for ^{19}F in teflon, measured at low temperature, is 120 ppm, similar to that of aryl fluorides. This value is a first order approximation for the CSA in 3,3-difluorocholestane, 5, which displays a powder linewidth ca. twice this value. In this case the ^{19}F-^{19}F dipolar and CSA interactions contribute comparably to the linewidth. The consequence of this broad powder line is that just 35% of the total resonance area is contained in the centerband in the MAS (6050 ± 50 Hz) spectrum, and intense first and second order sidebands appear in the spectrum.

^{19}F MAS NMR of DAST Fluorinated APC #8 North Dakota Lignite

E. W. Hagaman, S. K. Lee[1]

Our initial goal in designing the solid state ^{19}F MAS NMR experiment was to verify directly that the fluorination of low rank coal (Argonne Premium Coal No.8, North Dakota Lignite) with sulfur tetrafluoride, SF_4, generates alkyl fluorides in the organic matrix of the coal, and only to a limited extent forms acyl fluorides from potential carboxylic acid residues in the coal, as indicated from previous triple

resonance experiments. This objective has been achieved and with it we have shown that ^{19}F MAS NMR is a highly sensitive probe that has revealed stuctural details of coal that were previously unmeasurable. For example, we have shown that APC#8 contains a fraction of its organic oxygen in the form of primary alcohol functions. The treatment of lignite with an array of fluorinating reagents, chief among these being diethylaminosulfur trifluoride, DAST, has now shown that it is possible to fluorinate many different sites in the coal and to assign them to functional group classes using direct observation of the ^{19}F resonance.

Diethylaminosulfur trifluoride, $(Et)_2NSF_3$, is an easily handled liquid that is a cognate of SF_4. DAST effects a wide range of oxygen replacement chemistry. It is useful for the conversion of primary, secondary and tertiary alcohols into alkyl monofluorides. Aldehydes and ketones are converted into geminal difluorides, and free carboxylic acids into acyl fluorides. The major side reactions in the use of DAST are dehydrations that accompany conversion of alcohols into fluorides.

DAST reacts with sulfur species (sulfonates sulfoxides, hemithioacetals) resulting in products with fluorine bonded to carbon. For example, with dialkyl or alkyl aryl sulfoxides that contain at least one α-hydrogen, the reaction with DAST effects a rearrangement that produces α-fluoroalkylsulfides. This reaction is strongly catalyzed by the Lewis acid, anhydrous zinc iodide, and is a useful synthetic reaction. Similarly, the DAST reaction with hemithioacetals requires the presence of N-bromosuccinimide, and will be an insignificant pathway in the coal milieu. The dry mineral matter free ratio, O/S_{org}, is 27 for APC #8. This ratio and the experimental reaction conditions bias the reaction of DAST with the organic matrix of this lignite toward oxygen replacement chemistry. The byproducts of DAST in this chemistry are hydrogen fluoride, HF, and thionyl fluoride, SOF_2. The ^{19}F MAS NMR spectra of the fluorinated lignite reveal components from both organic and inorganic fluorides unless the coal is demineralized prior to the DAST reaction chemistry.

The ^{19}F MAS NMR spectra of demineralized APC #8 lignite that has been treated with DAST spans 280 ppm and contains evidence of at least six different chemically unique species. One of these is a sharp resonance at -130 ppm and arises from diethylamine hydrofluoride, a

byproduct of DAST hydrolysis. The remainder are coal derived and provide evidence for fluoride functional groups expected from DAST chemistry.

The appearance of ^{19}F resonances in spectra recorded at MAS = 6 kHz are distinguishable according to the breadth of their powder lineshape. Significantly, only difluoromethylene moieties have a large CSA and dipolar interaction resulting in obvious first and second order sidebands. The recognition of this pattern in the ^{19}F MAS NMR spectra of fluorinated lignite (DAST) allows the identification of ketonic oxygen in the coal. Hydroxylic oxygen and, in particular, primary alcohols are also apparent in the spectra as a well-resolved resonance band representing primary alkyl fluoride centered at -230 ppm. This resonance has no detectable first order sideband area as anticipated from model measurements. DAST chemistry also creates secondary alkyl fluorides and acyl fluorides in the APC #8 lignite.

The spectral characteristics of fluorinated lignite prepared from demineralized APC No.8 are a strong function of reaction conditions. At low temperature, -78°C, DAST reacts readily with carboxylic acid functions in the coal to produce acyl fluorides as the major species. Alkyl fluorides are the next most abundant functionality. At room temperature, the sum of resonances from both alkyl fluorides and difluorides is greater than the acyl fluoride peak. This kind of selectivity can be used to advantage to deconvolute complex spectra.

---

1. ORNL Postdoctoral Fellow.

3. AQUEOUS CHEMISTRY AT HIGH TEMPERATURES AND PRESSURES

This chapter summarizes basic research by the High Temperature Aqueous Chemistry Group on chemical reaction equilibria and thermodynamics, the thermodynamics of electrolyte solutions, the group's participation in programs to apply experimental results to the problems of acidity in geothermal streams at The Geysers and on the volatility of electrolytes in steam cycles of power plants, and finally a new program on a pending CRADA with Modell Development Corporation on the study of solubilities of phases important in supercritical water oxidation processes. The program is making great strides in the measurement of the detailed chemistry and thermodynamics of broad classes of electrolytes at high temperatures and pressures using a powerful arsenal of unique equipment developed over years at ORNL. The combination of results from measurements with potentiometry, calorimetry, isopiestic and conductance techniques, along with phase studies and spectroscopic measurements, provides definitive information for the processes occurring at high temperatures such as ion association and complexation. At an expanding rate, new applications of the power of this program are being found, leading to new research opportunities.

CHEMICAL EQUILIBRIA AND THERMODYNAMICS OF REACTIONS

Metal Chloride Complexation

M. R. Narkhede,[1] D. A. Palmer, K. E. Hyde[2]

The thermodynamics of formation of transition metal chloride complexes have been studied for decades because of their importance (1) as metal transport agents in natural hydrothermal systems, (2) in enhancing the solubility of corrosion products in commercial steam generators, and (3) because of their intrinsic scientific interest. These applications require knowledge of the stability constants of these complexes at high temperatures where data are still sparse. The measurement of stability constants of transition metal(II) chloride complexes has continued in this period using the unique high-temperature chloride-electrode concentration cell developed recently in this program. Zinc(II) chloride complexation was studied from 5 to 250°C at an ionic strength of 1.0 $mol \cdot kg^{-1}$ with sodium trifluoromethanesulfonate as the noncomplexing supporting electrolyte. The formation quotients for $ZnCl^+$ are larger than those for the corresponding $FeCl^+$ species measured recently in this laboratory, but are substantially smaller than

reported from an earlier solubility study cited in the literature. Attempts were made to improve the performance of the electrodes in terms of their response time and Nernstian behavior. These efforts had little effect, although the current electrodes are functional provided they are given a reconditioning period following each experiment. A manuscript was submitted and accepted for publication in *Geochimica Cosmochimica Acta* describing the experimental study of ferrous chloride complexation at high temperatures using the hydrogen-electrode cell and its response to a competitive reaction with acetate.

Magnesium Hydrolysis

D. A. Palmer, D. J. Wesolowski

Magnesium is a major component of some natural brines (Salton Sea and the WIPP nuclear repository site in New Mexico), and consequently there has been a long-standing interest in the aqueous chemistry of this divalent ion. However, the lower solubility of its hydrolysis products has thwarted efforts to determine the thermodynamics of the mononuclear-hydroxo species. Measurements of the first hydrolysis constant were made at four ionic strengths from 0.1 to 5 $mol \cdot kg^{-1}$ (NaCl) utilizing the hydrogen electrode concentration cell. The temperature was varied from 1 to 250°C, so this represents the first detailed study of this equilibrium to high temperatures. The degree of hydrolysis to form $MgOH^+$ was limited to 2% of the total magnesium in solution before precipitation of presumably brucite, $Mg(OH)_2$, occurred. These preliminary results are in good agreement with earlier published data at 25°C and high ionic strengths, but indicate there is considerable discrepancy between the values extrapolated to infinite dilution and the corresponding values reported in the literature at ambient temperatures. It was surprising to discover that the logarithm of the hydrolysis constant remained a linear function of the reciprocal temperature in Kelvins over the entire temperature range investigated, implying a zero heat capacity change. This observation, however, is in keeping with recent results on the analogous aluminum(III) hydrolysis reaction, indicating that these small, highly charged cations behave as larger species due to their tightly bound inner solvation shells. Therefore, the change in solva-

tion caused by hydrolysis, as manifested in the heat capacity of reaction, is minimal.

Uranyl Hydrolysis and Complexation

C. Nguyen-Trung,[3] D. A. Palmer

The thermodynamics of uranyl(VI) hydrolysis have been studied extensively by a wide variety of techniques, largely because of their importance in considerations of the possibility of migration of uranium from breached nuclear waste respositories into the surrounding ground water. However, none of the earlier investigations addressed the near neutral to moderately basic pH region due mainly to the insolubility of the uranate(VI) salt in this region. Therefore, a series of titrations of aqueous solutions containing UO_2^{2+} were carried out at 0.1 mol•kg^{-1} ionic strength at 25°C from pH 2 to 12. Tetramethylammonium trifluoromethanesulfonate was used to maintain the ionic strength because it provided a noncomplexing medium that was a strong electrolyte and had less tendency to form insoluble uranates than the more traditionally-used alkali metal salts of perchlorate, nitrate, and chloride. A glass combination electrode was used to monitor the pH change and was calibrated internally on the hydrogen molality scale. Hydrolysis quotients (i.e., $Q_{mn} = [(UO_2)_m(OH)_n^{2m-n}][H^+]^n/[UO_2^{2+}]^m$) were obtained for the well characterized species $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH_5)^+$, designated as the 2:2 and 3:5 species, respectively, which predominate in mildly acidic solutions, *viz.* pH 3-5. These quotients were in good agreement with the large volume of published data, which nevertheless show a scatter of *ca.* one log unit. The hydrolysis quotient for the 3:7 species, which is the most important uranyl(VI) ion at neutral pH for concentrations in the millimolar range, was almost five log units smaller than the value quoted in the literature at the same experimental condition. In addition, hydrolysis quotients were obtained for the 3:8 and 3:10 anions, which predominate under mildly basic conditions. The initial choice of the polynuclear uranyl(VI) ions considered in processing these data was based on the results of a complementary Raman study of uranyl(VI) hydrolysis. This work underscores the advantage of using two methods to investigate such complex systems, whereby in this case Raman

spectra provide the background information on speciation, and potentiometry establishes their relative stabilities. Finally, a manuscript describing the corresponding Raman study of uranyl(VI) complexation by a variety of inorganic and organic ligands was prepared and has been published recently in the journal *Inorganic Chemistry*.

Ion Association by the Conductance Method

P. C. Ho, D. A. Palmer

The high-temperature conductivity apparatus has provided much of the information currently available on the association of electrolytes at extreme conditions, *viz.* 800°C and 400 MPa. This information is invaluable in the interpretation of experimental results obtained in this program from calorimetric, potentiometric, and volatility studies, even at moderate conditions. The thermodynamics of ion association are also fundamental in understanding natural processes such as corrosion in commercial steam generating systems and the behavior of deep hydrothermal fluids, as well as in the fast emerging field of supercritical treatment of waste streams. The conductivities of dilute (<0.1 molar) aqueous solutions of sodium chloride were investigated intensively from 350 to 400°C up to pressures of 300 MPa using the recently updated conductivity apparatus. These measurements were initiated to determine the behavior of this electrolyte near the critical temperature of the solvent where controversy exists as to the density dependence of the association constant at low solvent densities. The earlier measurements of NaCl conductivity in aqueous solution by Quist and Marshall in this laboratory were made at >400°C. It was found that in calculation of the specific conductance of each NaCl solution, the measured contribution for the conductivity of water had to be used in the temperature range 300 to 400°C, rather than relying on the calculated theoretical values as was possible at higher and lower temperatures. Preliminary calculations indicate that the resulting equivalent conductivities and association constants differ from the linear density relationships established by Quist and Marshall. The current results to 370°C are in agreement with those obtained by Zimmerman and Wood at the University of Delaware using a new low-pressure flow-through conductance cell. The design of

the inner electrode in the cell currently in use at ORNL was altered. A double-layered configuration of zirconia and alumina is now used to provide improved corrosion resistance while maintaining the required degree of electrical insulation. Initial testing with NaCl solutions to 500°C is now complete, with improvements in the reproducibility of the measurements and lower hysteresis being observed during pressure cycling.

A Model for Prediction of Reaction and Standard State Thermodynamic Quantities

R. E. Mesmer

A model which originated at ORNL for the standard state thermodynamic properties of electrolytes and reaction thermodynamics in terms of the P-V-T properties of water has been successfully applied to extrapolations for many kinds of chemical equilibria and electrolytes. Generally, the model is based on the use of the principle for volumes such that the molar volume at temperature is related to that at 25°C by a simple linear function whereby substances with the same $\bar{V}^o$ at 25° (or reactions with the same $\Delta\bar{V}^o$ at 25°C) have the same temperature dependence for $\bar{V}^o$. In an analogous way, $\bar{C}_p^o$ (or $\Delta\bar{C}_p^o$) is a linear function of $T(\partial\alpha/\partial T)_p$, where α is the expansivity coefficient of the solvent. Electrolytes with the same $\bar{C}_p^o$ at 25° have the same temperature dependence. By this model, log K is a simple function of logarithm of the density of water. These relationships fit data remarkably well for reactions involving ions, acids, and bases to 300°C. In the supercritical region, only modest changes are needed for similarly good fits.

Some of the basis for this model can be seen as stemming from the fact that the electrostriction term in the molar volume of an ion $\bar{V}_i^o$ is proportional to β, the compressibility coefficient for water. The proportionality constant is independent of both temperature and pressure. At the critical conditions, β approaches infinity, leading to infinities for $\bar{V}^o$ or $\Delta\bar{V}^o$. This model is referred to as the "density" model and is clearly a powerful estimating tool.

THERMODYNAMICS OF ELECTROLYTES

Enthalpies of Dilution of Sulfates

J. M. Simonson, S. A. Milioto[4]

Solutions containing sulfate are present in a wide variety of natural and technological systems. Due to the high solubility of the alkali-metal and some alkaline-earth sulfates and the two ionization reactions of sulfuric acid, solutions of sulfates may extend to high ionic strengths over very wide ranges of temperature and pH. The thermodynamic properties of these solutions may have a controlling influence on solution reactions, including partitioning of solutes to the vapor phase, solubility of metal ions, and hydrolysis of various solute species. In particular, the partitioning of sulfates between liquid and vapor phases as sulfuric acid or as an ammonium sulfate or bisulfate is of considerable practical interest to the steam generator community. In light of both this practical interest and the incomplete basic thermodynamic information available on sulfuric acid and its ammonium salts at high temperatures, an extensive series of calorimetric measurements was begun on (H_2SO_4 - NH_4HSO_4 - $(NH_4)_2SO_4$) solutions.

To date, enthalpies of dilution have been measured for $(NH_4)_2SO_4$(aq) to 5 mol•kg^{-1} at temperatures from 30 to 250°C; for (NH_4HSO_4 + H_2SO_4)(aq) to 6 mol•kg^{-1} from 30 to 325°C; and for H_2SO_4(aq) to 6 mol•kg^{-1} from 30 to 325°C. All systems have been investigated at two pressures (to 400 bars) at each temperature in order to determine the effect of pressure on the excess thermodynamic properties. While experimental measurements extending to higher temperatures are in progress and analysis of the results is not yet complete, a number of conclusions and guidance for further experiments have been drawn from the available data.

Sulfuric acid is an example of a solute for which the excess thermodynamic properties apparently are less difficult to describe quantitatively at modestly high temperatures than at ambient temperature. As shown in an earlier potentiometric study in this program, the second ionization constant for sulfuric acid decreases relatively rapidly with temperature. At temperatures above 100°C, this ionization reaction contributes little to the total observed enthalpy of dilution

even for results ranging as low as 0.005 $mol \cdot kg^{-1}$. At lower temperatures, the representation of the dilution enthalpies is extremely sensitive to the calculated degree of dissociation of the bisulfate ion, due to the large enthalpy of this reaction. While the standard state thermodynamic properties for this reaction are well known from the previous potentiometric experiments, small changes in the assumed equilibrium speciation as calculated from available excess thermodynamic property values lead to large changes in the corrected dilution enthalpies, with the result that no currently available model for the excess thermodynamic properties of sulfuric acid is sufficiently precise at low temperatures to permit straightforward analysis of the observed dilution enthalpies. The goal of the modeling study currently in progress is therefore to develop a significantly more precise representation for $H_2SO_4(aq)$ excess thermodynamic properties over the complete temperature range of the present experimental results, consistent with the new values of dilution enthalpies in this temperature range.

The opposite behavior is observed for the enthalpy of dilution of $(NH_4)_2SO_4(aq)$: the observed enthalpies of dilution are consistent with strong electrolyte thermodynamics at low temperatures, but are significantly more complex at higher temperatures. Analysis of these results, which is complicated by the reaction $NH_4^+ + SO_4^{2-} = NH_3 + HSO_4^-$, will depend directly on both the known ionization thermodynamic properties for bisulfate ion and for ammonia, which have been determined in previous studies in this program. This holds also for the new results for $\{NH_4HSO_4 + H_2SO_4\}$ dilution enthalpies. These experiments are expected to give the most direct information on the formation of NH_4HSO_4 ion pairs at temperatures above 200°C.

Isopiestic Studies of Phosphates

H. F. Holmes, R. E. Mesmer

Phosphoric acid and its salts are of great commercial, geological, and scientific importance. However, quantitative data for the excess Gibbs energy of aqueous solutions of these compounds are seriously lacking, particularly so at elevated temperatures. Modeling of the behavior of phosphates in physical processes and in chemical reactions

cannot be realistically achieved without these fundamental data. We have completed, in the ORNL high-temperature isopiestic facility, a series of measurements on aqueous solutions of selected phosphates over the temperature range of 100 to 250°C. The chosen compounds were phosphoric acid and the mono- and dihydrogen phosphates of sodium and potassium. An equimolar mixture of sodium monohydrogen phosphate and sodium dihydrogen phosphate (a common buffer for the control of pH) was included in the experiment. Aqueous sodium chloride served as the reference electrolyte for the calculation of thermodynamic properties. Stoichiometric osmotic coefficients (based on four particles) of the phosphate solutions were quite reproducible and clearly indicate that analysis of the results (incomplete at present) will require consideration of the ionization equilibria of phosphoric acid.

Thermodynamic Model for $CaCl_2$(aq)

H. F. Holmes, J. M. Simonson, R. E. Mesmer, R. H. Busey[5]

A model for the thermodynamic properties of aqueous $CaCl_2$ as a function of temperature, pressure, and molality has been completed and a manuscript describing the results is ready for internal review. The model is based on the ion interaction treatment which has been used so successfully by investigators (including us) in this field of research. At low temperatures, the upper molality limit of about 4.5 $mol \cdot kg^{-1}$ is determined by the inability of three virial coefficients to reproduce results above an ionic strength of about 13.5 $mol \cdot kg^{-1}$. The model is capable of reproducing freezing temperatures down to approximately -15°C. The upper temperature limit of 250°C results from the increasing ion association in $CaCl_2$(aq) with increasing temperature. Below 200°C, ion association can be neglected, while at 200 to 250°C, it can be adequately approximated by use of the $\beta^{(2)}$ parameter to give increased ionic strength dependence to the second virial coefficient. The temperature and pressure dependencies of $\beta^{(2)}$ can be satisfactorily represented by the ionization constant of $CaCl^+$(aq) from earlier ORNL electrical conductivity work. Our model is valid for pressures through at least 400 bars, the upper limit for useful density and enthalpy

results for $CaCl_2$(aq). This work clearly indicates that aqueous calcium chloride should be treated as a mixed electrolyte solution above 250°C.

Low Temperature Isopiestic Studies

D. A. Palmer, S. A. Milioto [4]

This program is oriented toward supplementing needed osmotic coefficient data obtained from the high-temperature facility, which has a lower limit of 110°C. The electrolytes chosen for study at 25 and 50°C are consequently those that are involved in other facets of the Aqueous Chemistry Group's research agenda. During this period, the salts chosen for study were Na_2SO_4, NaF_3CSO_3, and $(NH_4)_2SO_4$, as well as two mixed electrolytes (H_2SO_4 and $(NH_4)_2SO_4$) in the mole ratios of 1:2 and 2:1. These measurements are virtually complete at 25°C using a NaCl reference solution. Knowledge of the activity coefficients of $(NH_4)_2SO_4$ and $(NH_4)HSO_4$ solutions will be required in the near future when the volatility of these solutions is measured in a parallel research program sponsored by EPRI. The two sodium salts have been studied in the past in this program, but discrepancies between these results and available literature data prompted these further measurements using different sources of the solid salts. The current study reaffirms the validity of the osmotic coefficients obtained in our previous work on NaF_3CSO_3 and Na_2SO_4. In the case of the other single electrolyte studied, namely $(NH_4)_2SO_4$, the osmotic coefficients proved to be in excellent agreement at molalities less than unity with those reported in two previously published works, but deviated increasingly at higher concentrations by *ca.* 1% at the concentration limit of 5 to 7 $mol \cdot kg^{-1}$.

VOLATILITY OF AQUEOUS ELECTROLYTES

HCl(aq) and NaCl(aq) to 350°C (Geothermal Division, OEE and RE)

D. A. Palmer, J. M. Simonson, R. W. Carter[1]

The production of acidic, chloride-bearing steam in both natural geothermal reservoirs (e.g., The Geysers) and steam generator systems has resulted in significant problems in the corrosion of the materials of construction of piping and turbine systems of power plants. In addition to these practical problems, experiments to determine the

partitioning of NaCl between liquid and vapor phases at high temperatures are of fundamental interest in light of the information which may be obtained from these experiments on the degree of association of the solute at high temperatures. In order to address these questions, measurements have been made of the partitioning of both HCl and NaCl between liquid and vapor phases over {HCl + NaCl}(aq) from 250 to 350°C at total ionic strengths to 6 $mol \cdot kg^{-1}$ and varying Na/H mole ratios. These experiments give unambiguous information on the partitioning of NaCl, as opposed to an unbuffered experiment in which both NaOH and HCl could be volatile species, by suppressing possible hydrolysis reactions at high temperatures. Liquid and condensed-vapor samples were analyzed by acidimetric titration and ion chromatography to determine total molalities of H^+, Na^+, and Cl^-.

A preliminary analysis of the experimental results was made based on the known values of the stoichiometric activity coefficients of HCl(aq) and NaCl(aq) over the temperature and molality range of interest, assuming that there are no effects of mixing of electrolytes on the individual stoichiometric activity coefficients. This approximation is expected to become increasingly unreliable at high temperatures, where ion association is known to occur in both NaCl(aq) and HCl(aq) and common ion effects may contribute significantly to the stoichiometric activity coefficients in mixed electrolytes. Even with this necessary approximation, values of the thermodynamic partitioning constant for NCl calculated from the measurements in mixtures with NaCl are in good agreement with those calculated from experiments on pure HCl(aq).

The calculated partitioning constants for NaCl, although necessarily less precise than those for HCl due to the much lower volatility of NaCl at all conditions investigated, indicate a significant, nearly linear dependence of the logarithm of the apparent partitioning constant on the total chloride molality in solution, with lower values of log K obtained at higher ionic strengths. The observed dependence is too large to be attributable to reasonable values of parameters of the ion interaction model which describe the effects of mixing of ions of like sign. Efforts are in progress to represent quantitatively the observed values of the partitioning constant for NaCl, based on (1) the develop-

ment of a fully speciated model for solute thermodynamic properties which takes into account the ion pairing of both HCl and NaCl at high temperatures, and (2) further consideration of the state of the solute in the steam phase, with renewed consideration of the assumption that the vapor phase solute exists as the undissociated molecule, with a unit activity coefficient.

Volatility of $NH_4Cl(aq)$ and Transport in Steam Generators

J. M. Simonson, D. A. Palmer, R. W. Carter,[1] R. E. Mesmer

Corrosion and deposition of solids in the turbine systems of power plants are major problems requiring expensive maintenance and resulting in lost power generation capacity in electric utilities throughout the United States. Many of the problems observed in operating steam generators are apparently specific to the design, construction, and operation of a particular system, with widely varying operating experience found by utilities using nearly identical water treatment methods and chemicals under similar conditions. In-plant monitoring of levels of treatment chemicals or contaminants in steam generator systems is severely limited due to the high cost of installing on-line analytical instrumentation, the inaccessibility of many components of the steam cycle, the very low levels of some of the troublesome compounds present, and the difficulty encountered in obtaining representative samples from a complex system operating at high temperatures, pressures, and flow rates of water or steam. Extensive operating experience has shown the need for strict control of treatment chemical and impurity levels in the water introduced into steam generators, and guidelines for water quality have been prepared by the Electric Power Research Institute (EPRI) based on operating experience at a number of plants.

For economic reasons, it is not practical to establish and maintain arbitrarily low levels of impurities, particularly of chloride, in the water used in steam cycles. It is therefore of great practical importance to perform laboratory measurements of the partitioning of common impurity compounds between liquid and vapor phases over a wide range of temperatures, including both the steam generation ($t > 350°C$) and condensate formation ($t < 100°C$) ranges. Since it is not practical to

perform precise experimental studies at the low solute levels encountered in steam cycles, measurements of the partitioning of these sparingly volatile solutes must be made at higher concentrations, and rigorous thermodynamic models used to extend the results of the laboratory measurements to concentrations of interest in steam cycle operation. The experimental and thermodynamic modeling expertise developed under Chemical Sciences sponsorship of the high-temperature aqueous chemistry program has led EPRI to commission a study of the partitioning of ammonium salts between liquid and vapor phases over wide ranges of temperature.

In a study recently completed and submitted for publication, measurements were made of the partitioning of ammonium chloride between liquid and vapor phases at temperatures from 120 to 350°C. This study has shown clearly both the complexity of the measurements and modeling involved in quantitative determination of solute partitioning to high temperatures, and the importance of accurate fundamental information on solution thermodynamic properties at high temperatures to the application of experimental results to steam cycle conditions. This complexity is reflected in the failure of widely used, overly simplistic descriptions of the temperature dependence of salt volatility to predict the partitioning observed in operating steam cycles. For ammonium chloride, the total partitioning of solutes to the vapor phase is the sum of contributions from ammonia, hydrochloric acid, and ammonium chloride. The relative amounts of these compounds in the steam depend directly on solution concentration and pH at high temperatures. Previous Chemical Sciences-sponsored studies at ORNL of the ionization of water and ammonia ro 300°C, the partitioning of hydrochloric acid between liquid and vapor to 350°C, and the liquid-phase thermodynamic properties of hydrochloric acid and ammonium chloride to high temperatures have provided the fundamental thermodynamic information essential to a quantitative description of the new measurements of ammonium chloride volatility. The overall model developed to describe the behavior of this solute, which indicates that steam formed over a low-chloride, high-pH liquid at high temperatures will produce an "early condensate" liquid at low temperatures having the extremely corrosive combination of

both high chloride and low pH, has been received with great interest by engineers and scientists directly involved in steam cycle chemistry, and is currently being used to estimate chloride concentrations in various parts of the steam cycle for comparisons with new data from operating plants.

TECHNICAL SUPPORT FOR SUPERCRITICAL WATER OXIDATION (SCWO) PROCESSES (CRADA - MODEC)

R. E. Mesmer, J. M. Simonson, R. C. Moore,[1] H. F. Holmes, H. D. Cochran,[6] G. F. Bloomingburg[6]

This program is the DOE part of a planned CRADA with MODEC to conduct research in support of the effort to evaluate and develop supercritical water oxidation as a viable method to handle mixed wastes at DOE sites. In the project, we are conducting proprietary research to facilitate the use of MODEC technology. MODEC has proprietary methods of mitigating problems associated with acid neutralization and solids deposition, but laboratory measurements of solubilities of certain inorganic materials will greatly facilitate the use of such technology. In addition, research is being conducted in the Chemical Technology Division to upgrade the ASPEN code to address SCWO conditions. We will incorporate properties of representative inorganics that are important to the process into models of the solution chemistry as well. Much prior experience with such experiments and thermodynamic modeling will be brought to bear on these tasks.

Two major problems which have been identified to date in the operation of SCWO pilot operations on simulated wastes are (1) deposition of inorganic solids at various points in the system, and (2) corrosion of structural metals. Organic compounds become highly miscible in the supercritical region facilitating the oxidation process, and, at the same time, inorganic compounds, especially salts, become quite insoluble at these temperatures.

High acidity is inherently produced during the oxidation of organics containing heteroatoms. The acid may cause severe corrosion of the metals in the system and may interact with other inorganic components. In addition, hydrolytic precipitation of hydroxides and oxides

of many metal ions is promoted by high temperatures and is accompanied by the production of acidity.

High miscibility of organics with water coupled with the high reactivity of hydroxyl radicals leads to rapid and complete oxidation of organics at temperatures on the order of 500°C. The low dielectric constant of water leads to the high miscibility of organics and at the same time low solubilities of inorganic salts. For the latter reason, it is difficult to provide chemical buffering against the acidity. Furthermore, the present state of knowledge and therefore the database in ASPEN are not yet adequate to provide a reliable basis for predicting the behavior of the important inorganic constituents in the SCWO process.

---

1. ORAU Postdoctoral Associate.
2. State University of New York, College of Oswego, Oswego, NY.
3. CNRS, France.
4. University of Palermo, Palermo, Italy.
5. ORNL, retired.
6. ORNL Chemical Technology Division.

4. GEOCHEMISTRY

This program provides fundamental geochemical information on fluid-rock interactions in the Earth's crust pertinent to magma/hydrothermal and hydrocarbon energy resources, large-scale fluid circulation, and remedial waste cleanup activities. Aqueous systems are investigated with a wide array of hydrothermal facilities that permit studies of metal complexation, mineral solubilities, acid and base dissociation, ion activity coefficients, and reaction kinetics. Studies of stable O, H, C, S isotope partitioning between minerals and fluids in experimental and natural systems help delineate the mechanisms and rates of fluid-rock reactions, fluid fluxes, and paleotemperatures. Silicate phase equilibria, crystallization kinetics, element partitioning, and melt/volatile interactions are studied under controlled redox conditions. Theoretical and empirical modeling complements the experimental approach by extending the results to experimentally inaccessible pressure-temperature-composition regions and by establishing the critical relationship between experimental and complex natural systems.

GEOCHEMISTRY OF CRUSTAL PROCESSES TO HIGH TEMPERATURES AND PRESSURES

D. J. Wesolowski, J. G. Blencoe, D. R. Cole, J. L. S. Bell,[1] D. A. Palmer

Hydrothermal Geochemistry

One of the most intriguing questions associated with aqueous and hydrocarbon fluid circulation in both sedimentary basins and geothermal systems is how aluminum is transported in brines to permit secondary porosity development, mineral alteration, and porosity occlusion via aluminosilicate dissolution and precipitation (feldspars, micas, clays, etc.). The most abundant potential organic complexing ligand encountered in sedimentary basin brines and some geothermal systems (e.g., Guaymas Basin) is acetate, a product of thermal degradation of buried organic matter.

To determine the importance of acetate in aluminum transport, an extensive series of potentiometric titrations of acetate buffers with aluminum chloride solutions was conducted using a high-temperature hydrogen-electrode concentration cell. The formation constants for $AlAc^{2+}$ and $AlAc_2^+$ were determined at temperatures of 25 to 125°C in 0.1 to 5.0 molal NaCl brines. Modeling of these results demonstrates that

$AlAc^{2+}$ may be the dominant aluminum species in solution in acetate-bearing sedimentary basin brines in the oil window.

Other organic acids reported in basinal brines include formate, malonate, and oxalate. The latter two are known to form extremely stable bidentate complexes with a variety of multiply charged cations, including aluminum, iron, calcium, and magnesium, at room temperature. In the past year, the dissociation constants of formic acid (25 to 200°C) and malonic acid (0 to 100°C, collaboration with R. M. Kettler of the University of Nebraska) were determined in 0.1 to 5.0 molal NaCl brines by potentiometry. Quantitative studies of metal complexation by these acids can now begin.

Because the thermal stabilities of organic acids are important in assessing their role in metal transport, a series of studies has been initiated in which the decomposition of formic and oxalic acids is conducted in the high-temperature potentiometric cell. Instantaneous rates of decomposition have been determined mathematically from the derivatives of functions of the organic acid concentration *vs.* time. In this way, the thermal stabilities of formic acid, formate, oxalic acid, bioxalate, and oxalate have been independently determined in the 150 to 250°C range.

A major study of the solubilities of calcite and dolomite was also completed in the 30 to 300°C range and 300 to 1300 bars in low-salinity H_2O-CO_2 solutions. Both calcite and dolomite exhibit retrograde solubility with increasing temperature and prograde solubility with increasing pressure. The equilibrium constants for both calcite and dolomite can be simply modeled as a function of temperature and the density of the solvent water, with dolomite being less soluble than calcite by approximately 0.5 log units at equivalent conditions. Extrapolation of the log K values for calcite to low temperature and pressure demonstrates quantitative agreement with the best available literature data. The effect of increasing pressure on the solubility of these minerals is significant, in that burial and uplift as well as lithostatic to hydrostatic pressure changes may exert a major influence on secondary porosity development in carbonate source rocks and reservoirs.

Stable Isotope Systematics of Fluid-Rock Interactions

Many hydrothermal systems exhibit varying degrees of fluid-rock oxygen isotope disequilibrium for the bulk rock. A detailed comparison of data from a variety of active geothermal and paleohydrothermal systems indicates that the degree of equilibration of the bulk fluid and rock is related to the temperature and salinity of the system, with higher temperatures and salinities promoting more rapid approach to isotopic equilibrium. This relationship is entirely consistent with calculations based on experimental studies completed in this laboratory and elsewhere and carried out for a simple closed system model that estimates the fraction of isotope exchange between rock and fluid as a function of temperature, rock type, salinity of the fluid, grain size, fluid/rock ratio, and the rate of isotope exchange.

Fluid composition plays a major role in determining the degree of isotopic equilibration in short-lived natural systems. Furthermore, the fact that many silicate-fluid exchange reactions are relatively fast compared to geologic time scales suggests that observed variations in the degree of isotopic exchange may have resulted from periodic, local self-sealing of the fracture network throughout the time of hydrothermal activity in a given system. This observation may explain, in part, the apparent discrepancy often reported between "field rates" of fluid rock reactions estimated from natural systems and "laboratory rates" of similar reactions studied in controlled experiments.

Stable isotope systematics can also be effectively employed in studies of Earth-surface processes in which insight is gained as to paleoclimatic conditions via rock-atmosphere-groundwater interactions. Pedogenic carbonates in well preserved paleosols in late Pleistocene alluvial fan deposits in south central New Mexico have elevated $^{13}C/^{12}C$ ratios relative to paleosols in overlying Holocene fans. The change from heavier to lighter carbon isotope ratios occurs rather abruptly at 9,100 years ago. The higher ^{13}C values in the late Pleistocene appear to reflect abundant C_4 grasses, which would have inhibited erosion in the upland areas, with a shift toward desertscrub (a low ^{13}C plant assemblage) in the Holocene. Pollen analyses of paleosols support this interpretation. The $^{18}O/^{16}O$ ratios in the carbonates are similar for

Holocene and late Pleistocene paleosols, reflecting a mean annual temperature of roughly 13.8°C, which apparently did not change significantly over the last 40,000 years in this region. It is known that high atmospheric CO_2 contents adversely affect C_4 plant metabolism. These observations, coupled with polar ice core CO_2 data, suggest that a combination of reduced rainfall and increased atmospheric CO_2 contributed to the decline of C_4 vegetation in the southwestern United States.

Studies of this system are being conducted in collaboration with G. H. Mack, T. H. Giordano, and C. Monger of New Mexico State University. Isotopic studies of the erosional source rocks of these alluvial fans—the Organ Cauldron and subvolcanic batholith, an early Oligocene volcanic sequence—are being conducted in collaboration with M. McCurry of Idaho State University and L. Farmer of the University of Colorado.

Thermodynamics of Rock-Forming Crystalline Solutions and Silicate Melts

Because plagioclase feldspar is the most abundant mineral in continental crustal igneous rocks and because water is the primary fluxing agent in igneous processes, the albite-water system is an excellent analog for modeling the behavior of granitic magmas. New, thermodynamically rigorous models have been developed for this system that employ a two-parameter Margules or a three-parameter Redlich-Kister formulation. These models accurately describe all thermodynamic properties and phase equilibria in the albite-water system in the range of 700 to 1200°C and 1 to 8 kbars. Calculated activity-composition relations are similar to those predicted by equations based on PVT data (but the model does not require such data, which are exceedingly difficult to obtain), excess enthalpies are in substantial agreement with data obtained from calorimetry, and calculated phase relations are fully compatible with the best available experimental data. Activities of melt species were calculated using a standard state in which the activity of molecular water in the melt is numerically equal to the activity of total water in the melt.

A major modeling effort, in collaboration with C. V. Guidotti of the University of Maine and F. P. Sassi of the Universitá di Padova, Italy, has also been focused on the solvus relations and thermodynamic

mixing properties of paragonite-muscovite crystalline solutions. These micas are abundant in many shallow to intermediate depth crustal metamorphic rocks and continental granites and play an important role in magma generation and crystallization in the crust. X-ray diffraction data on natural $2M_1$ paragonites and muscovites have been evaluated, and accurate unit cell dimensions have been determined. Derived equations for molar volume indicate that excess molar volume is positive for sodium-bearing muscovites but is either zero or slightly negative for potassium-bearing paragonites.

Solvus data obtained by Blencoe (1974) for synthetic, binary paragonite-muscovite micas have been re-analyzed to delineate the solvus and to develop a new thermodynamic model. The data indicate that at pressures between 2 and 8 kilobars and temperatures above 400°C, mutual paragonite-muscovite crystalline solution increases with increasing pressure, which helps to explain why most sodium-rich muscovites are found in high-pressure metamorphic rocks. This result further indicates that paragonite-muscovite micas are highly compressible, which is a new and unexpected finding. A polybaric, polythermal excess free-energy equation was developed from these data, which provides calculated paragonite-muscovite solvi for 1 bar to 10 kbars and temperatures >400°C. Numerical geothermometers based on solvus data for natural paragonite-muscovite pairs were also developed.

---

1. ORAU Postdoctoral Associate.

CRUSTAL STABILITY OF HYDROCARBONS AND C-O-H-N FLUIDS

J. G. Blencoe, J. L. S. Bell,[1] D. B. Joyce,[1] J. C. Seitz,[1] T. E. Burch[1]

The objective of this project is to determine the thermodynamic and kinetic properties of carbonaceous fluids over ranges of pressure, temperature, and composition encountered in the Earth's crust. Such fluids play a dominant role in the transport of energy and material in the crust, and are themselves energy resources, in the form of biogenic and abiogenic natural gas and other hydrocarbon fluids. The pressure-volume-temperature (PVT) relationships of C-O-H-N fluids and mixtures are evaluated to 500°C and 4 kbars to derive all other thermodynamic

properties. The equilibrium activity/composition relationships of C-O-H-N fluids up to 8 kbars and 1100°C are determined by employing novel experimental techniques. The thermal stability of organic compounds such as acetic acid are studied to identify unconventional biological inputs to C-O-H-N fluids encountered in natural gas reservoirs.

A unique high PT vibrating tube densimeter designed and constructed at ORNL has been used to obtain PVT data on binary and ternary mixtures in the system CO_2-CH_4-N_2 at 50, 100, and 200°C and at pressures of 100, 200, 400, 600, 800, and 1000 bars, encompassing the complete compositional range in this system, which is representative of natural gas reservoirs. Conservative estimates of accuracy are P, ±2.0 bar; T, ±0.2°C; and V, ±0.2%. Preliminary modeling of the results indicates that ternary molecular interaction parameters are small and that most of the binary data are well described by two-parameter Margules-type formulations.

At the higher temperatures and pressures, the deviation from ideal mixing of the pure end members of these gases are often less than 3% of the total volume. However, at lower pressures and temperatures (<200°C), mixtures containing CO_2 exhibit remarkably large excess volumes. For instance, an 80% CO_2, 20% N_2 mixture at 50°C has an excess volume greather than +20% of total volume at 100 bars and less than -10% at 600 bars. CO_2-CH_4 and $CO_2$0CH_4-N_2 mixtures also exhibit large and widely varying excess properties at these conditions. Such large deviations from ideal mixing exert a profound influence on derived thermodynamic properties of the components, such as activity. Moreover, such information is critical in reservoir engineering and the transmission of natural gas through pipelines.

A detailed comparison of various published equations of state for pure gases and mixtures in the CO_2-CH_4-N_2 system with the newly obtained data reveals that none of the currently available models adequately represent the actual behavior of these gases at all temperatures and pressures studied. Most of the equations break down near the critical point of CO_2 for mixtures containing this gas in any significant proportions. Furthermore, it is clear that the major source of error in most of the available formulations is in the numerical description of the PVT

properties of the pure end members. Of the equations of state investigated, DDMIX, the mixture property program available from the National Institute of Standards and Technology (Ely, 1988) is uniformly superior. However, most geoscientists and petroleum engineers are currently using some form of a modified Redlich-Kwong equation of state.

Activity-Composition Relationships of C-O-H-N Gases

Experimental studies of CO_2-H_2O mixtures are now under way, employing an internally heated pressure vessel specifically designed for hydrogen service and capable of precise redox control. Silver oxalate and water are loaded into $Pd_{75}Ag_{25}$ capsules with Ni/NiO or Co/CoO to control oxygen fugacity. Hydrogen pressure is controlled with a separate $Pd_{75}Ag_{25}$ membrane, and the activity of water is computed from the reaction $H_2O = H_2 + 1/2O_2$. The composition of the quenched capsules and the Gibbs-Duhem equation is then used to determine the activity-composition relationships of the mixtures. Measurements have been completed at 50° intervals from 400 to 650°C at 500 bars total pressure, with successful reversals at all conditions studied. The results demonstrate large positive deviations from ideal mixing at the lower temperatures for CO_2-rich mixtures, with the system approaching ideal mixing at 650°C.

Development of an equation of state for CO_2-H_2O mixtures is also proceeding, the new model incorporating experimental solvus relations, measured mixing enthalpies and volumes, and the activity-composition results described above. Margules, Van Laar, and Quasichemical models are being empirically fitted to these data. Preliminary results demonstrate that combining the derivative properties, enthalpy, and volume with phase equilibrium data and the activity-composition data previously described offers a much more powerful and reliable avenue to a quantitative and thermodynamically rigorous equation of state for this system than has been available in the past.

Thermal Stability of Acetic Acid

The kinetics of thermal decarboxylation of aqueous solutions of acetic acid and sodium acetate were evaluated at 335 and 355°C in the

presence of various potentially catalytic surfaces. Such high temperatures were needed to observe the decomposition in a practical time scale. The results were then extrapolated down to the more geologically relevant conditions of 100 to 200°C. Quartz, calcite, and pyrite were found to have minor catalytic effects, whereas calcium- and iron-bearing montmorillonite, hematite, and magnetite exerted a profound effect on rates of decomposition. The dependence of the rate on the surface area of pyrite per unit volume of solution was also studied. The results show that the decarboxylation of acetic acid is surface-catalyzed, with the cleavage of the carbon-carbon bond occurring while the acetate molecule is adsorbed. Entropies and enthalpies of activation for all catalytic substrates indicate the existence of a common rate-determining step.

In the absence of an effective catalyst, acetic acid survives indefinitely (>5 billion years) at 100°C. Iron-bearing phases such as magnetite and iron-montmorillonite rapidly catalyze the decarboxylation to CH_4 and CO_2, while minerals such as hematite induce an oxidative decomposition to CO_2 and/or complex polycondensates. The half-life of acetic acid in the presence of calcium-montmorillonite is approximately 410 years at 100°C. Thus, it is clear that both the host lithology and the production rate of acetic acid from thermal degradation of more complex organic material are significant in controlling the concentration of this carboxylic acid at any given time in a basinal brine. Furthermore, circulating brines containing acetate may encounter lithologies that could rapidly induce decomposition to produce CH_4, CO_2, or complex polycondensates.

FUNDAMENTAL RESEARCH IN THE GEOCHEMISTRY OF GEOTHERMAL SYSTEMS

D. J. Wesolowski, D. R. Cole, J. Horita[1]

The goal of this research is to provide quantitative experimental data and theoretical models for fluid/rock interaction processes that bear a direct application in the discovery and exploitation of active geothermal systems. Simple analogs are studied to develop useful generalizations of the behavior of more complex systems in which Na-K-

Mg-Ca-Cl-SO_4-HCO_3 brines react with mineral assemblages in the system Na-K-Ca-Mg-Fe-Al-Si-S-O-C-H at elevated temperatures and pressures.

Geochemistry of Aluminum in Natural Waters

Brine chemistry and the development and occlusion of porosity in most geothermal systems are highly dependent on the stability of aluminosilicate minerals in the rock matrix, such as feldspars, micas, and clays. An exact description of the distribution of the species Al^{3+} and $Al(OH)_y^{3-y}$ ($y = 1$ to 4) is required to predict the solubilities of these phases in natural waters. During the last year, a detailed study was completed on the hydrolysis of Al^{3+} in NaCl brines using a unique, high-temperature potentiometric cell. The equilibrium quotients for the reaction $Al^{3+} + H_2O = Al(OH)^{2+} + H^+$ were obtained at 25-degree intervals from 25 to 125°C in 0.1 to 5.0 molal NaCl solutions. Because of the exceedingly low solubility of most aluminum minerals, these two species will dominate the transport of aluminum in acidic brines to at least 150°C. A quantitative model for this reaction as a function of temperature and ionic strength has been developed.

These results, combined with previous studies completed in this project and the aluminum acetate complexation study described in the first part of this section, provided the means to interpret the extensive gibbsite–$Al(OH)_3$cr–solubility data in near-neutral pH solutions reported in previous years. The formation constant for the reaction $Al(OH)^{2+} + H_2O = Al(OH_2^+ + H^+$ has been modeled to 200°C using these results and critically evaluated literature data.

Oxygen and Hydrogen Isotope Systematics in Brines

Studies of the distribution of stable oxygen and hydrogen isotopes in geothermal waters and mineral assemblages provide quantitative information on reservoir temperatures, fluid sources and fluxes, and the extent of subsurface processes such as steam separation. However, the effect of dissolved ions on the partitioning of these isotopes between brines, steam, and minerals, although known to be significant, has largely been ignored because of uncertainty in the magnitude of the effect at high temperature. During the past year, measurements of the

effect of pure salts in the system Na-K-Ca-Mg-Cl-SO_4 on the water liquid-vapor partitioning of hydrogen and oxygen isotopes have been completed for 0.5 to 6.0 molal salt solutions in the range 50 to 100°C. The effect of 1.0 to 5.0 molal NaCl has been determined to 200°C.

Sodium and potassium salts have little or no effect on the partitioning of oxygen isotopes at temperatures up to 200°C. On the other hand, calcium and magnesium salts of chloride and sulfate exhibit large salt effects, to the extent that isotopic studies of systems involving brines containing less than 1 molal of these cations must take into account the salinity effect in the derivation of temperatures and water/rock ratios.

All the salts studied exert significant effects on the partitioning of hydrogen isotopes between brines and vapor. Chloride salts affect the partitioning by 1 to 2 per mil per molal chloride, with only minor effects related to the nature of the cation. Sulfate salts exhibit a smaller salt effect, indicating that the doubly charged anion is not more strongly hydrated than the singly charged chloride ion. Both oxygen and hydrogen isotope salt effects are linear with the molality of the dissolved salt. For chloride salts, the hydrogen isotope salt effect decreases with increasing temperature to about 100°C and remains constant at approximately 1 per mil molal chloride in the 100 to 200°C range.

STABLE ISOTOPE SYSTEMATICS DURING BURIAL DIAGENESIS IN THE ALBERTA BASIN: AN ION MICROPROBE STUDY

D. R. Cole, L. R. Riciputi,[1] W. H. Christie[1]

In this project, the micron-scale spatial resolution, elemental and isotopic imaging, and quantitative trace element and isotope ratio analytical capabilities of a state-of-the-art Cameca 4f ion microprobe are being developed and used in a study of the fluid/rock interactions associated with burial and hydrocarbon generation in carbonates and clastics of the Alberta Deep Basin. A detailed study has been initiated on the trace element distributions in primary and diagenetic calcites and dolomites of the Nisku Formation, an important petroleum host rock in the Alberta Basin. Distributions of iron and manganese indicate

changes in redox conditions during early diagenesis and later fluid-flow events. Barium, B, Na, Mg, Si, and Al changes with time suggest significant changes in fluid source coincident with dolomitization of the calcite reefs, a process leading to increased permeability. In general, the chemical variability on a fine scale revealed by the ion probe indicates that the chemical composition of the diagenetic carbonates responds to a complex interplay between primary composition; changes in chemistry, temperature, and flux of fluids through time; and the variable chemistry of small, rock-dominated microenvironments.

Sulfur isotope ratios (precision of 0.5 per mil) have been measured in a variety of pyrite grains, some as small as 40 μm, from both the Nisku and the sour gas province located farther west in the Alberta Basin. Very large variations in the ratios (up to 40 per mil) appear to reflect differences in sources of reduced sulfur—either thermogenic or bacteriogenic reduction of seawater sulfate. Considerable progress was also made during this period on the development of oxygen isotope ratio measurement techniques. Precisions of 1 per mil have been obtained on magnetite standards with spatial resolution on the order of 10 μm. Because the remnant magnetism of diagenetic magnetites can be used to date late diagenetic events, coupling such observations with oxygen isotope and trace element analyses offers the opportunity to develop a time-temperature-fluid source history of the Alberta Basin and other hydrocarbon-bearing systems.

---

1. ORNL Analytical Chemistry Division.

ADVANCED CONCEPTS

D. R. Cole, D. J. Wesolowski

This project explores topics in the geosciences that offer the opportunity to open new frontiers of scientific inquiry or methodology. These goals are often achieved by developing unique laboratory facilities, techniques, and theoretical models. The benefits of this exploratory research impact many areas related to the domestic energy supplies.

Design and construction of a new high pressure-temperature, flowing emf cell was completed this year. The new cell will enable the measurement of pH in aqueous solutions to at least 400°C and 1 kbar, an accomplishment never before achieved. This capability will enable the study of the hydrogen ion activity in supercritical brines such as those encountered in magma/geothermal systems and will permit measurements of the pressure dependence of protolytic aqueous reactions relevant to deep sedimentary basin settings.

Geologic applications of the Cameca 4f ion microprobe are being developed. A new method for the quantitative analysis of rare earth elements in a variety of silicate structures, involving the use of doubly charged ions of odd mass isotopes, was demonstrated that is four times faster than current methods, with sensitivities of 5 to 50 ppb. Energy offset techniques have also been developed that allow linear calibration curves to be generated for B, Na, Al, Ca, Mg, Mn, Fe, Sr, and Ba in carbonates, with detection limits of <1 ppm and precisions of approximately 10% on spot sizes of 15 to 30 μm. Elemental imaging using the probe has been expanded to enable trace element imaging of fields up to 500 × 500 μm with resolution of about 10 μm.

A collaboration with the Advanced Inorganic Materials Group continues to explore novel methods of materials synthesis using geochemical experimental techniques. Attempts to synthesize covalently bonded carbon-nitride compounds, expected to have a hardness similar to diamond, demonstrate that extremely high pressures are required. However, potential precursor materials with short-range, trigonal, layered structures were formed at 700°C and 2.25 kbars.

A collaboration was initiated with L. A. Odom of Florida State University to investigate the potential use of paramagnetic defect centers in natural quartz as a geochronometer. Such defect centers are stabilized in quartz as a result of gamma irradiation from natural unstable isotopes (uranium, thorium, etc.) as well as cosmic rays. Extremely high dose rates available at the High Flux Isotope Reactor at ORNL are needed to test hypotheses regarding the annealing rates of defect centers and also to help distinguish between centers resulting

solely from radiation damage and those associated with trace impurities, such as aluminum and iron, in the quartz matrix.

5. CHEMISTRY OF ADVANCED INORGANIC MATERIALS

This program consists of four related research tasks: (I) the exploitation of surface modification and electrochemical techniques to prepare mixed-oxide films with useful catalytic and electronic properties, (II) novel synthetic routes to prepare compounds with appropriate morphologies (whiskers, platelets, etc) for use as reinforcing agents in composites, (III) synthesis and characterization of advanced nonoxidic ceramic materials, particularly as films or coatings, with emphasis on plasma-enhanced CVD, and (IV) the determination of composition/structure/property relationships in high T_c superconducting oxides and application of the results to optimization of synthesis/processing procedures. Multiple spectroscopic and electrochemical probes are being applied in Task I to determine the oxidation states and depth profiles in anodically grown films of $M_xTi_{1-x}O_2$ on ion-implanted M-Ti near-surface alloys. Use of STM and AFM to probe surface morphology and spatial variations in electronic properties is being developed. Research in Task II is focussed on production of oxidic precursors, such as Na_xWO_3 and ZrO_2, in desired morphologies by thermal and molten salt reactions and on their pseudomorphic conversions by reducing/carburizing and nitriding agents to carbides and nitrides. Preparations of several metal nitrides of moderate stability (Sn_3N_4, Cu_3N, Ni_3N) as thin films by reactive sputtering in a nitrogen plasma and their conversion to metallic lines by maskless laser decomposition illustrate the approach of Task III. Plasma-enhanced CVD approaches to other materials in the metal-C-N-B regime are in progress. Synthetic work on high T_c superconducting oxides in Task IV emphasizes the optimization of aerosol synthesis of complex powders for the powder-in-tube approach to conducting wires and the doping and phase behavior of Tl-based compositions.

PREPARATION AND CHARACTERIZATION OF ELECTROCATALYTIC SURFACES

XPS Characterization of Anodic Layers Grown on Ir- and Rh-Implanted Titanium[1]

C.E. Vallet, A. Choudhury[2], P.E. Sobol[3] and C.W. White[4]

X-ray photoelectron spectroscopy is used to complement the array of *in situ* techniques applied to the study of anodic layers formed on

titanium implanted with a noble metal, and allows the chemical characterization of the mixed oxides.

The (RuO_2-TiO_2) anode and, to a lesser degree, the (IrO_2-TiO_2) anode are good electrocatalysts for the production of chlorine from chloride solutions. In the ongoing study, the electrochemical oxidation of titanium implanted with Ru (or Ir) has produced catalytic surfaces for the chlorine evolution reaction[5]. It was assumed that a surface layer of mixed dioxide was formed and that the ratio of Ru (or Ir) to Ti at the oxide surface was directly related to the implant profile. With these assumptions it was possible to determine an electrocatalytic efficiency of iridium to ruthenium of the order of 0.4-0.45. The large difference in electrocatalytic efficiency cannot be attributed to difference in size or electronic structure of Ru^{4+} and Ir^{4+}, or to different structures in $Ru_xTi_{1-x}O_2$ and $Ir_xTi_{1-x}O_2$. The lower electrocatalytic efficiency of iridium, however, could possibly stem from an incomplete oxidation of surface iridium, with only a fraction of (Ir^{4+}) iridium sites active in the chlorine evolution reaction.

In order to test this hypothesis, the surface of an electrochemically oxidized iridium-implanted titanium electrode, with good catalytic activity, was investigated by X-ray Photoelectron Spectroscopy (XPS). Measurements were done by the angle dependent method and by depth profiling with argon ion sputter etching using a Perkin Elmer model 5600 spectrometer at the Perkin Elmer Laboratory (Eden Prairie, MN). The measurements were made at electron emission angles of 15° and 70° which probe depths of 20Å and 70Å, respectively. The positions of the $Ti_{2p\ 3/2}$ line at 458.6 eV and of the $Ir_{4f\ 7/2}$ line at 62.2-62.5 eV, shown in Figure 5.1, were identical in both configurations and indicated no large variation with depth of the valence states of Ir or Ti for layers between 20 and 70Å. The positions of the $Ti_{2p\ 3/2}$, the $Ir_{4f\ 7/2}$ and O_{1s} lines are consistent with TiO_2 and IrO_2 present at the surface. A better knowledge of the extent of the mixed oxide layer was obtained by depth profiling measurements through the oxide during 4 keV argon ion sputter etching. Figure 5.2 shows the estimated depth of the mixed oxide layer and of the Ir metal implanted layer. The value of 350 Å for implanted Ir metal is consistent with that measured by Rutherford

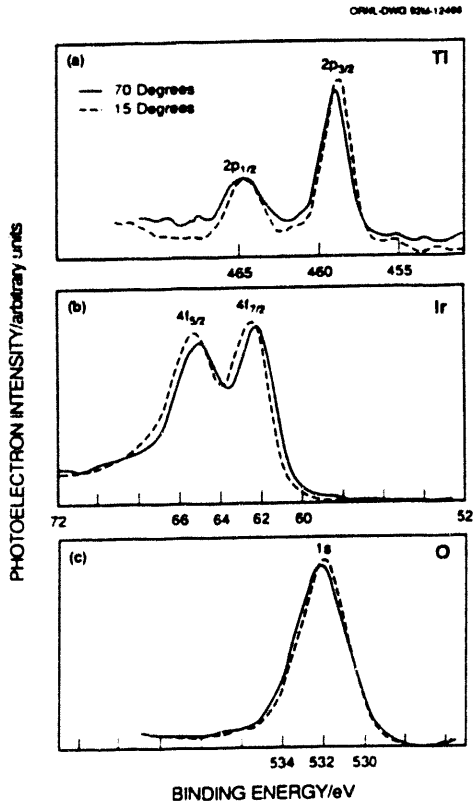


Fig. 5.1. Photoelectron spectra taken at emission angles of 15 degrees (—) and of 70 degrees (---).

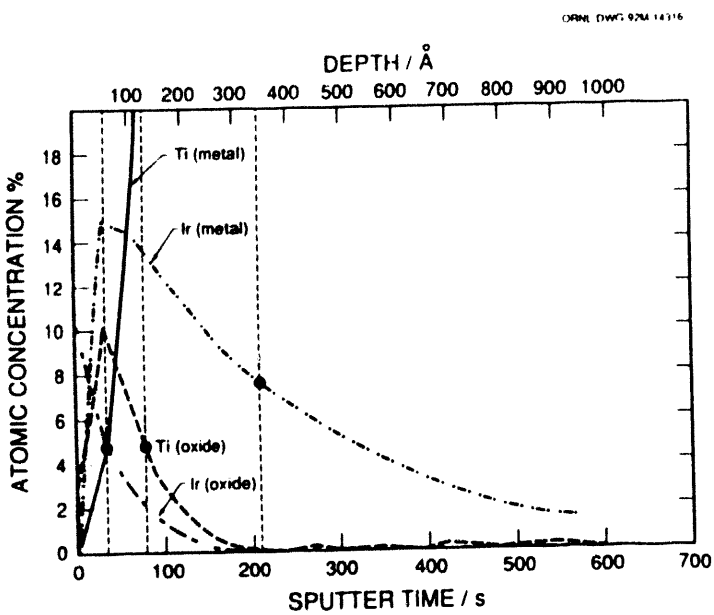


Fig. 5.2. Estimate of the thickness of the implant layer and of the TiO_2/IrO_2 layer from depth profiling results. The distances in the upper scale were calculated for a sputter rate of 100Å min^{-1}.

backscattering. The anodic layer thickness is estimated to be 60-130 Å which is consistent with the angle dependent results.

These measurements show a mixed dioxide layer with both Ti and Ir in only the 4+ valence state and a layer thickness of about 100Å. The XPS measurements provided the first chemical analysis of an oxide layer anodically grown at implanted titanium. The results indicate that the lower catalytic efficiency of iridium relative to ruthenium is not attributable to the incomplete oxidation of surface iridium, but rather may come from different rates in the adsorption and electrochemical desorption steps involved in the chlorine evolution reaction.

A rhodium-implanted titanium electrode with a gaussian implant profile measured by Rutherford backscattering (peak concentration of 12.5×10^{21} Rh atoms cm^{-3} and half height width of 400-500Å) was oxidized at a potential of 1.1 V vs SCE in a 1M $[Cl^-]$ solution of pH = 1.0 over a time period of 5-6 months. The *in situ* tests to monitor the progress of corrosion through the implant profile consisted of measurements of the exchange current and potentiodynamic polarization curves from 1.1V to 1.5V vs SCE to study the rate and mechanism of the chlorine evolution reaction as well as *in situ* photoacoustic measurements of the optical absorption of the layer. A very small current, 300-500 times smaller than with similar doses of iridium or ruthenium, was recorded for chlorine evolution over extended periods of time and identical results were obtained with several electrodes. In addition, the polarization curves gave Tafel slopes in the 51-60 mV range at 30°C which may be attributed to an incomplete metallization of the electrode. Concurrent *in situ* photoacoustic measurements of the (n-TiO_2) bandgap absorption gave values of 0.4 to 0.6, intermediate between near unity measured for TiO_2 anodic layers and less than 0.1 measured for metallic $Ir_xTi_{1-x}O_2$ layers. After removal from the electrochemical cell, the electrode was submitted to Rutherford backscattering analysis in order to confirm that corrosion had moved the surface through the implant profile. The remaining dose of Rh was 17% of the initial dose indicating that during the experiment the profile peak had been brought to the surface. The electrode was then submitted to XPS analysis in a VG Escalab II electron spectrometer with no preliminary sputtering in order to inspect a surface as close as possible to the electroactive surface which had been

probed by electrochemical and photoacoustic measurements. The binding energy for the $Rh_{3d\ 5/2}$ line was compared to spectra obtained for dioxide ($RhO_2.2H_2O$) and for sesquioxide ($Rh_2O_3.5H_2O$) powders and to spectra reported in the literature. The $Ti_{2p\ 3/2}$ line was observed at 458.37 eV and indicated that the X-ray beam probed the oxide layer. The spectrum of rhodium in the region of the $3d_{5/2}$ and $3d_{3/2}$ lines consisted of two broad peaks. The best peak fit, shown in Figure 5.3, was obtained by using two peaks at 306.7 and 308.2 eV with full widths at half height of 1.79 and 2.09 eV, respectively. These results are in best agreement with rhodium metal and Rh^{1+}. The large breath of the peak at 308.2 eV suggests that small quantities of Rh^{3+} may also be present in the layer.

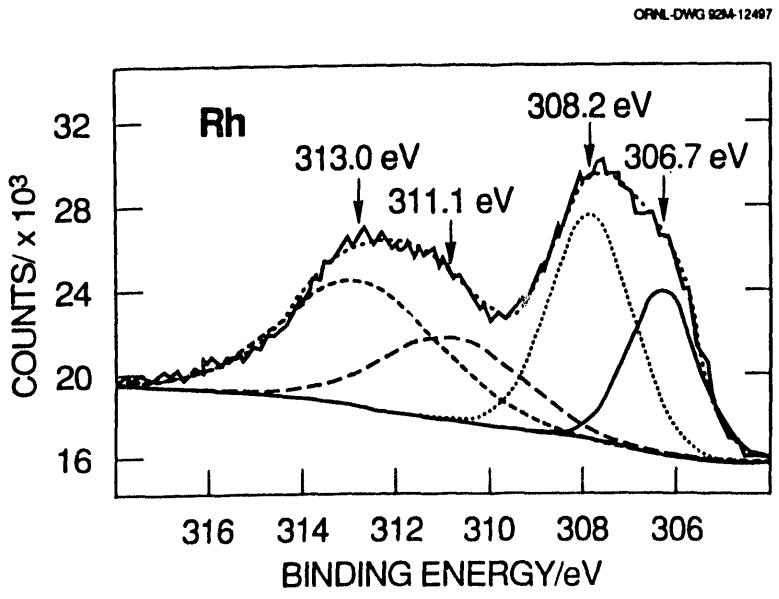


Fig. 5.3. Rhodium 3d photoelectron spectrum and peak analysis.

The XPS technique was invaluable in confirming the scheme for the formation of a $Ir_xTi_{1-x}O_2$ layer from Ir-implanted titanium samples. On the other hand, the XPS results showed that the similar procedure applied to a rhodium-implanted titanium electrode did not lead to the formation of a RhO_2/TiO_2 mixed oxide. The absence of metallic RhO_2 at the surface may explain the lack of activity of the electrode toward the chlorine evolution reaction.

1. C.E. Vallet, A. Choudhury, P.E. Sobol and C.W. White, Electrochim. Acta (1993) *in press*.
2. ORNL Metals and Ceramics Division.
3. Physical Electronics Laboratory, Perkin Elmer, Eden Prairie, MN.
4. ORNL Solid State Division.
5. C.E. Vallet and C.W. White, Nucl. Instrum. Methods, B1. 855 (1991).

RESEARCH ON NOVEL INORGANIC COMPOUNDS, NONOXIDIC CERAMICS, AND HIGH T_c SUPERCONDUCTORS

Elongated Crystals of ZrO_2 by Flux Evaporation

C. E. Bamberger, G. M. Begun[1]

The preparation of ZrO_2 needles was explored using the flux evaporation method which had been used with success earlier for the preparation of TiO_2 needles. The method consists of dissolving ZrO_2 in a potassium borate ($K_2B_4O_7$) melt to form a colorless, transparent glass. This glass was then kept at high temperatures (1150° - 1300°C) in air for several days; the potassium borate evaporated as such or as species involving K_2O and B_2O_3 leaving a residue of ZrO_2. This residual ZrO_2 was obtained mainly as relatively large rods, e.g., 40 μm per side of a square cross section by 500 μm or more long. Some rods were seen with holes of diameters close to 10 μm along the longest axis. This together with the shape of cross sections of broken rods leads to the speculation that the rods were formed by a screw dislocation mechanism of growth. Identification by XRD and Raman spectroscopy revealed that the rods had crystallized in the monoclinic system. Attempts to change the crystal structure by adding MgO or Y_2O_3, known to produce tetragonal or cubic powders, did not have an effect. Monoclinic rods were obtained from mixtures 0.01 Y_2O_3-0.99 ZrO_2 to 0.11 Y_2O_3-0.89 ZrO_2, 0.09 MgO-0.91 ZrO_2 and 0.11 Yb_2O_3-0.89 ZrO_2. The minimum values of ratios of $B_2O_3/(K_2O + ZrO_2 + \text{additives})$ that produced single phase ZrO_2-containing glasses was about 1.70. Examination of single rods by XRD indicated that they exhibited significant polysynthetic twinning.

1. ORNL Chemistry Division, retired.

Synthesis of Acicular Crystals of Sodium-Tungsten Bronzes; Candidates for Pseudomorphic Reactions

C. E. Bamberger, O. C. Kopp[1]

In the search for pseudomorphic reactions additional to the earlier reported conversions of $K_2Ti_6O_{13}$ to TiN and Cr_2O_3 to Cr_3C_2 and CrN, the possibility of synthesizing fibers or whiskers of sodium-tungsten bronzes, Na_xWO_3, for subsequent conversion to WC was explored. The literature on tungsten bronzes, stemming from the 1950's and 1960's, is quite extensive because there was an interest in explaining their electrical and magnetic properties and in finding applications for them. It was during that time that preparative methods, crystal structures, and some chemical properties were described. Current interest in superconductors, electrochromic displays, and catalysts has brought about additional research on tungsten bronzes, A_xWO_3, and the closely related intercalated alkali tungstates, $A_xWO_{3+x/2}$. A seminal paper by A. S. Ribnick, B. Post, and E. Banks presented in 1962 at an ACS symposium reported a type of phase diagram (T vs x, in Na_xWO_3) which has not been drastically modified since then. According to this phase diagram, at temperatures up to 1000°C, there should be two phases (tetragonal I and II) present for $x = 0.11 - 0.28$, only the tetragonal II phase for $x = 0.28 - 0.34$, and a cubic phase for $x \geq 0.40$. According to other references: a) the tetragonal phases occur as needles, b) the tungsten bronzes are extremely inert to aqueous solutions of acids and bases, and c) alkali metal tungsten bronzes decompose and may lose the alkali metal by evaporation above 1000°C. In view of the aforementioned facts, a search was undertaken for the preparative conditions (value of x, temperature, duration of reaction, and gaseous atmosphere) that would yield morphologically pure phases of fibrous material. The synthetic route consisted of preparing a mixture [$5WO_3$ (or H_2WO_4) + W^0 + 3 Na_2CO_3] equivalent to 6 $NaWO_3$, and subsequently mixing portions of "$NaWO_3$" with adequate amounts of WO_3 (or H_2WO_4) to yield Na_xWO_3 (e.g., $NaWO_3 + 2WO_3 \rightarrow 3Na_{0.33}WO_3$). In some cases Na_2WO_4 was used instead of the equivalent (Na_2CO_3+WO_3). The conditions found for obtaining only fibers were: $0.20 \leq x \leq 0.36$, ramping to 1020° ± 20°C in 4 h and holding for 1 h, and an inert gas atmosphere (N_2, Ar). The first deviation from the data in the literature was found when comparing the XRD patterns of the above

preparations with those reported. Although part of the patterns matched some in the literature, there were no really good matches. Our compounds exhibited more lines, as if pertaining to a mixture of compounds. While the occurrence of more than one phase may be the result of conducting the synthesis at a temperature above the thermal stability of the major phase, lower temperatures did not produce crystals with the desired needle morphology. Examination of the products by means of a scanning electron microscope (SEM) showed that they were morphologically homogeneous, i.e., they consisted mainly of bundles of needles, some loose needles, and very little particulate matter. To ensure that some of the XRD lines were not due to tungsten compounds other than bronzes, the preparations were leached with hot water, hot dilute HCl, and hot NH_4OH in accordance with procedures described in the literature. Since the first two leachings removed very little weight while the NH_4OH removed a significant amount, subsequent preparations were leached with NH_4OH only. Because leaching conditions were not available in the literature, different NH_4OH concentrations and ratios of solid/solution were tried. All gave high percentages of dissolution (30-50%). Neutron activation analyses (NAA) were made on bronze preparations with $x = 0.25$ and 0.33 before and after NH_4OH leaching. The results allowed us to also calculate the amounts of Na and W that had been leached; the ratio of W/Na in the leachate decreased with the number of successive leachings and approached constancy. After about three leachings, the XRD patterns of the residues did not change further. Purified phases with a final composition of $x = 0.16$ gave XRD patterns which were different from any known tungsten compound and thus remain unidentified. Needles with initial composition of $x = 0.33$ produced simpler XRD patterns after purification by NH_4OH solution leaching; the remnant needles were identified as having tetragonal symmetry. The positions of the lines were similar to the phase identified in the literature as "tetragonal II" but the intensities were very different. It was concluded that the data in the literature were probably affected by preferred orientation of the crystals. Because of their phase purity, precursor needles with composition $Na_{0.33}WO_3$ are the ones favored to be tested for pseudomorphic conversion to WC and, to a lesser extent, to WN.

1. Consultant from the Department of Geological Sciences, University of Tennessee, Knoxville, TN.

Carbon-Nitrogen Pyrolyzates: Attempted Preparation of Carbon Nitride

L. Maya, D. R. Cole, E. W. Hagaman

Precursors for the preparation of carbon nitride were selected from a number of relatively high nitrogen content organic materials. The precursors were pyrolyzed in a closed system at 700°C under 225 MPa. The resulting residues showed little nitrogen loss, but were amorphous with relatively low densities. Raman spectroscopy and ^{13}C NMR indicated the presence of trigonal carbon.

Nitrogen and/or Boron-Containing Polymers as Precursors of Ceramic Materials

L. Maya

The use of polymeric precursors to produce ceramic materials affords considerable flexibility to control the morphology of the desired product. We have examined derivatization reactions of preformed polymers as a synthetic approach to produce precursors. Boron moieties have been bound to either polyethyleneimine or polybutadiene. In a different approach, polymeric cyanoborane, $(CNBH_2)n$, has been used as a single source for the chemical vapor deposition of boron nitride films on a variety of substrates. Attempts have been made to synthesize carbon nitride, an hypothetical compound predicted to have extreme hardness. These attempts have involved the pyrolysis of nitrogen containing precursors such as polymerized hydrogen cyanide.

Plasma-Enhanced Chemical Vapor Deposition of Boron Nitride Using Polymeric Cyanoborane as Source

L. Maya

The plasma-enhanced chemical vapor deposition (PECVD) of boron nitride films was studied using polymeric cyanoborane, $(CNBH_2)n$, a material previously examined by thermally activated CVD. The PECVD procedure yields boron nitride coatings containing ≈20 wt % paracyanogen

as a contaminant. This impurity can be removed by heat treatment under vacuum or in an ammonia atmosphere. The boron nitride coatings are hexagonal and appear to be boron deficient. The PECVD process takes place at 300°C, measured at the backside of the substrate, as compared with 600°C in the thermally activated CVD process.

Preparation of Tin Nitride via an Amide-Imide Intermediate

L. Maya

Tin nitride was prepared by the thermal decomposition of an intermediate amide-imide derivative which, in turn, was prepared from tin (IV) bromide and potassium amide in liquid ammonia. Tin nitride is an amorphous solid that undergoes decomposition into the elements at a maximum rate at 420°C. Ammonia release from the amide-imide reaches a maximum at 125°C and conversion into the nitride is essentially complete at 300°C. The nitrogen and tin binding energies derived by XPS show electron density transfer similar to that typical of the metallic interstitial nitrides in spite of the covalent character of this semiconductor. The electrical resistivity of the nitride determined on a film prepared by CVD from $(Et_2N)_4Sn$ is 0.15 Ω cm.

Deposition of Crystalline Binary Nitride Films of Tin, Copper, and Nickel by Reactive Sputtering

L. Maya

Films of tin, copper, and nickel nitride were deposited by reactive sputtering in a nitrogen plasma generated by a potential drop of about 400 V and a 10 mA current between two stainless steel electrodes. The cathode made contact with a thin foil of the metal to be sputtered while the second electrode, at ground, acted as a pedestal to hold the substrate to be coated. In a typical run, lasting 20 h, a flow of 20 sccm ultrapure nitrogen was passed through the system while holding a pressure of 2 torr. The amount deposited was established by weighing in a microbalance. The films were characterized by FTIR, XRD, Temperature Programmed Thermal Decomposition (TPTD), four probe electrical resistivity, and direct chemical analysis. The TPTD was conducted in an enclosed tube, placed in a furnace programmed to ramp at 10 °C/min,

under a stream of helium which was monitored by a mass analyzer. The decomposition of each nitride could be readily observed and quantified on the basis of the nitrogen evolved. The nitrogen content of each specimen examined was determined from a calibration curve developed earlier by decomposing known amounts of sodium azide. The metal content of each sample was determined subsequent to the nitrogen analysis by dissolution of the residue in acid and atomic absorption analysis by Inductively Coupled Plasma (ICP). The nitrogen and metal analyses accounted for 100 ± 1 wt% of the nitrides examined in this study.

Tin nitride has a chemical composition corresponding to Sn_3N_4. The TPTD showed a maximum rate of decomposition at 615 °C with nitrogen, as expected, being the only volatile component observed. The IR spectrum of tin nitride consists of a weak broad band, 100 cm^{-1} wide, centered at 660 cm^{-1}. The electrical resistivity of a Sn_3N_4 film deposited on quartz was determined at room temperature and found to be 0.02 Ω cm. An additional measurement performed on a film deposited on silicon showed a value of 0.017 Ω cm which is essentially the same. A value of 1.85 eV was obtained as an estimate of the band gap of this semiconductor from the optical spectrum of a film deposited on quartz. The band gap was obtained from a plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$, where α is the absorption coefficient and $h\nu$ the photon energy. The x-ray diffraction pattern observed at a grazing angle showed the following lines with d spacings in nm and relative intensities in parentheses: 0.519 (91), 0.319 (19), 0.272 (48), 0.260 (99), 0.173 (11), and 0.160 (10). This pattern agrees for the most part with the electron diffraction data reported in the literature.

The chemical composition of copper nitride corresponds to Cu_3N. Maximum nitrogen evolution takes place at 465 °C. The IR spectrum of Cu_3N shows a single band at 643 cm^{-1}. The x-ray diffraction pattern of Cu_3N films differs from that of the registry of the International Centre for Diffraction Data in that some of the lines are weak or missing while some are particularly strong. This suggests a preferred orientation. The most prominent line in the pattern derived from the film is the 100 reflection at 0.382 nm which corresponds to the lattice parameter of this cubic structure. Also observed, but much weaker, were the 200 and

210 reflections at 0.191 and 0.171 nm, respectively. The electrical resistivity of this compound proved to be too high to be measured by the four probe method. On the other hand, an estimate based on a direct resistance measurement gave a value of 2 kΩ cm.

Films of nickel nitride were found to have a composition corresponding to Ni_3N. The profile of the thermal decomposition was unusual in showing two nitrogen evolution events with maxima at 305 and 405 °C and relative intensities of 1.0 and 2.3, respectively. These observations can be explained on the basis of a previous study conducted by Bernier [Ann. Chim. **6**, 104, (1951)], who found through the use of x-ray diffraction and magnetic measurements the existence of a Ni_4N phase as an intermediate in the thermal decomposition of Ni_3N, i.e., the hexagonal paramagnetic phase Ni_3N converted into a cubic ferromagnetic Ni_4N phase which however was nitrogen deficient. Apparently Ni_4N is a limiting composition that is achieved only with full nitrogen occupancy. These observations are consistent with the behavior observed in the TPTD profile of the present study with the first nitrogen evolution corresponding to the conversion of Ni_3N into Ni_4N. The difference between the observed relative areas of the integrated peaks for evolved nitrogen and the idealized ratio of 1.0:3.0 might be explained by the formation of a nitrogen deficient phase. In the present study, the x-ray diffraction pattern of the film did not coincide with the known hexagonal pattern of Ni_3N; a cubic phase was observed instead. This cubic phase showed a very strong line at 0.223 nm corresponding to the 200 reflection. Additional reflections of about one tenth in intensity were as follows: 0.135 (311), 0.141 (310), 0.119 (321), 0.112 (400), 0.099 (420), 0.089 (500), and 0.088 (510). The IR spectrum of Ni_3N proved to be featureless in the range of 4000-400 cm^{-1}.

Paracyanogen Reexamined

L. Maya

Paracyanogen, a polymer of cyanogen, $(CN)_2$, is one of the earliest synthesized polymeric materials. It has attracted attention for possible electronic uses as a dielectric. This material has also been of interest as a potential precursor of carbon nitride. A study was

undertaken to better characterize paracyanogen which apparently can be synthesized by different routes; thus, samples were prepared by the pyrolysis of silver cyanide, the photolysis of cyanogen, and by sputtering a carbon electrode in nitrogen. The products were characterized by FTIR, ^{13}C NMR, and through temperature-programmed thermal decomposition. Paracyanogen derived by the different routes was indeed spectrally and thermally similar. Paracyanogen is a polymer that incorporates carbon, mostly sp2, and nitrogen in a disordered structure. Cyanogen is the main volatile component released in the thermal decomposition of paracyanogen. The cyanogen released was identified by FTIR and Mass Spectrometry. The rate of release reached a maximum at 700 °C. The paracyanogen derived from silver cyanide still contained residual elemental silver and decomposed during attempts to convert it to carbon nitride at 700 °C and 0.3 GPa in a sealed system.

Maskless Laser Writing of Microscopic Metal Lines

L. Maya

Maskless laser writing was performed by passing a flat-bottomed cell containing a specimen of silicon, quartz or sapphire coated with the metal nitride in front of a focused beam of an argon ion laser (green 514 nm line) operating at power levels of 0.5 to 2.0 watts. Focusing was achieved by means of microscope objectives of either 20X or 10X magnification power. The cell containing the specimen was evacuated prior to writing to prevent oxidation of the metal lines at the time of formation. The cell was manipulated with a simple manual x-y stage. Metallic lines a few microns wide were generated. The metal lines were examined by optical microscopy as well as SEM in the case of those derived from Cu_3N. The resistance of the lines was measured directly after attaching electrical leads by means of copper wire and a liquid alloy composed of tin, indium, and gallium. Resistivity values were calculated on the basis of the width observed by microscopy and a calculated thickness that considered the thickness of the initial nitride coating and its metal content. The resistivity of the copper, and nickel lines was 10 $\mu\Omega$ cm while that for tin was 0.43 mΩ cm. The resistivity of the tin metal lines was considerably higher than that of

the bulk metal. This is due to the fact that some of the metal formed in the process coalesces into microscopic beads leaving areas where constrictions are evident. This phenomenon is quite likely due to the relatively low melting point of tin (232 °C) which is evidently exceeded during the writing process. No attempt was made to optimize the laser writing process which, in principle, is limited by the wave length of the laser light and the optics used to concentrate the laser beam.

Study of High T_c Superconductors

J. Brynestad, D. E. Heatherly, Staff Members of the ORNL Metals and Ceramics Division, ORNL Solid State Division, and the University of New Mexico

The research on high T_c superconductors has continued. Emphasis has been placed upon the development of the aerosol synthesis techniques for the synthesis of precursor powders, especially of "BiPb 2223" ($Bi_{2-\alpha}$ Pb_{β} $Sr_{2+\gamma}$ $Ca_{2+\delta}$ Cu_3 $O_{10+\epsilon}$) powders for use in the "Powder in (silver/silver alloy) Tube" (PIT) approach to the production of superconducting wires with sufficiently high critical current densities for practical applications. This work also has contributed to the filing of a patent application ("Method of Producing Pb-Stabilized Superconductor Precursors and Method of Producing Superconducting Articles Therefrom" by D. M. Kroeger, H. S. Hsu, J. Brynestad). The efforts to optimize the properties of the end product have brought many surprises, and yet there probably is a long way to reach the goal. The challenge of this part of the wire program is to synthesize a precursor powder with the "optimal" properties for the subsequent operations that lead finally to a multifilament conducting wire with appropriate properties. The feedback time of information is long, 3-6 weeks, and the number of experimental parameters very high. The parameters for the synthesis of precursor powders are: composition (6-7 components), concentration of the starting solution, droplet size distribution of the aerosol, temperature profile(s) of furnace, composition(s) of carrier gas(es), residence time(s) at various temperatures in the furnace, powder collection variables, and post-treatment variables. An aerosol synthesis system has been built for a systematic study and identification of the most important parameters in the pyrolysis process. Work has been initiated

on the synthesis of "Tl 1223" ($(Tl_{1-\alpha}\ Pb_{\beta}\ Bi_{\gamma})\ Sr_{2-\delta}\ Ba_{\epsilon}\ Ca_{2+\omega}\ Cu_3O_{8.5+\Delta}$) powders by aerosol pyrolysis for general and PIT studies. A 4-zone furnace has been built for the incorporation of thallium into precursor films and coatings by means of $Tl_2O + O_2$ gas mixtures. This furnace also is used for the study of the stability ranges of the various phases in the Tl-Pb-Sr-Ba-Ca-Cu system as a function of Tl_2O- and O_2- pressures and temperature. Research on "BiPb 2223" and "Tl 1223" systems was conducted in cooperation with the Superconductor Technology Program for Electric Energy Systems, while that on thallium-based superconductors was performed as part of the BES program, "Superconductors with High Critical Temperatures" (Solid State Division, ORNL).

6. STRUCTURE AND DYNAMICS OF ADVANCED POLYMERIC MATERIALS

In the main part of this program, we pursue fundamental structural and dynamic studies with the intent of providing a better understanding of advanced polymeric materials. Our approach is based on a combination of experimental and theoretical efforts. To characterize the structure of bulk polymers and fibers at the molecular level, we use small-angle and wide-angle x-ray and neutron scattering; the motion and disorder in polymers is probed by NMR and neutron spectroscopy; scanning tunneling, atomic force, and optical microscopies can map out surface morphologies; and the bulk mechanical, transport and thermodynamic properties are characterized with thermal and mechanical analysis. The theoretical aspects are addressed with state-of-the-art molecular dynamics and neural networks to simulate chain conformations, dynamics, and energy flow in polymers, with the simulations closely linked to experiment.

Although alloying of metals has been practiced for centuries, analogous intimately blended polymer systems are just emerging as engineering materials. The second part of our program aims to contribute to the development of a scientific basis for the molecular design of polymer blends in order to optimize physical and end-use properties. The primary objective is to provide a foundation for multiphase materials development similar to the knowledge base in small molecule chemistry that underlies single-phase polymers. Our approach involves polymer characterization by small-angle neutron scattering (SANS) using isotopic polymer mixtures as model systems to explore the limitations of Flory-Huggins theory, and to test the predictions of new integral equation polymer theories on chemically distinct species. Our ultimate focus will be on multicomponent polymer systems where mixing occurs on molecular length scales (e.g., nanophase composites) in contrast to conventional composites and filled polymers.

A third component of our program is a Cooperative Research and Development Agreement between ORNL and Hoechst Celanese (HC) that will lead to new methods for the prediction and analysis of high-performance materials. The goal is to use a novel scheme based on combining neural networks, genetic algorithms, and graph theoretical structure methods to relate the chemical structure of materials to their mechanical, physical and chemical properties. A desired result is the creation of an accurate and rapid computational method for the prediction of a host of properties, such as the melting or boiling points, sublimation or pyrolysis temperatures, glass transition temperature, dielectric constant, poisson ratio, tensile strength, thermal and electrical conductivity, etc., for materials like polymers, metals, ceramics, or composites,

density functional theory, and molecular dynamics calculations in order to investigate chemical, physical, and mechanical behavior under a variety of ambient conditions. Success in this endeavor is expected to substantially increase our ability for producing high performance materials and provide advances in pattern recognition and image analysis.

ADVANCED THERMAL ANALYSIS

The Advanced THermal Analysis System (ATHAS) Data Bank

B. Wunderlich[1]

The ATHAS data bank saw a large increase in volume, and the 1993 copy is available on request. A number of new polymers were analyzed, and the 1990 data bank of experimental heat capacities was published. Of particular interest are a large series of aliphatic polyesters, some polysilylenes, a number of polysulphones, all naturally occurring poly(amino acid)s and some of their copolymers. The heat capacities of all these poly(amino acid)s, basic for the understanding of the thermodynamic properties of proteins were either not known or existed in the literature with unacceptably large errors (as much as 50%). A number of polymers with special mesophases were analyzed and compared to the mobility known from solid state NMR. The prior work on nylon was extended with a discussion of the observed disorder using, besides calorimetry, also quasielastic neutron scattering. To better handle the fitting and prediction of data, a neural network technique was investigated.

New Instrumental Thermal Analysis Techniques

B. Wunderlich[1]

The single-run heat capacity measurement technique, earlier predicted to be possible and developed in our laboratory, was completed and presented at the NATAS Meeting. New research into the understanding of the reversing heating and cooling method, developed by TA Instruments, is underway (using an instrument on loan from TA Instruments).

The Mesophases of the Tetra-*n*-alkylammonium Halides

B. Wunderlich[1]

The analysis of a large number of tetra-*n*-alkylammonium salts is drawing to a close. The remaining research deals with the X-ray structure (discussed below). It was found that all analyzed samples had regions of mesophase stability of a plastic- or condis-crystalline nature. In addition, some samples showed development of disorder outside of well-defined transition regions. The structural reasons of the latter are being sought through the present X-ray investigation. This research served as a training ground to distinguish condis crystals from plastic crystals. Small molecules are particularly suited for this research since they only rarely show partial crystallinity. Solid state NMR and calorimetry could resolve the deviations from the general rules of entropy changes on disordering.

Thermal Analysis of Miscellaneous Materials

B. Wunderlich[1]

Other small molecules analyzed included the newly discovered fullerenes, which fit our research program because of their plastic crystalline nature. Complete thermodynamic characterization of C_{60} was possible, and measurements on C_{70} are in progress. Epoxides at various stages of polymerization have been analyzed to make progress toward the understanding of these technologically important composite components. Future work depends on the availability of well-characterized samples. The thermal characterization of all available *n*-paraffins, completed in 1991, was followed in 1992 with a similarly complete study of all available *n*-perfluoroparaffins. The thermal properties, as well as the mesophase transition behavior, could be traced from the small molecules to polytetrafluoroethylene. Finally, our old small-molecule proving ground for 100% crystallinity mesophase behavior, OOBPD, could be used to define signature tests for the distinction of smectic and condis phases, an ongoing research effort in our laboratory. A collaboration with Professor Lebedev of Russia is progressing well. The originally proposed low temperature heat capacity measurements on six samples were completed and a second set of six is in the preparation stage.

STRUCTURE AND THERMAL PROPERTIES OF POLYMER FIBERS

B. Wunderlich, B. K. Annis, Y. Fu[2]

The fiber diffraction effort has met with considerable success in the past year. The original full-pattern refinement program for characterizing the crystalline portion of polymer fibers treated the amorphous regions as background, which was then discarded. This procedure proved to be unsatisfactory insofar as the portions of the background (the amorphous part) near and under Bragg peaks were not correctly modeled. In addition, the amorphous part of the scattering is of considerable interest in its own right since it appears to be important in determining the properties of fibers. A newly developed Fourier filter technique succeeds in separating the total scattering into crystalline and amorphous portions. This separation of the crystalline and amorphous scattering has now been extended to a three-domain model, originally suggested by thermal analysis. The fibers could be shown to consist of at least three parts, and their fractions have been quantitatively established (crystalline, oriented amorphous, and random amorphous *via* X-ray diffraction; and crystalline, rigid amorphous, and mobile amorphous *via* thermal analysis). Considerable interest has been expressed by the fiber industry for the newly developed characterization methods.

Fourier Filter for Separating Crystalline and Amorphous Scattering

B. Wunderlich,[1] Y. Fu[2]

A key problem in fiber structure analysis is the separation of the crystalline diffraction from the noncrystalline scattering. To address this problem, an iterative Fourier filter method has been developed. This method separates the crystalline scattering and the noncrystalline scattering based on the intrinsic difference in sharpness of the two patterns: the Bragg scattering from the crystalline region is sharper than that from the amorphous region. By choosing a suitable Fourier filter, the patterns can be separated. Errors in the separation were minimized by an iteration procedure.

The Separation of Oriented and Isotropic Amorphous Phases in PET Fibers

B. Wunderlich, Y. Fu[1]

Ten poly(ethylene terephthalate) (PET) fiber samples have been studied. Both morphology and crystal structure of the crystallites are accurately determined, and these parameters depend on the processing history of fibers. More important, we have shown that the PET fiber is composed of at least three domains: a crystalline domain, an oriented amorphous domain, and an isotropic amorphous region. It is tempting to identify the oriented amorphous domain from diffraction with the "rigid amorphous" fraction obtained by thermal analysis. Although the three-domain model was proposed two decades ago in order to satisfy the mechanical behavior of PET fibers, this is the first time that the three fractions have been determined quantitatively with the diffraction method.

Full-pattern Refinement of High-modulus PE Fibers

B. Wunderlich,[1] Y. Fu[2]

Several ultra-drawn high-modulus polyethylene (PE) fibers have also been studied by the full-pattern refinement method, combined with the other techniques. Although the tensile modulus of these fibers nearly approaches the theoretical value, other important properties such as shrinkage and tensile strength are more influenced by the non-isotropic amorphous domains, which are poorly characterized. The current PE fiber two-phase structural model cannot explain the properties. Our study shows that these PE fibers consist mainly of crystallites and oriented, noncrystalline chains. The volume fraction of these oriented, noncrystalline chains is larger than that of crystallites. The misorientation of the crystallites, the orientation, and the density of the oriented chains all affect fiber properties. A possible new structural model is being developed to explain the diffraction results.

SAXS from PET and PE Fibers

B. K. Annis

Small angle x-ray scattering data from both the PET and PE fibers were obtained to complement the fiber diffraction effort. Analysis of

the data in terms of the paracrystalline model gives an estimate of the spacing between crystallites and their sizes. In general the crystallite dimensions are somewhat smaller than those obtained by wide angle scattering. In the case of gel-spun PE the conventional picture is that the fibers are composed of extended chains with ends occurring at random positions along the fiber axis. In this picture there would be no crystallites periodically spaced along the axis and the small angle scattering typically observed from fibers would not occur. However, to the contrary, preliminary SAXS data indicate that for some of the samples, the type of scattering pattern which implies an axial arrangement of crystallites is observed.

AMORPHOUS AND SEMICRYSTALLINE POLYMERS

X-ray Diffraction Studies of Symmetric Tetra-*n*-alkylammonium Halides (TAAH)

A. Habenschuss, B. Wunderlich,[1] A. Xenopoulos,[2] A. H. Narten[3]

The interest in these materials stems from the fact that these relatively small molecules display some of the same mesophases encountered in polymers. Previously, the changes in the x-ray diffraction patterns as a function of temperature were correlated with calorimetrically observed first-order transitions. For short alkyl-chain lengths, orientationally disordered (plastic) mesophases were obtained, while for longer alkyl chains only conformationally (condis) disordered mesophases are possible as the cation is too large to reorient as a whole. The patterns can generally be separated into a set of peaks corresponding to the ionic framework lattice made up of the ammonium ion and the halide ions, and a second set of peaks with *d*-spacings starting at 4 Å, that correspond to the paraffinic substructure within the ionic framework. The former set of peaks correlates with alkyl chain length, especially for the longer homologs. This indicates that the ionic framework for the TAAH with longer alkyl chain lengths is the same; only the structure of the paraffinic regions changes with temperature and chain length. Some of the diffraction patterns have now been indexed and unit cell parameters determined. Plausible structural models are being sought. The plastic-crystalline structures are characterized by a diffuse back-

ground similar to the melt pattern and can be indexed as face-centered or simple cubic. The melt patterns consist of two peaks, corresponding to an average interchain distance independent of the alkyl-chain length (the inter-chain distance), and to a distance increasing monotonically with the chain length (the average ion-ion distance).

Some quasi-elastic neutron scattering (QNS) data has been collected on tetra-*n*-ethylammonium iodide below its disordering transition at the IPNS at Argonne. The purpose of this was to gain information on the methyl motion and/or motion of the cation as a whole. This is another route to the dynamics of segmental motion, which complements the NMR work already completed on these materials.

Crystal Folding in Poly(ethylene oxide)

A. Habenschuss, S. Z. D. Cheng[4]

We have been studying the crystallization of low molecular weight poly(ethylene oxide) (PEO), with the aim of understanding the energetics and kinetics of crystal growth in these polymer systems. In previous work using time-resolved small angle x-ray scattering (SAXS), transmission electron microscopy (TEM), and differential scanning calorimetry (DSC), we have shown that low molecular weight, monodisperse PEO initially forms lamellar crystals with thicknesses which are not an integral fraction of the extended chain length (non-integrally folded crystals, NIF). With time, these NIF crystals then thicken and/or thin to form integrally folded crystals (IF) where the lamellar thickness corresponds to extended, once-folded, twice-folded, etc., chains.

We have now extended this work to examine how the kinetics of PEO crystallization depends on molecular weight, crystallization temperature, and the nature of the chain end-groups. With increasing molecular weight, the annealing of the NIF crystals to the IF crystals slows down, apparently due to the increasing difficulty of molecular chain motion along the crystallographic c-direction (normal to the lamella), which is necessary in forming IF crystals. Thus with increasing molecular weight the NIF crystals may remain permanently as a final metastable state. The fold length of NIF crystals is proportional to the reciprocal of the supercooling for each fraction as predicted by nucleation theory.

Introduction of increasingly bulky end-groups (methoxy, phenoxy) can severely block the thickening and thinning processes.

The Phase Diagram of Poly(oxybenzoate)-co-poly(oxynaphthoate)

A. Habenschuss, B. Wunderlich,[2] M. Varma-Nair[2]

The commercially promising polyester poly(oxybenzoate) (POB) suffers from the absence of a melt regime, where convenient processing could take place. Our previous work has shown that a small transition just below decomposition was not melting but a disordering crystal transition. Others have shown that co-polymers of POB with poly(oxy-naphthoate) (PON) show more tractable processing properties. We have therefore extended the x-ray diffraction phase analysis to PON and POB-co-PON. PON does indeed melt, as do most of the co-polymers near the PON side of the phase diagram. However, this melt phase is anisotropic, analogous to a liquid crystal. In the POB-rich region, the co-polymers resemble POB, but with a small anisotropic melt region. Thus, the ease of processing of POB-co-PON is due to this mobile phase.

SCANNING PROBE MICROSCOPY

Comparison of STM and AFM Imaging

B. K. Annis, B. G. Sumpter, D. Pedroza[5]

The influence of atomic level defects upon polymer properties is a concern of polymer science. Atomic force (AFM) and scanning-tunneling (STM) microscopies have the capability of imaging surface structure at the atomic level, and an opportunity arose which enabled a comparison of the two techniques for the investigation of this scale of surface defects. The samples were highly oriented pyrolytic graphite (HOPG) irradiated with various doses of C^+ ions to produce a range of surface and subsurface damage. In general STM was found to produce better images of the surfaces at the atomic level than AFM. The STM images included defects of a few atoms on the least irradiated materials. As the dose increased the surfaces consisted of alternating patches of order and disorder, had a glassy carbon appearance, and, finally, displayed no recognizable features. No examples of small regions of atomic scale defects were found by AFM.

During this work both techniques found complex surface morphologies on a scale of a few to several hundred nanometers. Some of this was detectable by optical and scanning electron microscopies but these techniques are often ambiguous as to whether or not surface features are elevations or depressions. This issue is easily resolved by AFM or STM. Interpenetrating networks of cracks and two types of ridges were identified and characterized as a function of irradiation dose. In the AFM study of one of the ridge networks, unusual images were produced which appear to be interpretable in terms of variations in surface friction. Since this phenomenon may occur in polymer systems containing different types of components and may also relate to adhesive properties, an effort to quantify the observations was begun.

Atomic Structure in Selenium

B. K. Annis, B. Wunderlich[1]

Another effort intended to obtain atomic scale information was directed at selenium. Crystallites of this material consist of helical chains of atoms, and AFM was able to resolve atomic size rows of about the correct spacing. However, so far we have been unable to resolve the direction of the helices.

Surface Morphology of PET and PE Fibers by AFM

B. K. Annis, B. Wunderlich[1]

Polymer fiber surfaces were also investigated by AFM. The surfaces of as spun PET fibers are fairly flat and devoid of any characteristic features. However, on annealing and subsequent etching by hydrolysis, lamellar and isolated fibril fragments could be made visible by AFM. The latter are preferentially aligned parallel to the fiber axis with lengths of 50-100 nm and widths of 20-50 nm; these sizes could be related to detailed fiber x-ray diffraction (domain size analysis). The surface of a high modulus, gel-spun polyethylene fiber known as Spectra was found to have features aligned parallel to the fiber axis. These resembled the bundles of molecular chains observed on the faces of lamellae of extended-chain PE crystals.

COMPUTER SIMULATION OF POLYMER STRUCTURE AND DYNAMICS

Simulation of Scanning Microscopy Probe Tip-Sample Interaction

B. G. Sumpter, B. Wunderlich[1]

An important issue related to the techniques of scanning tunneling (STM) and atomic force microscopes (AFM) is in the interpretation of the images obtained from a typical surface scan. Most images of surfaces have been simply interpreted as exact topographies of the probed surface. However, this is the ideal case, and recently it has become increasingly clear that the interaction between the microscope probe and the sample is much more complex, greatly affecting the results obtained. Both the structural and dynamical processes of the AFM tip and sample surface must be examined in order to obtain relevant information on the types and magnitudes of distortions that may occur from a typical AFM or STM scan. By combining the resources of molecular dynamics (MD) simulations and AFM experiments, progress has been made toward developing a better understanding of the complex interactions between the AFM probe and polymer crystals and any subsequent changes that may occur in the AFM tip or the sample. The interaction of several probes appropriate to AFM, STM, or Nanoindentation with a crystalline polyethylene surface were examined using extensive computer simulations. The microscopic details of the dynamics and structure of a polyethylene surface caused by the interactions and any subsequent changes or perturbations on the images produced were elucidated. The ongoing experimental characterization of polymer morphology using electron and optical microscopy, AFM, STM, as well as thermal analysis techniques were linked to the theoretical study.

Probe Load-force Level. The general feature of a large degree of structural reversibility in polymers was observed and it was concluded that this makes it possible to perform nondestructive AFM experiments on a given polymer surface. However, it was shown that there is a distinct threshold to the probe load-force level that could be exerted without causing structural deformations and that this threshold could be related to the rate and pathways of internal energy flow. Based on an extensive study of various AFM load-force levels and tip radii of curvature, a suggested optimum working range of 10^{-8} to 10^{-11} N was determined in

order to avoid irreversible structural damage of the polymer sample and to obtain well-resolved surface images.

Stick-slip Phenomena. Surface contaminants such as those caused by adsorbed polar molecules (water for example) can cause significant perturbations on the images produced. From our calculations, it appears that when the AFM tip encounters such a defect, it is initially attracted (or repelled) to a greater extent and ultimately becomes "trapped" for a short period of time. This type of stick-slip phenomena leads to an enhanced frictional dissipation which in turn causes an increase in the surface temperature of both the AFM tip and the polymer surface. The increase in temperature can subsequently induce rotational defects in a polymer chain which can lead to crystal deformation(s) on a microsecond timescale.

Image Distortions. In addition to this surface perturbation caused by frictional dissipation, the presence of adsorbed polar molecules causes a substantial change in what the AFM attempts to image. In this case, the adsorbed polar molecules act like attractors and cause the AFM tip to adjust to a much larger degree than the average forces felt by the surface atoms. This in turn can lead to an image which appears to have large and sharp features imbedded on the surface topology. Such structural distortions were also observed in AFM images obtained from experimental studies of crystalline polyethylene. Although the size of the observed distortions in the experimental observations are most likely due to a much larger defect than that which could be caused by adsorbed polar molecules (probably sharp protrusions on the surface or tip), it has clearly demonstrated that care must be used in interpreting AFM images of polymeric surfaces.

Modeling the Fermi Resonance Interaction in Polyethylene

D. W. Noid, B. G. Sumpter

Another area of fundamental importance is the spectroscopic description of polymers. For example, there has been considerable interest in developing methods to model the Fermi resonance interaction in polyethylene. In the past, most of calculations used the normal mode method and the resonance interaction term(s) were added using a pertur-

bation theory based on the normal coordinates. Recently we have examined the internal dynamics of polyethylene from an "exact" classical mechanical point of view using an accurate potential energy surface.

Based on our previous work, it was known that nonlinear resonances such as a Fermi resonance have characteristic shapes in coordinate space. This type of interaction can be accurately treated by using appropriate semiclassical quantization conditions, eigentrajectories which correspond extremely well with quantum mechanical eigenvalues, and wavefunctions. We have extended these ideas from the current field of nonlinear dynamics to the study of nonlinear resonances in polymers.

Two types of resonance interactions were observed in the internal dynamics of the polyethylene model. A 1:1 resonance was found between one CH stretch to the next CH along the polymer chain and was independent of the total energy of the system. However, a Fermi resonance between the C-H stretch and HCH bend vibrations was not observed until approximately zero point energy was placed into these modes. At that point, the two characteristic C-shaped semiclassical trajectories appeared. It should be stressed that a classical normal mode analysis cannot probe this energy regime nor the required potential couplings, and is not particularly appropriate for studying this well-known spectral phenomenon. Only by carrying out molecular dynamics calculations on the potential energy surface are we able to determine the actual anharmonic-mode structure. To obtain the frequencies of vibration from the molecular dynamics data, the MUSIC method (a signal/subspace spectral estimator) was employed and has proven to be an invaluable tool for computing spectra from very short-time molecular dynamics calculations.

BLENDS OF MACROMOLECULES WITH NANOPHASE SEPARATION

B. K. Annis, A. Habenschuss, G. D. Wignall,[6] J. D. Londono,[7] J. G. Curro,[8] K. S. Schweitzer[9]

Experiments and Analysis

A. H. Narten,[2] G. D. Wignall,[6] G. D. Londono,[7] A. Habenschuss, B. K. Annis

A wide range of SANS measurements have been initiated on the ORNL 30m facility, including some which were started before this proposal was funded. One such experiment, conducted in collaboration with the University of Minnesota on model polyethylene-propylene isotopic mixtures, established the scaling relationship between the degree of polymerization, N, and the critical chi-parameter for phase separation, $\chi_c \sim N^{-\delta}$, where $\delta = 1.01 \mp 0.05$.

A series of SANS measurements on isotopic polyethylene (PE) blends has been commenced to study the statistical segment length, effective chi-parameter and phase stability as a function of N, T and ϕ. Further measurements on PE are being undertaken in the intermediate-angle region to determine the intrachain form factor and Kratky plateau behavior as a function of N. The results will be compared with theoretical models.

Theory

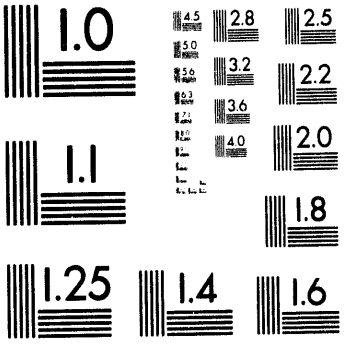
A. H. Narten,[3] J. G. Curro,[8] K. S. Schweitzer[9]

In its original form, PRISM theory used the mean spherical approximation (MSA) closure to supplement relations between intermolecular site-site correlations and the corresponding direct and intramolecular correlation functions. The MSA has been widely used to model the structure and interactions in systems where chain connectivity effects may be neglected (e.g., small molecules, colloids, micellar solutions, etc.). However, when applied to high molecular weight polymers, it failed to account for the scaling between χ_c and N observed at ORNL via SANS. PRISM theory has since been fundamentally reformulated to account for chain connectivity in describing the consequences of attractive forces on structure and phase behavior. The resulting theory has been systematically applied to simple symmetric and isotopic-like binary blends, and in the long chain limit agrees with the observed (mean

field) scaling behavior ($\delta = 1$). However, a rich *non*-mean field dependence of the effective chi-parameter and interchain pair correlations on polymer density, composition, and local chemical structure is found which is in good qualitative agreement with available Monte Carlo simulations. Preliminary applications to isotopic polyethylene mixtures using simplified molecular models are being undertaken to interpret current and future experiments at ORNL. Generalization of the PRISM theory to include compressibility effects and single chain structural asymmetries (e.g., aspect ratio differences) present in real chemical blends has been initiated. An approximate analytical treatment of the PRISM theory for such blends reveals a complex and nonlinear dependence of miscibility on chain structure and intermolecular forces. The predictions are consistent with recent work reported in the literature on polyolefins which find that the degree of branching, backbone stiffness, and deuteration labeling strongly influence the effective chi-parameter and critical temperature.

Generally, the new PRISM results suggest novel strategies for manipulating phase behavior. Applications of the blend theory to treat segregation of polymer mixtures near a surface have also been performed. Which component preferentially segregates to a solid surface is found to be a sensitive function of polymer structure, interchain interactions, and proximity to a bulk phase transition. The PRISM theory has been used to calculate the equation of state properties of alkanes and PE melts employing X-ray scattering derived interchain potential parameters measured at ORNL. The new theoretical predictions are in excellent agreement with the experimental PVT properties. A "self consistent" PRISM theory of polymer solutions and melts has been developed. This permits an *ab initio* calculation of the influence of condensed phase environment on single chain conformation. This approach will be generalized to treat polymer blends where single chain dimensions may significantly deviate from their melt values, and hence strongly influence miscibility, in a composition and chemical structure dependent fashion.

The efficacy of PRISM as a modeling tool has been recognized by a 1992 R&D 100 Award given jointly to SNL, BIOSYM, and UI by the R&D


1.0
4.5
2.8
2.5
5.0
3.2
2.2
5.6
3.6
6.3
4.0
2.0
1.1
1.8
1.25
1.4
1.6

2 of 3

Magazine for "the 100 most technologically significant products of the year." Similarly, the ORNL SANS experiments [PRL, 68, 2452 (1992)] to establish scaling relationships between χ_c and N were honored by Martin Marietta Energy Systems, Inc. as one of the eight best technical publications at ORNL in 1992.

ATOMISTIC SIMULATIONS OF MATERIALS: A NEURAL NETWORK APPROACH

B. G. Sumpter, D. W. Noid

Computer simulations of the atomic motions involved in materials (such as polymers, metals, ceramics, or composites) provide much of the needed insight to understand the origin of their thermodynamic, kinetic, spectroscopic, and mechanical properties. From this type of detailed information one can begin to derive or manipulate the chemical structure in order to optimize certain properties (a materials by design formalism). In recognition of the number of possible compounds and their isomeric forms (for example, the number of possible monomers and combinations to form co-polymers), it becomes essential to have a method to sort out the most appropriate structure in order to provide the desired properties. In this regard, new methodologies must be developed which both exploit presently available information and provide the ability to make accurate estimates of other types of essential information. A particularly promising approach is a novel technique which couples artificial neural networks with genetic algorithms, graph theory, quantum mechanics, and molecular dynamics. This methodology provides a route to an efficient and accurate molecular-based computational scheme for predicting chemical, physical, and mechanical properties of high-performance materials and for understanding their structural and dynamical characteristics under various ambient conditions. Our recent results have demonstrated the feasibility of obtaining accurate predictions for properties such as heat capacity, molar volume, refractive index, glass transition temperature, change in heat capacity at the glass transition temperature, dielectric constant, and molar polarization for as many as 320 different polymers. The average error that was obtained for all predicted properties was 2% and the maximum error was 10%, far surpassing other types of predictive schemes such as pure graph

theory approaches or quantitative structure/property relationships. The new methodology provides the essential tool for designing new materials and for predicting properties on materials for which no experimental data are available.

---

1. ORNL/UT Distinguished Scientist.
2. The University of Tennessee, Knoxville, TN.
3. ORNL Chemistry Division, deceased.
4. University of Akron, Akron, OH.
5. ORNL Metals and Ceramics Division.
6. ORNL Solid State Division.
7. ORAU Postdoctoral Associate.
8. Sandia National Laboratory, Albuquerque, NM.
9. University of Illinois, Urbana, IL.

7. CHEMISTRY OF TRANSURANIUM ELEMENTS AND COMPOUNDS

The primary objective of our transuranium studies is to promote the chemistry, physics and material science of the actinides and their compounds through systematic investigations. This goal is pursued by determining experimentally thermochemical, structural, and electronic properties of the f-elements and their compounds and is supplemented by theoretical calculations. Results are frequently interpreted as a function of electronic configurations, which permits an understanding of f-element chemistry in terms of the framework of the entire Periodic Table. Studies include the 4f-elements, or selected transition elements, for comparative purposes or when they are incorporated in compounds or alloys with the actinides. Overall the intent is to fundamentally define and understand actinide science, to establish important scientific data bases, and to provide scientific information that is relative to a diversity of technological areas. Examining the high-pressure behavior of the actinides yields unique information concerning bonding, phase behavior and interatomic interactions. Thermodynamic information is acquired primarily via high-temperature mass spectrometry, differential thermal analysis, and theoretical calculations. The high-temperature vaporization of oxides is pertinent to both fundamental and practical science. Relativistic calculations have provided ionization potentials, electronic structures, radii, etc. for elements through Z = 105, which aids in establishing a fundamental understanding of the actinides in relation with other elements of the Periodic Table. Solid-state spectroscopy (Raman, luminescence, fluorescence, absorption) studies are used to define structural environments and electronic energy levels and transitions in actinide materials. These spectral techniques provide sensitive investigative tools which complement X-ray analysis. New thrusts include defining the electronic structure and dynamics of free actinide atoms and molecules via electron spectroscopy and carrying out photoionization studies of actinides via mass spectrometry employed in conjunction with tunable-laser ionization.

Studies of Actinide Materials under High Pressure

R. G. Haire, M. M. Gensini [1], U. Benedict[2]

One of the principal effects of pressure on a material is to decrease the separations between atoms and between their electronic orbitals. These reductions may induce significant changes in their electronic nature, and/or alter critical atom-atom distances, which may be reflected in the chemistry and physical properties of the material. To explore the effect of high-pressure on actinide materials, we have employed diamond anvil cells and X-ray diffraction analysis to follow crystal changes with pressure. Frequently we attempt to deduce from the structural and symmetry changes what alterations in bonding and electronic nature may have occurred in the materials due to the pressure.

Our recent investigations have been with actinide monopnictides and mono-chalcogenides which exhibit the NaCl-type crystal structure at ambient temperature and pressure. These two groups of compounds lend themselves to systematic studies as a function of the anion and/or the actinide present and have potential for displaying valence fluctuations under pressure. One facet of these studies has been to ascertain the role of the actinide's 5f-electrons in either the bonding or in other electronic interactions, and whether pressure can affect or change their role. The involvement of the other electrons (e.g., s,p,d) in the behaviors under pressure are also pursued.

Studies of the high-pressure behavior of UBi and CmBi have now been completed and have yielded the first pressure data for NaCl-type actinide bismuthides. The monobismuthides contain the pnictogen with the highest Z; also bismuth has the largest radius and p-orbitals with the highest quantum numbers of the pnictogens and is more prone to anion-anion interactions. Thus, knowledge of the monobismuthides' pressure behavior becomes important in developing, comparing and understanding the systematics of actinide pnictides themselves as well as for comparison with other actinide compounds, such as the chalcogenides.

We have determined that both UBi and CmBi (see Fig. 7.1) undergo first-order transitions from their NaCl-type structures to a CsCl-type structure with accompanying volume collapses. UBi transforms at 5 GPa with an 11% volume decrease and CmBi changes at 12 GPa with a 16% volume

collapse. With CmBi, a subsequent second-order transition to a tetragonal phase occurred at 19 GPa; there was no accompanying volume collapse with this transition. The latter structural change involved a distortion of the CsCl-type lattice. These monobismuthides also displayed different hysteresis behavior upon release of the pressure.

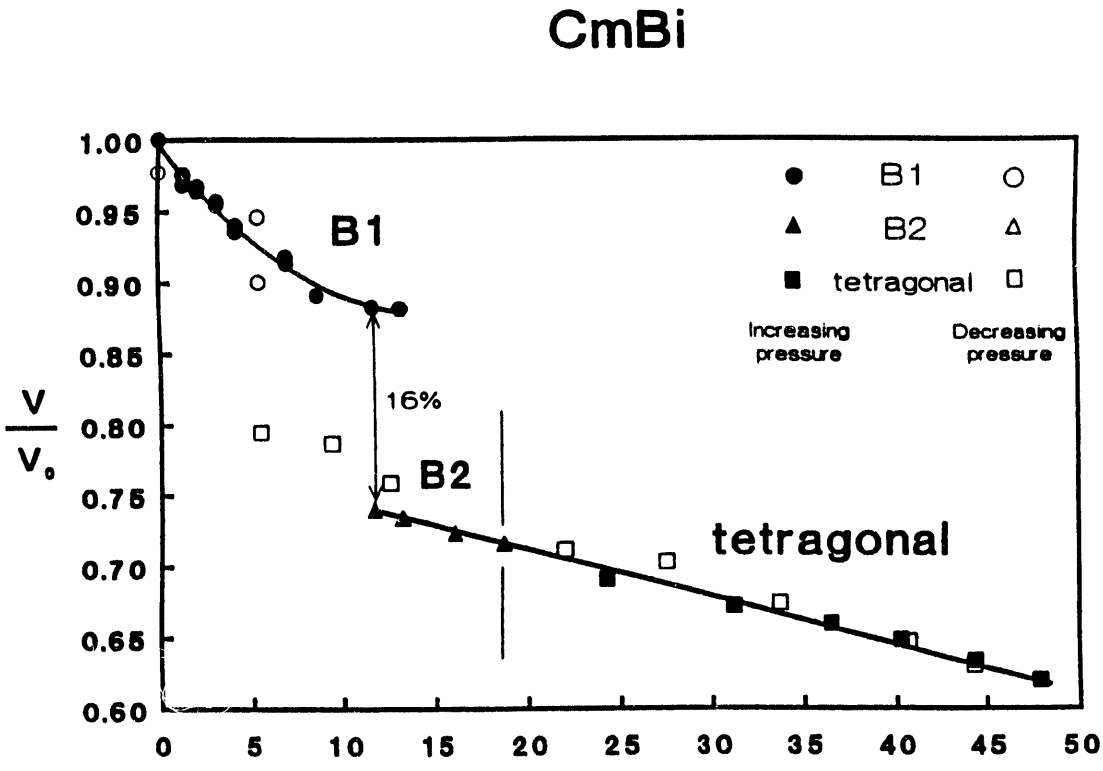


Fig. 7.1. Relative volume of CmBi with pressure.

The bulk moduli and its pressure derivatives were determined for both materials. Such parameters can be correlated with the nature of the bonding that is present and therefore are pertinent to our objectives. UBi was found to have a modulus of 91 GPa and a derivative of -5, while the values for CmBi were 53 GPa and 8. The modulus for CmBi is very similar to the moduli of the monobismuthides, CeBi and LaBi (50 and 55 GPa, respectively). The higher bulk modulus and the negative derivative calculated for UBi arise from the anomalous compression curve observed for its NaCl form. One interpretation of such behavior is that

it reflects a continuous electronic interaction with pressure. Examples of comparable behavior are known with certain lanthanide chalcogenides (e.g., SmS, SmSe, and SmTe).

The decrease in the volume and the interatomic distances in materials often cause significant changes in their bonding. A significant aspect for understanding actinide chemistry is the concept of 5f-electron involvement in bonding (e.g., localized versus itinerant 5f-electrons). With the Pa-Pu compounds it is possible to estimate the probability for localized/delocalized states for their 5f-electrons from the actinide-actinide interatomic distances that exist in the compounds, as proposed by the concept of the Hill Limit. Estimates for such distances in transplutonium compounds can also be made but these values are not as well established. In addition to the potential bonding role of the f-electrons, interactions between them and/or the other orbitals are also likely to be affected by changes in the interatomic distances. These interactions may involve the f-electrons with the metalloid's p-electrons, the actinides' 6d7s electrons with the metalloid's p-electrons, involve only between the p-orbitals of the metalloid, etc.

The interatomic distances, Cm-Cm and Cm-Bi, calculated for CmBi as a function of pressure are given in Table 7.1. These distances in the NaCl structure (B_1) and in the CsCl structure (B_2) were found to decrease regularly with pressure. However, the Cm-Bi distance increases significantly (over 3%) at the transformation of the NaCl structure to the CsCl structure, which also brings about a change in coordination number of the Cm from 6 to 8. In the CmBi tetragonal phase, two different Cm-Cm distances exists; one distance is considerably smaller and the other slightly larger than found in the CsCl phase at the second transformation. With additional pressure the two Cm-Bi distances in the tetragonal phase were then found to decrease regularly with pressure up to the maximum pressure.

Based on several considerations, it seems unlikely that the minimum Cm-Cm distance found, even at the maximum pressure studied (48 GPA), was small enough to consider that 5f-5f overlap had occurred. Since the Cm-Bi distances changed at the NaCl to CsCl transition, it is possible that this transformation may have been influenced by the Cm-Bi distances. The formation of the tetragonal phase may also have been

influenced by the Cm-Bi distances and/or the Bi-Bi distances (second neighbor interactions).

In Table 7.2 are given the U-U and the U-Bi interatomic distances calculated from the data obtained for UBi. In the study of UBi only the NaCl and CsCl structures were observed. A constant decrease in the U-U distances was found with pressure and the behavior of the U-Bi distances under pressure was similar to the situation observed for the NaCl and CsCl forms of CmBi. As a Hill Limit for 5f-5f overlap has been established for U compounds (340-360 pm), this "limit" can be compared to the minimum U-U distance (350 pm) found in UBi at the maximum pressure reached in this study (42 GPa). Although the U-Bi distance does fall within the Hill Zone, given the highly symmetrical structures (cubic NaCl and CsCl) observed, as well as other considerations, it is not likely that 5f overlap occurred in UBi.

Several other considerations can be addressed in interpreting these data but one of the important conclusions reached from the study was that 5f-electrons were not likely to have influenced the pressure behavior of either of these monobismuthides. Rather, it is probable that the contributing electronic interactions resulting from pressure were limited to those between the 6d7s orbitals of the actinides and the p-orbitals of the metalloid and/or between the p-orbitals of the metalloid atoms themselves (second neighbor interactions).

Table 7.1. Interatomic distances at ambient pressure (p_o), at the transition pressures (p_{trans}) and at the highest pressure (p_{max}) for CmBi.

Pressure (phase)	d_{Cm-Cm}, pm	d_{Cm-Bi}, pm
p_o (NaCl)	447	316
p_{trans}^1 (NaCl)	429	304
p_{trans}^1 (CsCl)	360	312
p_{trans}^2 (CsCl)	357	309
p_{trans}^2 (Tet)	370 and 322	309
p_{max} (Tet)	356 and 309	296

Table 7.2. Interatomic distances at ambient pressure (p_o), at the transition pressure (p_{trans}) and at the highest pressure (p_{max}) for UBi.

Pressure (Phase)	d_{u-u}, pm	d_{u-Bi}, pm
p_o (NaCl)	450	318
p_{trans} (NaCl)	439	311
p_{trans} (CsCl)	376	326
p_{max} (CsCl)	350	303

Hill Limit for uranium compounds: 340-360 pm.

1. ORNL Physics Division.
2. Institute for Transuranium Elements, Karlsruhe, Germany

High-Pressure Spectroscopy Studies

C. Chen [1], N. Stump[1], J. R. Peterson[1,2] R. G. Haire

Raman, luminescence, and emission spectroscopy have also been used to monitor changes in materials under pressure and complement our high-pressure X-ray diffraction studies. These spectroscopic investigations employ "fingerprint" techniques and site symmetry analyses to ascertain structural changes by optical characterizations. These spectral studies have concentrated on lanthanide materials.

One application of this spectral approach has been the study of the phase transitions of Eu_2O_3 under pressure via luminescence and the effects of pressure on the electronic energy levels of the Eu^{3+} in its sesquioxide. It was observed that at a pressure of ~8 GPa the C-form (cubic) of Eu_2O_3 transformed to the A-form (hexagonal), while during the release of pressure the latter form reverted to the B-form (monoclinic) of the oxide. With increasing temperature at normal pressure, the sequence is C- to B- to A-form. The B-form of this oxide was found to transform to the A-form at 4 GPa of pressure and the B-form reformed during the release of the pressure (2 GPa). This behavior

shows the reversible nature of the A- and B-transition for the oxide, in contrast to that between the C- and B-forms. In studies of the C-form of the oxide, spectral shifts observed under pressure were used to calculate the effect of pressure on the spin-orbit and Coulomb interactions of the 4f-electrons, which can be correlated with the expansion of the 4f-electron wave functions. This expansion results in both the variation of the effective electronegativity and radius of the Eu^{3+}. Additional high-pressure studies have been performed using both pure and doped compounds. Europium is especially suited to such studies as a result of its fluorescence and luminescence properties. Studies of several lanthanide vanadates under pressure employed these spectral monitoring methods. The compressibilities of $TbVO_4$ and $DyVO_4$ were calculated from spectroscopic data collected as a function of pressure while the pressure-induced phase transitions in $EuVO_4$ and $YVO_4:Eu^{3+}$ were studied by using the luminescence of Eu^{3+}.

The compressibilities of the Dy and Tb compounds were estimated indirectly from the pressure dependence of the Raman stretching frequencies of the V-O bonds through an empirical correlation. This approach provided a method to estimate the compression and equation of state of the samples via Raman spectroscopy. Volume compressibilities of 6.71×10^{-3} and 6.23×10^{-3} GPa^{-1} and bulk moduli of 149 and 160 GPa were calculated for $TbVO_4$ and $DyVO_4$, respectively.

The pressure dependence of the emission from the Eu^{3+} in doped and pure $EuVO_4$ has been investigated to 14 GPa using spectral measurements. Abrupt changes in the luminescence spectra at 7 GPa, which were not reversible when the pressure was released, were taken to signify the phase transition in the $EuVO_4$ from a zircon-type structure to a scheelite-type structure. The latter structure is the established crystalline form of the heavier lanthanide vanadates.

---

1. Chemistry Dept., University of Tennessee, Knoxville.
2. Part-Time employee of the Chemistry Division.

Spectroscopic Investigations of Structural and Electronic Properties

J. R. Peterson,[1,2] N. A. Stump,[1] G. Chen,[1] R. G. Haire

The primary emphasis in this work has been the application and enhancement of optical characterization for the f-elements. Certain aspects of this work were reported in the section dealing with pressure. The information appearing here is limited to studies at ambient pressure. A major portion of the work has involved the use of luminescence, or luminescence lifetimes, and Raman spectroscopy to characterize the structural and electronic nature of f-element materials.

The thrust of our recent efforts has been to use spectroscopy for characterizing structural and electronic environments of f-element materials. Lanthanide and actinide compounds characteristically exhibit narrow emission and absorption features as a result of transitions between outer electronic levels. These features are very sensitive to the near environment of the f-element; small changes in the environment can produce spectral shifts, intensity variations, changes in the nature of the luminescence, and alter the luminescence lifetimes. Such variations can lead to establishing characteristic "finger prints" for the f-element in particular environments.

We have employed the Eu^{3+} ion in both pure and doped materials for luminescence studies due to its simple yet destructive spectrum, which allows definitive assignments. Using these optical characteristics of Eu^{3+} we have investigated thermal chemical reactions involving halides, oxalates, organic complexes, etc. We have also used this approach for investigating the phase behavior of oxides, and phase transition in both pure and doped vanadates, as well as $EuVO_4$ and YVO_4 doped with Eu. We have completed an abbreviated characterization of the luminescent properties of three room-temperature forms of several lanthanide sesquioxides using Eu as a dopant in the different oxide forms. We have also investigated the effects of temperature on the electronic levels of Eu^{3+} in its sesquioxide. The lanthanide oxyhalides have also been investigated to ascertain their structural characteristics and correct errors reported in the literature with regard to symmetry assignments for the oxyhalides.

Several europium chelates have been studied to determine if slight changes in their composition and structure can be monitored by spectros-

copy. One example involved the europium-tris (2,6-pyridinedicarboxylato) ion coupled to different cations. The europium site symmetry and energy-level diagram of this material is well established and therefore these data could be used in studies involving this chelate. Spectra obtained for the chelate with different cations showed that the variations in the spectra could be used to correlate composition (waters of hydration; specific cation) as well as ascertain structural variations that occurred with the salts.

The application of fiber optics has also been pursued in our spectral studies. Fiber optics offer interesting potentials for use as probes in inhospitable environments, such as at high- or low-temperatures, liquid nitrogen, etc. These fiber optic probes have several potential applications for extensive studies with actinide compounds, and we have initiated the application of such probes in our studies.

---

1. Chemistry Dept., University of Tennessee, Knoxville.
2. Part-Time employee of the Chemistry Division.

Theoretical Chemistry

Elijah Johnson

Theoretical calculations are undertaken to provide both a predictive basis for designing experiments and also to assist in the interpretation of experimental results. For example, estimates of thermodynamic properties of selected actinide compounds can be made by using ionic radii and ionization potentials calculated by using relativistic Dirac-Fock quantum calculation models.

Efforts during this period can be placed into four areas. These are: quantum mechanical calculations on atoms and molecules; development of computational techniques; application of molecular dynamics methods of statistical mechanics; and neutron transport calculations. The main motivation for modifying current calculation methods is to develop new approaches for producing satisfactory results for atoms or molecules which contain a large number of electrons.

Our efforts to calculate ionization and electrode potentials for element 105 have now produced a manuscript that has been accepted for publication. In order to calculate these values it was necessary to use

different approaches for calculating the electrode potentials. One of these was to use ionization potentials and a Born-Haber cycle; the other employed ionization potentials in conjunction with the periodic law of the chemical elements. Both approaches predicted that the +5 oxidation state of element 105 would be the most stable valence state for it.

The enthalpy of sublimation for element 105 was determined using multiconfigurational Dirac-Fock values for the energy of excitation for two low-energy electronic configurations for this element together with the enthalpies of sublimation for V, Nb and Ta (group V elements; 105 is assigned as a extension of this group). The enthalpy of sublimation calculated for element 105 is 924 kJ mol^{-1}. An earlier estimate for this value was much lower (795 kJ mol^{-1}).

The J-P Desclaux computer program for the solution of atomic problems considering relativistic quantum mechanics was used to consider atomic americium. These data are needed for proposed experiments involving electron spectroscopy experiments with americium vapor. The current version of the computer program was not practical due to its tremendous computational time. A single configuration calculation is rapid but the multiconfigurational calculation is desired for its accuracy. There are two solutions to this problem: one is to use a modification of the Desclaux (applying certain restrictions); the other approach is to use a program employing a self-consistent field that has been written for molecules.

We have used the self-consistent field program for calculating the binding of ions to crown ethers but have not been satisfied with the results. The problem appears to be with the Monte Carlo integration procedure. An attempt is in progress to modify this procedure so that it may become suitable for our calculations.

In most approaches for the solution of the Schroedinger or Dirac-Fock equations, some or all of the basic functions are given in an analytical form. Some modifications to this approach can improve the accuracy obtained; efforts to devise a method for performing these calculations has now been developed sufficiently to apply it to some problems. However this approach still takes significant time and for systems containing greater than ten electrons parallel computer systems will be needed.

The uncertainties in the calculated electrode potentials (e.g., those for element 105) can be reduced by other calculational approaches to obtain thermodynamic quantities. The implementation of this approach has been started in calculations involving low concentrations of NaCl in aqueous media near the critical point of water. This approach is presently being evaluated and may be expanded to other materials.

We have also tested a computer program involving a Monte Carlo integration for solving the Boltzmann equation for neutron transport. These calculations are aimed at developing the optimum geometry and conditions for producing the greatest number of cold neutrons from a given quantity of Cf-252. This calculational approach will be pursued and modified as needed.

Photoelectron Spectrometry

M. O. Krause

Photoelectron spectrometry provides a powerful tool to determine exactly the 5f- and 6d-electron binding energies, which provides among other things a measure of the relativistic and many-electron effects in the actinides. One of the present goals of these studies with the actinides is to delineate the electronic structure of the free atoms, and ultimately to determine the response of the bound electrons to an electromagnetic perturbation. Very little information is available for the actinide electronic structure and dynamics, except for their outermost and the innermost electrons. Even a basic property as the binding energies of the 5f-electrons has not been measured or established for these elements in the atomic state.

The latter point is illustrated by Table 7.3 where it can be seen that experimental data do not exist for the 5f- and 6d-electrons in Am or Cm, and theoretical predictions based on a single-particle model are suspect and are often considerably different than expected. A comparison between theory and experiment can be made for the 7s level (the only level that has been experimentally determined) where a discrepancy of about 1 eV is observed. On a chemical scale, a 1 eV difference is equivalent to an uncertainty of 84 kJ.

Table 7.3. Comparison of theoretical and experimental binding energies (in eV) for Am and Cm.

Level	Theory	Experiment	
	Atom	Atom	Solid
	$_{95}$Am		
$4f_{7/2}$	450.8	-	448.5
$6p_{3/2}$	23.3	-	18
$5f_{5/2}$	5.58	-	4.9
$5f_{7/2}$	2.99	-	4.9
7s	4.88	5.99	-
	$_{96}$Cm		
$4f_{7/2}$	480.9	-	472.4
$6p_{3/2}$	26.1	-	18
$6d_{3/2}$	4.97	-	-
$5f_{5/2}$	10.64	-	5.6
$5f_{7/2}$	7.48	-	5.6
7s	5.470	6.02	-

To make these proposed measurements on free atoms requires the formation and study of atomic vapors. Americium has been chosen as the actinide for the proof-of-principle experiment and preparations are in progress to determine its 5f-electron binding energies. An electron spectrometer equipped with an electrostatic electron energy analyzer has been designed and constructed. A special high-temperature oven to produce a beam of atomic Am atoms has also been acquired. A similar oven has been successfully tested with 10 mg of Ag in a spectrometer at the Synchrotron Radiation Center at the University of Wisconsin and this

quantity was found to be sufficient for reliable measurements of the energies of the Ag atoms' 4d-electrons. Silver requires a similar temperature as Am for achieving the same vapor density, which suggests that 50 mg of Am should suffice for the proposed studies of Am.

A helium discharge lamp will be employed as a source of photons for the initial experiments at our laboratory; the photon energies available from this lamp will however limit the levels that can be studied. The studies will provide the first measurements of the 5f-electron binding energies for Am. They will also serve as a prototype for future work on other lightly-bound electrons and on the many-body effects prevalent in such multi-electron atoms. A significant aspect of this initial work will be to establish procedures for comparable studies in the future with tunable photon energy sources (e.g., synchrotron source), which will be essential for elucidating the dynamic properties of such atoms (e.g., the photoionization cross section of Am). In this regard, we are continuing our efforts to establish the Actinide Research Station at the Advanced Light Source at Berkeley, CA. This facility would permit high-resolution ESCA spectrometry and would offer a tremendous potential for exploring and solving many basic and applied questions in actinide science.

Vaporization of Actinide Oxides

R. G. Haire

The study of the vaporization behaviors of oxides is one aspect of determining the chemical and physical properties of actinide materials from their high-temperature behaviors. In many cases the final goal is to derive primary thermochemical properties from the studies. We have used high-temperature mass spectrometry as the major investigative tool in these studies.

Although the oxides are one of the primary classes of compounds of the actinides, they have not been thoroughly characterized. Crystal forms and lattice parameters have been established for the majority of the actinides but several questions remain about high-temperature phase behaviors, melting points, etc., especially for the transplutonium oxides. The high-temperature behavior and properties of the actinide oxides are important not only to establish the basic chemistry of these

elements but also because they are relevant and important in technologies where oxides are encountered.

The actinides display a variety of oxidation states in their oxides, due in part to the close proximity of the 7s-, 6d-, and 5f-electron energy levels. The highest oxide stoichiometries and the largest variation in oxidation states are found with the earlier members of the series. The first sesquioxide (if actinium is excluded from the series) occurs with plutonium and this stoichiometry become the stable one for the transplutonium elements at high temperatures. Thus, the electronic nature of the actinide plays an important role in oxide formation and behavior. The goal of our vaporization experiments was to systematically explore the high-temperature behavior of the sesquioxides in terms of the electronic configurations of the actinides.

Two major vaporization processes have been recognized for the actinide sesquioxides from our studies to date: one produces the monoxide while the other involves the effusion of atomic actinide vapor. Studies of these oxides have been initiated for the actinides from Am through Es. We have determined that the particular vaporization process can be correlated with the electronic configuration of the actinide. The critical factor is the promotion energies for the f-electrons (e.g., $f^n s^2$ to $f^{n-1}ds^2$) in the actinide, which determines the magnitude of the dissociation energies for the actinide monoxides. Establishing the correlation between these promotion energies and the monoxide dissociation energies provides both a predictive and a correlative approach to understanding the actinide oxide's stability and vaporization mode.

We have determined that Am, Cf and Es oxides vaporize via the effusion of atomic vapor, Cm oxide by evolving Cm monoxide, and Bk oxide by both processes. These findings are in perfect accord with predictions based on the calculated promotion energies and the correlation referred to above. Additional work is necessary to finalize our studies, to establish thermodynamic parameters (e.g., enthalpy of decomposition, enthalpy of formation, etc), and to fully understand the phase behavior of these oxides.

The results from these high-temperature studies offer the benefit that other thermodynamic data can also be indirectly derived from them. For example, the enthalpy of formation of the M^{3+} ion can be established

for Bk, Es, Fm, etc. via a correlation with the enthalpy of formation of the oxide, which is obtained in the high-temperature vaporization work. The enthalpies of solution for these three actinide sesquioxides, and those of higher actinide oxides, have not been determined experimentally and would be very difficult or impossible to measure.

The High-Temperature Chemistry of Technetium Vapors

J. K. Gibson

Mass spectrometry studies have been used to characterize gaseous species of technetium evolving from condensed phases of technetium under vacuum or under low-pressures of oxygen and other reactants at elevated temperatures. These studies explore the vapor species and vapor transport mechanisms for technetium, an important fission-product. One specific interest was the existence and stability of gaseous alkali pertechnetates (e.g., $MTcO_4$, where M = an alkali metal). Condensed phases of technetium and cesium or potassium were studied up to 900°C with this goal in mind. Rhenium, the 5d-homolog of technetium, was included in these studies in order to compare the chemistries of these two transition metals under identical conditions. We have determined that important and unexpected differences exist between the high-temperature vaporization chemistries of these two elements' binary oxides.

Among the technetium-containing gaseous species observed in these studies were $KTcO_4$, its dimer $(KTcO_4)_2$, and $CsTcO_4$. Inclusion of rhenium into the solid phases showed that technetium (VII) had a greater oxidizing capability than rhenium (VII) and established the existence of novel mixed metal oxide species (e.g., $TcReO_5$, $TcReO_7$). Other technetium vapor species identified in these studies consisted of various oxides, hydroxides, halides, and oxyhalides.

Earlier investigations of the rhenium-oxygen system had revealed ReO_3 and Re_2O_7 as the important gaseous species but provided no evidence for Re_2O_5. Therefore, it was anticipated that the Tc isologs of the two former oxides would dominate the technetium system; the observance of Tc_2O_5 as an important vapor species was unexpected. The existence of this latter species mandates that vapor transport models for technetium consider the existence of the pentoxide as a major species and that

caution must be exercised in concluding that the high-temperature chemistry of rhenium and technetium are nearly identical.

The existence of volatile alkali pertechnetates is a significant factor when explaining the synergistic vapor transport of cesium and technetium during high-temperature processes (e.g., vitrification of fission-product wastes). Our studies have demonstrated that not only do these gaseous species of Tc exist but also that they are substantially stable and may be very important in high-temperature transport mechanisms.

Studies of Np Alloy Systems

J. K. Gibson, R. G. Haire, M. Gensini[1]

We have initiated studies of binary alloy systems that involve two actinides as well as actinides with lanthanides or with transition metals. Due to the scarcity and radioactivity of several of the actinides, information regarding their alloying behavior is often limited, although the phase relations in several systems of Th, U and Pu have been well characterized. We have employed differential thermal analysis and X-ray diffraction (at ambient temperature) to characterize the phase relationships in neptunium, americium, and the binary alloy systems, Np-Am, Np-Ln (Ln = La,Nd,and Lu) and Np-Zr.

Each of the three Np-Ln systems studied here has been found from the DTA results to be characterized by limited solubility or miscibility of the components. The effect of alloying upon the Np and the Ln elements transition temperatures suggest these systems behave similarly to the Pu-Ln systems. That is, these Np-Ln systems appear to form two-phase systems in which there is limited mutual solubility. A similar conclusion was reached in the case of the Np-Am system. Neither element appeared to be completely miscible in the other; at best there may only be a very limited solubility of each component in the other (e.g., an Am-rich, Np phase and a Np-rich, Am phase, with each retaining the essential features of the pure host element).

We have also studied the Np-Zr system. DTA studies were carried out with Np-Zr samples ranging from 10 to 90 atom percent of Zr as well as with pure Np and Zr. The main impetus for studying these various alloys was to promote our general understanding of actinide bonding and

the bonding behavior of f-elements with d-transition metals. Thus a specific goal was to gain an overall understanding of the role of the f-electrons in the bonding of such alloys.

The different Np-Zr alloys were prepared both by in situ heating of the components in DTA cells and by arc melting. Cyclic DTA runs were made on materials formed by both modes of preparation. X-ray diffraction data at room temperature were also acquired for these Np-Zr samples; for materials prepared both by arc melting or directly in the DTA cells; and for arc-melted materials after they were subjected to DTA cycling (i.e., annealing cycles).

The essential findings of these studies was that Np and Zr are immiscible in the solid phase, even though both were expected to form a single bcc phase at elevated temperatures (it was suspected that these bcc forms of each would exhibit mutual solubility). Another important finding was that melting, or a partial fusion of a Np-rich phase following the decomposition of a material assigned to be $NpZr_2$, occurs at temperatures very close to the melting point of pure Np. These results were also unexpected based on the behaviors of the U-Zr and Pu-Zr systems where elevated melting temperatures for these alloys are observed.

Using data from these studies it is possible to speculate about the general features of the Np-Zr phase diagram. The apparent invariance of the melting points and the atomic volumes, and the retention of the α-Np phase and of the α-Zr phase, support the immiscibility of the two metals. These findings also suggest a phase diagram that is void of details, indicative of extensive formation of a solid solution. The retention of the α-to-β and the β-to-γ transitions for Np, which are essentially unaffected by the presence of Zr in the system, supports this contention. The X-ray data support the existence of the $NpZr_2$ phase as one phase; the DTA peak observed at 540°C is believed to represent the decomposition of this phase to Np-rich and Zr-rich phases.

Since the bonding in a metal is disrupted or altered by alloy formation, a consideration of the nature of the bonding is pertinent to predicting and/or understanding the miscibility or alloying of two or more metals. The cohesive energies of the metals should provide a measure of each metal's bonding in the pure metal and it is reasonable

to consider these cohesive energies in projecting potential solubilities for different metal pairs. The cohesive energies of U, Np, Pu and Zr are all similar, which alone would suggest mutual miscibility. However these cohesive energies include a contribution from 5f-electron overlap and this is a maximum for Np (e.g., the atomic volume of Np is considerable smaller than the volumes of U or Pu, which suggests greater f-bonding). Thus, the greater this 5f-interaction the greater should be the resistance of the metal to alloy formation, where such 5f-bonding would be altered. To expand on this concept will require the determination of how this 5f-interaction changes with temperature, structure, and alloy composition. This will be a future facet of our studies with alloy systems.

---

1. ORNL Physics Division.

Studies of Thermal Decomposition Mechanisms of Oxalates

J. K. Gibson and N. A. Stump[1]

We have explored the use of Raman and luminescence spectroscopies as tools to investigate mechanisms involved in thermal decomposition of f- element materials. For these exploratory studies we characterized the high-temperature decomposition of europium oxalate employing the luminescence of the Eu^{3+} or Eu^{2+} ions and Raman spectra. The luminescence spectra can provide information on the Eu valence (+2 or +3) as well as the local site symmetry and bonding of the Eu. The vibrational Raman spectra provide complementary characterization of the ligands around the Eu ion. The interest in the oxalates arises from their importance in separation and preparative schemes.

The mechanisms for the thermal decomposition of hydrated lanthanide sesquioxalates have been studied by others using various thermal and spectroscopic techniques as well as by X-ray diffraction. It has been found that the thermal decomposition process generally proceeds by the following processes; first, dehydration, which is then followed by decomposition to the sesquioxide via a dioxycarbonate. However, the mechanism for the Eu sesquioxide remains enigmatic, presumably reflecting the potential availability of a divalent state in the case of Eu. Several novel mechanisms have been postulated for this Eu sesquioxide.

The decomposition of Eu oxalate was followed at various temperatures and conditions. The luminescence data obtained during heating are consistent with the occurrence of two trivalent intermediates; evidence for a divalent intermediate was not obtained in our work. The Raman spectra showed that both intermediates have vibrational modes at energies close to that observed for pure Eu carbonate. We have proposed that the decomposition mechanism consists of the sequential formation of monoxy-dicarbonate and dioxy-monocarbonate intermediates prior to formation of the final sesquioxide. If correct, this sequence would be unique for Eu oxalate as compared to the decomposition of similar lanthanide compounds.

---

1. Chemistry Dept., University of Tennessee, Knoxville

Laser-Mass Spectromet y

J. K. Gibson

A laser photoionization time-of-flight mass spectrometer (TOFMS) system is being developed for studying actinide vapors and solids. The system consists of a Reflectron TOFMS which will have an electron impact ionization source in addition to the Excimer (XeCl) pumped dye laser used for photoionization of vapors and photo ablation of solids. Detection and mass analysis of the ions produced will be accomplished with the TOFMS; the mass resolution ($\Delta M/M$) is greater than 1000 for ions generated by electron impact and even larger for photoions. In addition to its high resolution, the system also offers maximum experimental flexibility by having two different ionizing mechanisms which can provide numerous combinations of techniques for comparative studies.

The novel design of the system has resulted in some delays in development delivery of instrumentation and has required the vendors to make modifications in their products. The laser system has been installed, has undergone testing and is operational. The reflection TOFMS has not been received although a linear TOFMS has been provided by a vendor for the interim period, and initial testing and further development of the system have been carried out with this linear instrument. When operational, this TOFMS instrument will greatly enhance our abilities to perform a variety of important high-temperature

research with exceptionally high sensitivity for detection of dilute and novel species.

8. CHEMICAL AND STRUCTURAL PRINCIPLES IN SOLVENT EXTRACTION

Crown ethers, ionizable lariat ethers, and related multidentate compounds are being synthesized and studied to gain insights leading to the selective recognition and separation of metal cations. Principles of thermodynamics and structure pertaining to energy-related separation techniques, especially solvent-extraction and ion exchange, receive primary consideration. An important thrust aims at combining neutral and ionizable functionalities in one extractant molecule as represented by the class of ionizable dibenzo-14-crown-4 lariat ethers, selective extractants for small alkali metal cations. Alternatively, neutral macrocycles are used alone or in synergistic combination with organophilic sulfonic and carboxylic acid extractants to achieve novel systems for selective separation of alkali, alkaline-earth, and transition metals. Questions being addressed through the synthesis and testing of new substituted crown-ether extractants pertain to the influence of preorganization, metal-ligand complementarity, lipophilicity, inductive effects, and steric factors on extraction selectivity and behavior. Structural aspects are probed extensively by the methods of X-ray structure determination of crystalline model compounds, and spectroscopy (e.g., FTIR, NMR, and UV/vis). Thermodynamic aspects are probed by distribution measurements, titration calorimetry, potentiometry, and other physical measurements. Multiequilibrium modeling techniques employing the program SXLSQA aid interpretation of extraction results.

BINDING OF ALKALI METAL CATIONS BY CROWN ETHERS AND IONIZABLE LARIAT ETHERS

Motivation, Approach, and Target Compounds

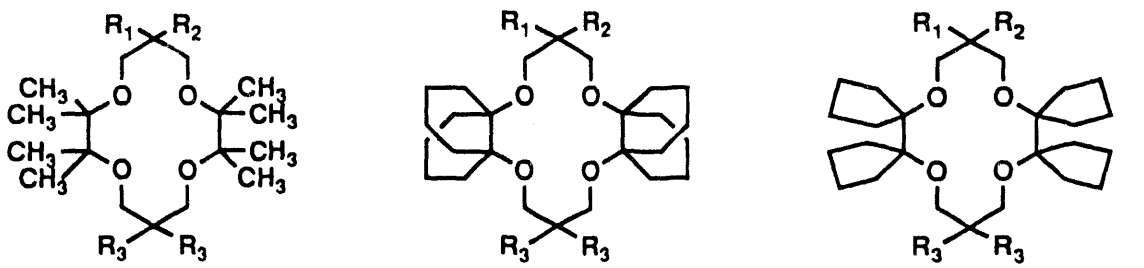
R. A. Sachleben, J. H. Burns, and B. A. Moyer

The broad purpose of this program is to strengthen the underlying foundation of thermodynamic and structural principles from which advanced separation systems based on solvent extraction and related techniques will be developed. Impetus stems especially from the many technical challenges facing the DOE and the nation in the next half a century in the area of separation science and technology, especially as pertaining to the areas of environment and waste.[1-4] In this program, fundamental questions related to selectivity, equilibria, and structure in metal-ion coordination and extraction by novel multifunctional extractants are primary topics of inquiry.

Among the large body of extractant types known, the crown-ether class of macrocycles affords the unique ability to selectively complex

and separate the alkali and alkaline-earth metals. Two key principles governing selectivity are optimization of complementarity or "fit" between the ligand and the target ion and preorganization of the ligand binding sites. Clearly, the macrocyclic geometry of appropriately sized crown ethers satisfies the first of these requirements. However, most of the known crown ethers have been very nonrigid or "floppy," and therefore preorganization has not always been optimum. Imposing conformational constraints on the ring appears to be a reasonable means for building in higher selectivity and binding strengths. In particular, relatively rigid lariat ethers based on the parent dibenzo-14-crown-4 ether represent a convenient vehicle for probing this effect. Here, the presence of two benzene rings in a relatively small macrocycle results in a conformation where the ether donor atoms are preorganized toward the convex face of the molecule. The lariat sidearm provides both a "capping" functionality on the axial position of the metal together with cation-exchange ability. Salient questions we have been addressing[5-8] concern how the cation held in the macrocycle and the anionic sidearm interact and how this interaction influences extraction behavior as governed by such variables as a) substitution at the position geminal to the ionizable sidearm, b) arm length, c) type of anionic functionality, and d) sidearm attachment via O or CH_2 linkages.

Recently, our efforts have progressed toward the less rigid 14-crown-4 systems represented by compounds 1 - 10 (Fig. 8.1).[9,10] Although they possess less rigidity than the dibenzo-14-crown-4 system (and probably less preorganization), these compounds may, in fact, provide a more constrained binding site in their complexes due to the steric demands of having substituents extending outward from both faces of the macrocyclic ring. In examining the structures of complexes in this series of crowns,[9] we have been gaining additional insight into the role of molecular constraints, including rigidity, on preorganization and on optimization of complementarity for selective complexation by crown ethers. Complementary thermodynamic studies on the extraction and complexation of metals by these compounds provide data for understanding structure-function relationships.[10] Additional candidates for synthesis include derivatives of 14-crown-4 lariats containing additional alkyl groups on the propylene bridges (compounds 7 - 9 in Fig. 8.1).



1 $R_1 = R_2 = CH_2$, $R_3 = H$
2 $R_1 = H$, $R_2 = CH_3$, $R_3 = H$
7 $R_1 = H$, $R_2 = CH_3$, $R_3 = alkyl$

3 $R_1 = R_2 = CH_2$, $R_3 = H$
4 $R_1 = H$, $R_2 = CH_3$, $R_3 = H$
8 $R_1 = H$, $R_2 = CH_3$, $R_3 = alkyl$
10 $R_1 = R_2 = R_3 = H$

5 $R_1 = R_2 = CH_2$, $R_3 = H$
6 $R_1 = H$, $R_2 = CH_3$, $R_3 = H$
9 $R_1 = H$, $R_2 = CH_3$, $R_3 = alkyl$

Fig. 8.1. Alkyl-substituted 14-crown-4 ethers.

In continuing our investigations into the relationship between macrocycle structure and cation binding, we have recently expanded our efforts toward the synthesis of selective extractants for other alkali metals. It is natural to ask to what degree can the insights we have gained on lithium binding by crown ethers be extended to the binding of alkali metals at the opposite extreme of size and charge density. Recent studies have indicated that bis(*tert*-butylbenzo)-21-crown-7 can act as a synergist to separate cesium from other alkali and alkaline earth cations.[11] Beyond this isolated study, however, little is known concerning how the extraction selectivity of crown ethers toward large alkali metals may be optimized. We have begun to investigate the selective complexation of cesium by variants of dibenzo-21-crown-7 by synthesizing compounds that contain structural units expected to influence the organization of the binding site of this macrocycle. Since cesium is a large, "soft" (relatively low charge density) cation, a reasonable strategy is to incorporate structures that form a large open binding cavity with sufficient rigidity to prevent the cavity from closing in to accommodate smaller cations; at the same time, aromatic substituents could be chosen that would lower the electron-donating

ability of the ether oxygens. These goals may be accomplished by modification of the 21-crown-7 macrocycle (see Fig. 8.2), or possibly by developing new systems containing conformationally oriented binding sites.

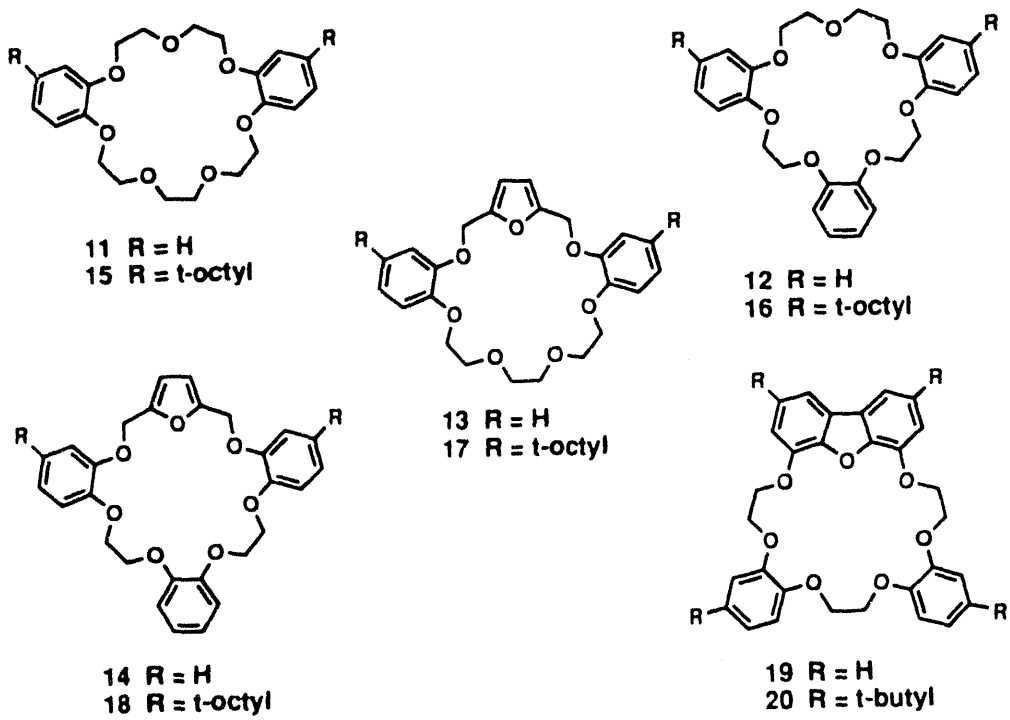


Fig. 8.2. Substituted 21-crown-7 ethers

---

1. "Separation & Purification, Critical Needs and Opportunities," National Research Council Report, Board on Chemical Sciences and Technology, National Research Council, 2101 Constitution Avenue, N.W., Washington, DC 20418; 1987.
2. Proc. First Hanford Workshop on Separation Science and Technology, Richland, WA, July 23-25, 1991.
3. "Basic Research for Environmental Restoration," Report DOE/ER-04 82T, Office of Energy Research, U.S. Department of Energy, Washington, DC 20585; Dec., 1990.
4. "Basic Research Needs for Management and Disposal of DOE Wastes," Report DOE/ER-0492T, Office of Energy Research, U.S. Department of Energy, Washington, DC 20585; Apr., 1991.
5. J. H. Burns and R. A. Sachleben, *Inorg. Chem.* 29, 788-795 (1990).
6. J. H. Burns and R. A. Sachleben, *Acta Crystallogr.* C47, 2339-2344 (1991).

7. R. A. Sachleben, B. A. Moyer, F. I. Case and S. A Garmon, *Sep. Sci. Technol.* 28, 1-23 (1993); Proc. Seventh Symp. on Separation Science and Technology for Energy Applications, Knoxville, TN, October 20-24, 1991.
8. R. A. Sachleben, B. A. Moyer, F. I. Case, and J. L. Driver, *Proc. International Solvent Extraction Conference (ISEC '93)*, to be held in York, England, Sept. 9-15, 1993, Society for Chemical Industry, London (in press).
9. R. A. Sachleben and J. H. Burns, *J. Chem. Soc. Perkin 2*, 1971-1977 (1992).
10. R. A. Sachleben, J. H. Burns, M. C. Davis, J. L. Driver, Z. Chen, Y. Deng, and B. A. Moyer, 205th ACS Nat. Mtg., Denver, Colorado, Mar. 28 - Apr. 2, 1993.
11. W. J. McDowell, G. N. Case, J. A. McDonough, and R. A. Bartsch, *Anal. Chem.* 64, 3013-3017 (1992). Work done in collaboration with R. A. Bartsch, Texas Tech University.

Synthesis of Crown Ethers

R. A. Sachleben, D. R. Bailey,[1] J. J. Bruce,[1] M. C. Davis,[1] E. S. Ripple[1]

We have completed the syntheses of compounds **1** - **6** shown in Fig. 8.1, using the synthetic scheme outlined in Fig. 8.3.[2,3] This method represents a significant improvement in time and yield compared to literature methods for the preparation of related crown ethers. For example, according to the literature, didecalino-14-crown-4, **10**, an analog of **4**, was prepared in 0.2% yield in six steps compared to 70% yield in four steps using the synthetic procedure outlined for **4** below. Our method is also useful for the preparation of other crown systems, as exemplified by the synthesis of tetraethyl-16-crown-4 (not shown) in 55% yield. Results from structural and thermodynamic studies on some of these compounds are reported in separate sections below.

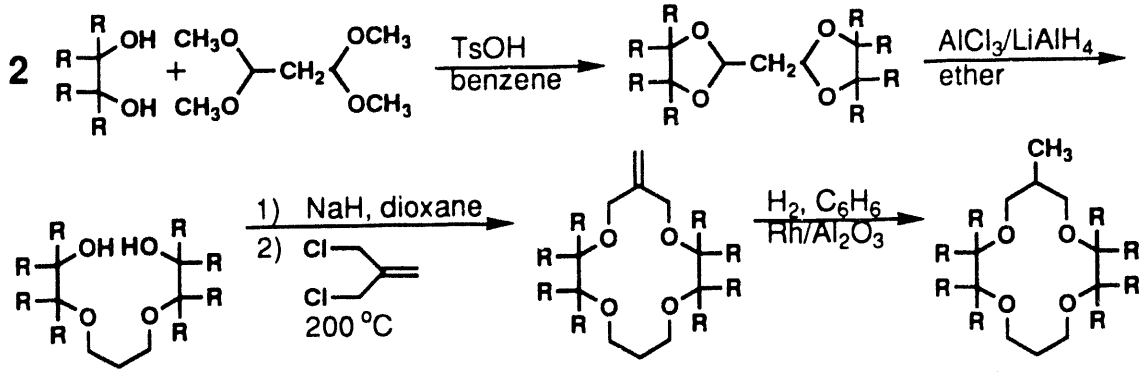


Fig. 8.3. Preparative route to substituted 14-crown-4 ethers.

We have initiated a project to study the effect of substituents on the selective extraction of large alkali metal ions, especially cesium, by 21-crown-7 ethers. We have synthesized compounds **11** - **14** for our initial structural studies (Fig. 8.2). Although compounds **11** and **12** have been reported previously, they are not commercially available, while **13** and **14**, which contain both benzo and furano substituents, are new compounds. Subsequently (see below), we plan to prepare the lipophilic derivatives **15** - **20** for extraction studies.

---

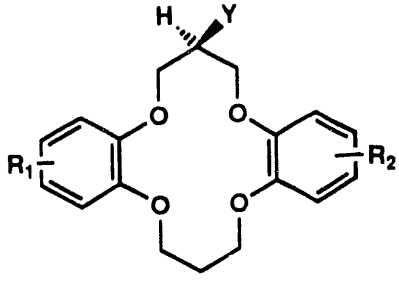
1. Undergraduate Research Participant.
2. R. A. Sachleben and J. H. Burns, *J. Chem. Soc. Perkin 2*, 1971-1977 (1992).
3. R. A. Sachleben, J. H. Burns, M. C. Davis, J. L. Driver, Z. Chen, Y. Deng, and B. A. Moyer, 205th ACS Nat. Mtg., Denver, Colorado, Mar. 28 - Apr. 2, 1993.

Structural Studies of Crown Ethers and Complexes

J. H. Burns, R. A. Sachleben, Z. Chen[1]

Crystals of **2** - **6**, **21** (Fig. 8.4), **2**•LiSCN, **4**•LiSCN, and **6**•LiSCN were prepared and analyzed by X-ray diffraction in order to compare the conformations of these crowns to each other and to assess the changes they undergo upon complexation.[2-4] Previously reported structures of **21**•LiSCN[5] and dicyclohexano-14-crown-4•LiSCN[6] were included in this comparison. X-ray structures for **4**•LiSCN and **6**•LiSCN and are shown in Fig. 8.5. In every case except **21**, the 14-crown-4 ring of the free ligand, regardless of its substituents, adopts a conformation in which there is no cavity, and the O atoms are in contact only in pairs. However, complexation with LiSCN results in rearrangement of the crown to where the 14-crown-4 ring adopts a pseudo-chair conformation and the O atoms form a planar rectangle. The Li^+ ion is 0.55 to 0.79Å from this plane, and the N atom of the SCN^- ion completes the pyramidal coordination of Li^+. The free **21** ligand adopts a conformation similar to that observed in the LiSCN complexes of **2**, **4** and **6**, where the oxygen atoms form a planar rectangle which is preorganized for the complexation of Li^+, as found in the structure of **21**•LiSCN. However, in **21** and **21**•LiSCN the 14-crown-4 ring adopts a pseudo-boat conformation, in contrast to the pseudo-chair form found for **4**•LiSCN and **6**•LiSCN, where the propylene

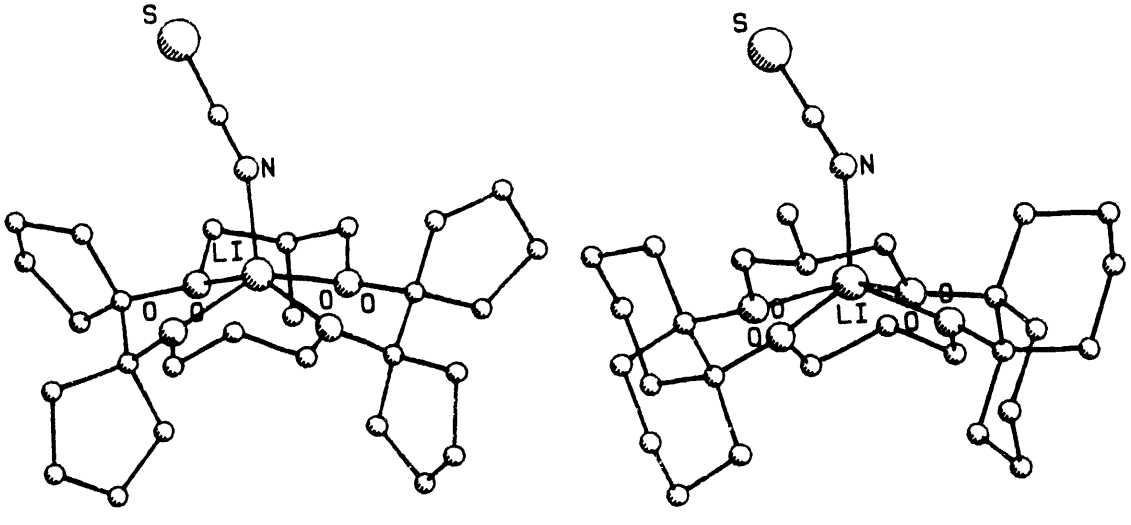
bridges are oriented towards the same face of the molecule to which the Li^+ is coordinated.



Y	$R_1 = R_2 = H$	$R_1 = R_2 = t\text{-}C_8H_{17}$
H	21	31
OH	22	32
OCH_3	23	32
CH_3	24	34
CH_2OH	25	35
CH_2CH_2OH	26	36
OCH_2CH_2OH	27	37
CH_2CO_2H	28	38
$CH_2CH_2CO_2H$	29	39
OCH_2CO_2H	30	40

Fig. 8.4. Dibenzo-14-crown-4 ethers synthesized for structural studies.

We have also obtained the structure of one complex containing the larger Na^+ ion, *cis-syn-cis*-dicyclohexano-14-crown-4•NaSCN. The observed structure is quite different from the Li^+ analog. Dimers are formed in which each Na^+ ion attains 6-fold coordination by complexation to the four oxygens of a crown (at 1.37Å from their plane) and by coordination to the two N atoms of a pair of shared SCN^- ions. The 14-crown-4 ring adopts a flattened pseudo-boat conformation, with the propylene bridges oriented away from the coordinated Na^+; the oxygen atoms are more widely separated than is the case in the Li^+ complex.



(a) (b)

Fig. 8.5. Structures of (a) tetracyclopentyl-14-crown-4•LiSCN (4•LiSCN) and (b) didecalino-14-crown-4 (6•LiSCN).

Clearly, all these substituted 14-crown-4 ligands, except **21**, are flexible and respond to the presence of the cation by changing their conformation to accommodate it. As larger cations are introduced, the conformational changes required to accommodate them are expected to become more demanding, contributing to the selectivity of 14-crown-4 ethers for the small Li^+ ion.

The solution structures of model compounds **22** - **28** and **40** (Fig. 8.4) have been studied by NMR spectrometry, revealing the configuration of the sidearm. Over the temperature range 183 - 323 K, these compounds adopt a single low-energy conformation in which the orientation of the sidearm relative to the crown cavity depends on the atom linking the sidearm to the macrocyclic ring. When the linking atom is oxygen, the sidearm adopts a pseudo-axial conformation and is oriented above and towards the crown cavity. When the linking atom is carbon, the sidearm adopts a pseudo-equatorial position and is oriented away from the crown cavity. The structure of the favored conformations, as determined by ^{13}C chemical shifts, ^1H-^1H coupling constants, and 2-D NOESY experiments, correlate well with the solid-state structures determined previously by X-ray diffraction studies. These results may have significance in understanding the extraction behavior of lipophilic compounds **32** - **34** (see below).

---

1. ORNL Postdoctoral Research Associate.
2. R. A. Sachleben and J. H. Burns, *J. Chem. Soc. Perkin 2*, 1971-1977 1992).
3. R. A. Sachleben, J. H. Burns, M. C. Davis, J. L. Driver, Z. Chen, Y. Deng, and B. A. Moyer, 205th ACS Nat. Mtg., Denver, Colorado, Mar. 28 - Apr. 2, 1993.
4. The structure of **21** has simultaneously been reported by others: N. K. Dalley, W. Jiang, and U. Olsher, *J. Incl. Phenom. Mol. Recogn.*, 12, 305 (1992).
5. G. Shoham, W. N. Lipscomb, and U. Olsher, J. Chem. Soc., Chem. Commun., 208 (1983).
6. G. W. Buchanan, R. A. Kirby, and J. P. Charland, *J. Am. Chem. Soc.*, 110, 2477 (1988).

Solution Thermodynamic Studies on Lariat Ethers

B. A. Moyer, R. A. Sachleben, J. B. Abreu,[1] F. I. Case,[2] J. L. Driver,[3] S. A. Garmon[1]

We have completed a series of extraction studies using the lipophilic, ionizable lariat ethers **38** - **40**.[4-6] Extractions of mixtures of

the chloride salts of Li - Cs as a function of pH were carried out by two-phase potentiometry with a glass electrode, and the organic phases were intermittently sampled for ion chromatographic analysis. It was found that compounds **38** and **39** in *n*-octanol diluent extract lithium selectively from an aqueous mixture of alkali metal chlorides. In contrast, **40** extracts sodium and potassium more strongly than lithium. All three crowns extract rubidium and cesium less strongly than sodium or lithium. It may thus be concluded that the presence of the oxygen atom linking the sidearm to the macrocycle in **40** reverses the lithium/sodium extraction selectivity obtained with the α-carbon linkage. It was also observed that **40** acts as a stronger acid in its extraction behavior by 1 - 2 pH units. In view of the difference in pK_a between propanoic acid (pK_a = 4.88) and glycolic acid (pK_a = 3.83), the effective acidity enhancement in **40** relative to **38** and **39** may therefore partly reflect the inductive effect of the α-oxygen atom. In addition, X-ray structures reported by us and others have demonstrated the role of the α-oxygen atom in providing an additional coordination site for the bound metal cation. Together, the inductive and coordinative effects of the oxygen link appear to impart a significant preference for sodium binding.

Interestingly, selectivity in extraction by **38** - **40** contrasts with selectivity in complexation by the truncated analogs **28** - **30** in homogeneous solution. In collaboration with R. A. Bartsch (Texas Tech University), we have obtained calorimetric measurements of the complexation of **28** - **30** with the alkali metal halides in aqueous methanol, revealing a more favorable free energy of complexation for sodium and potassium than for lithium. Thus, at this stage of our progress, selectivity of lariat ethers in two-phase extraction systems appears to be significantly different than the selectivity in homogeneous methanol media.

Experiments to determine the acidity constants of compounds **28** - **30** and **38** - **40** by potentiometric titration in homogeneous solution (90% methanol) have been performed, and analysis of the data is in progress. These results, in combination with the calorimetric results, will allow more complete characterization of the single-phase thermodynamic properties of this series of compounds.

1. Undergraduate Research Participant.
2. Chemistry Division, ORNL (Retired).
3. Staff Chemist, Oak Ridge Research Institute.
4. R. A. Sachleben, B. A. Moyer, F. I. Case and S. A Garmon, *Sep. Sci. Technol.* 28, 1-23 (1993); Proc. Seventh Symp. on Separation Science and Technology for Energy Applications, Knoxville, TN, October 20-24, 1991.
5. R. A. Sachleben, B. A. Moyer, F. I. Case, and J. L. Driver, *Proc. International Solvent Extraction Conference (ISEC '93)*, to be held in York, England, Sept. 9-15, 1993, Society for Chemical Industry, London (in press).
6. R. A. Sachleben, J. H. Burns, M. C. Davis, J. L. Driver, Z. Chen, Y. Deng, and B. A. Moyer, 205th ACS Nat. Mtg., Denver, Colorado, Mar. 28 - Apr. 2, 1993.

MULTIEQUILIBRIUM MODELING IN SOLVENT EXTRACTION

C. F. Baes, Jr.,[1] B. A. Moyer

The FORTRAN least-squares modeling program SXLSQA (written by C. F. Baes, Jr.) represents the most advanced treatment of solvent-extraction equilibria available.[2,3] Improvements in SXLSQA continue to be made as dictated by the needs of current systems under investigation in extraction experiments. Recently, the asymmetric mixing effect has been added to the Pitzer treatment applied by the program.[4] For the organic phase, species activity coefficients are now calculated by use of the Hildebrand-Scott treatment with inclusion of the Flory-Huggins correction for the effect of the volume of species on the entropy of mixing.[5] In addition, the user may now elect to have all activity coefficients set to unity in the event that experimental conditions ensure constant activity coefficients. The ability of the program to treat calorimetric and spectral data has also been upgraded. Ease of use continues to improve with implementation of greater flexibility in output such as plots and tables of species concentrations and activity coefficients. Convergence criteria and memory requirements may now be set by the user. The usefulness of the program has attracted interest from others in the separations community.

1. Chemistry Division, ORNL (Retired); presently Consultant.
2. C. F. Baes, Jr., B. A. Moyer, and G. N. Case, *Sep. Sci. Technol.* 25(13-15), 1675-1688 (1990); Proc. Sixth Symp. on Separation Science and Technology for Energy Applications, Knoxville, TN, October 22-27, 1989.

3. B. A. Moyer, L. H. Delmau, G. J. Lumetta, and C. F. Baes, Jr., *Solvent Extr. and Ion Exch.* (in press).
4. K. S. Pitzer, in Activity Coefficients in Electrolyte Solutions, 2nd ed., K. S. Pitzer, Ed., CRC Press, Boca Raton (1991), pp. 75-153.
5. E. J. Henley and J. D. Seader, Equilibrium-Stage Separation Operations in Chemical Engineering, John Wiley & Sons, New York, 1981, p. 185.

CROWN ETHERS AS SELECTIVE EXTRACTANTS FOR TRANSITION METAL CATIONS

Extraction Studies

B. A. Moyer, J. H. Burns, C. F. Baes,[1] Jr., L. H. Delmau,[2] G. J. Lumetta[3]

Our study of the complexation and extraction of transition-metal cations by macrocyclic compounds is directed toward understanding the origin of selectivity when ligands having controlled donor-atom sets in controlled geometries interact with cations having highly specific bonding requirements. While ionic radii and electrostatic considerations dominate strategies for separating alkali and alkaline earth metals, d-orbital occupancy with its attendant influence on bonding becomes an additional, often pivotal variable in separating members of d-transition series. Our attention has been focused on complexation equilibria and selectivity in the series of divalent, high-spin 3d transition metals Mn(II) - Zn(II) as a model system because of the broad base of theoretical and experimental knowledge concerning the coordination chemistry of this series and because of the importance of this series in hydrometallurgical separations.

Our earlier studies of the extraction of the 3d transition metals revealed a unique selectivity for Mn(II) and Zn(II) ions when the crown ether *tert*-butylcyclohexano-15-crown-5 (tBC15C5) is combined synergistically with cation exchangers.[4] Recently, FTIR[5-7] and X-ray crystallographic[8] studies have revealed direct 1:1 coordination of Mn(II) and Zn(II) cations by the crown ether under the extractive conditions. Formation of such complexes is remarkable because it is the first example of a crown ether complexing divalent first-row transition metal ions in competition with water.

By use of the program SXLSQA, it has been possible to model available data on the extraction of Mn(II) from nitric acid by didodecylnaph-

thalene sulfonic acid (HDDNS) in combination with either *t*-butylbenzo-15-crown-5 (tBB15C5) or tBC15C5 in toluene.[7] Overall, only 1:1 metal: crown ether interactions have been found, and HDDNS acts both as a cation exchanger and as a solvating agent leading to small aggregates. The crown ethers used alone extract Mn(II) weakly. When combined with HDDNS, tBB15C5 depresses the extraction of the metal, and no complex of Mn(II) with the macrocycle was found. However, tBC15C5 synergizes the extraction of Mn(II) by HDDNS with formation of a family of 1:1 metal: crown ether complexes of the form $MnBH_{a-2}A_a$ (a = 2 to 4). Opposing extraction was the solvation of the crown ethers by HDDNS to give families of species of the form $(HA)_a{\cdot}B$. Infrared spectra of the extraction complex $MnBA_2$ (B = tBC15C5) in CCl_4 were compared with infrared spectra of the crystalline model complex $[Mn(C15C5)(DtBNS)(H_2O)](DtBNS){\cdot}C_7H_8$ (where C15C5 = cyclohexano-15-crown-5 and DtBNS = 3,7-di-*t*-butylnaphthalene-1-sulfonate), whose structure was known from X-ray diffraction.[8] The spectral results indicate encirclement of the extracted Mn^{2+} ion by tBC15C5 in solution, and sulfonate anions probably compete weakly with water for the axial coordination sites.

---

1. Chemistry Division, ORNL (Retired); presently Consultant.
2. Undergraduate Research Participant.
3. ORNL Postdoctoral Research Associate.
4. W. J. McDowell, B. A. Moyer, G. N. Case, and F. I. Case, *Solvent Extr. Ion Exch.* 4, 217-236 (1986).
5. G. J. Lumetta, B. A. Moyer, and P. A. Johnson, *Solvent Extr. Ion Exch.* 8, 457-475 (1990).
6. G. J. Lumetta and B. A. Moyer, *J. Coord. Chem.* 22, 331–336 (1991).
7. B. A. Moyer, L. H. Delmau, G. J. Lumetta, and C. F. Baes, Jr., *Solvent Extr. and Ion Exch.* (in press).
8. J. H. Burns and G. J. Lumetta, *Acta Crystallogr.* C47, 2069–2073 (1991).

Calorimetric Investigations

B. A. Moyer, J. H. Burns, Y. Deng,[1] G. G. Wu,[1] R. M. Izatt[2]

The remarkable extraction selectivity for Mn(II) and Zn(II) ions when the crown ether *tert*-butylcyclohexano-15-crown-5 (tBC15C5) is combined synergistically with cation exchangers suggests the existence of unusual bonding effects (see above). The selectivity order Mn(II) > Fe(II) ~ Co(II) ~ Ni(II) < Cu(II) < Zn(II) is essentially the inverse of the Irving Williams Order (IWO). If the IWO may be ascribed to an

increase in ligand field stabilization energy (LFSE) of the non-spherically symmetric metals Fe(II) - Cu(II) in the reaction, then it may be reasonably postulated that the observed selectivity entails a *decrease* in LFSE for these metals leading to depressed complexation. To test this idea, X-ray and calorimetric investigations have been conducted.

The calorimetric experiments were performed on a model system in which 2 - 5 mM Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) nitrate or trifluoromethane sulfonate salts in propylene carbonate (PC) containing 30 - 50 mM H_2O were titrated with the crown ether cyclohexano-15-crown-5 (C15C5) at 25 °C. After correction for dilution heats and heat leakage, the thermograms for Mn(II), Co(II), Ni(II), and Zn(II) followed 1:1 M:L stoichiometries, giving values of log$K$ and ΔH by regression procedures. The titration of Cu(II) followed an unusual 2:1 M:L stoichiometry; this stoichiometry was also found in conductometric and polarographic studies of the complexation of Cu(II) and other divalent metal cations by crown ethers in methanol.[3] For the 1:1 reactions, the strength of complexation of the metals by C15C5 followed the order Mn(II) > Co(II) > Ni(II) < Zn(II), paralleling that observed in our solvent-extraction studies.[3,4] More importantly, this order was found to be enthalpy based, supporting the postulated ligand-field effect.

The structure of the crown-ether complex bis(trifluoromethanesulfonato)Mn(II).cyclohexano-15-crown-5 was established by X-ray crystal-structure analysis. Crystals are comprised of isolated molecules linked only by van der Waals forces. Each Mn^{2+} ion is coordinated by a pentagonal bipyramid of oxygen atoms. The five atoms of the equatorial plane belong to the crown ether molecule, and the apical atoms are contributed by monodentate triflate ions. This molecular configuration is similar to that found previously in $Mn(DtBNS)_2$.cyclohexano-15-crown-5.H_2O in which one apical oxygen atom is from the di-*tert*-butylnaphthalene sulfonate ion (DtBNS), and the other from a water molecule.[4] The present crystalline compound contains no water nor has any hydrogen bonding. While the cyclohexano-15-crown-5 ligands in the two compounds have different conformations, neither is very strained compared to the free ligand.

1. ORNL Postdoctoral Research Associate.
2. Department of Chemistry, Brigham Young University.
3. L. Chen, M. Bos, P. D. J. Grootenhuis, A. Christenhusz, E. Hoogendam, D. N. Reinhoudt, and W. E. van der Linden, Anal. Chim. Acta, 201, 117-125 (1987).
4. J. H. Burns and G. J. Lumetta, *Acta Crystallogr. C47*, 2069-2073 (1991).

Thia Crown Ethers as Extractants for Cu(II)

B. A. Moyer, C. F. Baes, Jr.,[1] S. Bajo,[2] G. N. Case,[3] L. H. Delmau,[4] G. J. Lumetta,[5] N. M. Wilson[4]

Ligand-field reasoning similar to that given above has led us to consider polydentate ligands that have higher ligand-field strength than the oxygen donor atoms of the oxa crown ethers. Previous experiments[6] with tetradentate thia macrocycles have indicated a marked selectivity for Cu(II) over the other metals in the series Mn(II) to Zn(II), including additionally Fe(III), a common contaminant in many important separation systems. Here, the "soft" sulfur donor atoms represent a key advantage in producing this desirable selectivity.

Recent efforts have focused on modeling the extraction of Cu(II) from sulfuric acid at 25 °C by combinations of the strong-acid cation exchanger didodecylnaphthalene sulfonic acid (HDDNS) in toluene with and without tetrathia-14-crown-4 (TT14C4). In the case of the "baseline" extraction of Cu(II) by HDDNS alone, trivariate extraction data were modeled within experimental error by assuming only the equilibrium extraction of Cu^{2+} ion by the aggregate $(HDDNS)_4(H_2O)_{22}$ together with the equilibrium dissociation of the aggregate to the monomer.[7] On the other hand, TT14C4 used alone gives practically undetectable extraction of Cu(II), presumably owing to the unfavorable transfer of aqueous anions, but in combination with HDDNS gives strong enhancement of Cu(II) extraction. Preliminary results on the modeling of extraction and spectral data for the synergistic system show that TT14C4 coordinates to the metal ion to form a 1:1 complex in the organic phase. This complex is associated with 3 or 4 HDDNS molecules, two of which are in the anionic form for charge neutrality. Thus, the extraction may be described as ion exchange coupled with selective coordination by the macrocycle.

The relationship between thia ligand structure and ability to synergize the extraction of Cu(II) from aqueous sulfuric acid solution by HDDNS has been surveyed.[8] Among the 12-, 14-, and 16-membered macrocyclic tetradentate thia ethers, the strongest enhancement was found with the 14-membered ring. Weak enhancement was observed for one monodentate and two bidentate alkyl thia ethers. Two acyclic tetradentate thia ethers exhibited stronger enhancement than expected from the aqueous-phase macrocyclic effect. It was shown that the weakening of the macrocyclic effect upon extraction may be reasonably attributed to differential solvation effects leading to greater partitioning of the linear tetradentate thia ligands to the aqueous phase relative to the macrocyclic analog TT14C4. In practical terms, a weak macrocyclic effect implies that, with an inexpensive acyclic ligand, one may achieve extraction effectively comparable to that obtained with the corresponding expensive macrocycle.

---

1. Chemistry Division, ORNL (Retired); presently Consultant.
2. Guest Scientist, Paul Scherrer Institute, Wurenlingen, Switzerland.
3. Chemistry Division, ORNL (Retired).
4. Undergraduate Research Participant.
5. ORNL Postdoctoral Research Associate.
6. B. A. Moyer, C. L. Westerfield, W. J. McDowell, and G. N. Case, *Sep. Sci. Technol.* 23, 1325-1344 (1988)
7. B. A. Moyer, C. F. Baes, Jr., G. N. Case, G. J. Lumetta, and N. M. Wilson, *Sep. Sci. Technol.* 28, 81-113 (1993); Proc. Seventh Symp. on Separation Science and Technology for Energy Applications, Knoxville, TN, October 20-24, 1991.
8. B. A. Moyer, R. A. Sachleben, and G. N. Case, *Proc. International Solvent Extraction Conference (ISEC '93)*, to be held in York, England, Sept. 9-15, 1993, Society for Chemical Industry, London (in press).

SYNERGISTIC EXTRACTION PHENOMENA IN RESIN SYSTEMS

B. A. Moyer, G. N. Case,[1] A. A. Kriger,[2] and S. D. Alexandratos[3]

A novel interpenetrating polymer network (IPN) having both carboxylic acid and pyridine functionalities has been characterized by tracer distribution measurements and IR spectrophotometry.[4] As shown by the following selectivity order, soft metals were preferred: Cd(II) > Ag(I) > Hg(II) > Ni(II) > Zn(II) > Co(II) > Eu(III). By comparison of distribution coefficients determined for this IPN and control IPNs having either carboxylic or pyridine groups, synergistic extraction of

the transition metals Ni(II), Zn(II), and Co(II) has been demonstrated at pH = 5.

By analogy to our synergistic solvent extraction systems, we have recently shown that it is possible to impregnate cation exchange resin beads with appropriate ligands and thereby obtain selectively synergized enhancement of the cation exchange process.[4,5] In the most effective example, a novel extractive resin employing the tetradentate macrocyclic ionophore tetrathia-14-crown-4 (TT14C4) has been demonstrated via impregnation of strong-acid polystyrene divinylbenzene cation exchange beads. Following uptake of several weight percent TT14C4, the sulfonic acid resin exhibits a 10-100-fold enhancement in the cation-exchange extraction of Cu(II). Best results were obtained with a resin that was approximately 30% sulfonated. Since extraction of Cu(II) by a control incapable of cation exchange (completely unfunctionalized polystyrene divinylbenzene impregnated with TT14C4) was too low to be detectable, the enhancement in cation exchange may be attributed to a synergistic effect involving coordination of the Cu(II) by the mobile macrocycle and cation exchange by the immobile sulfonic acid groups. The cation exchange behavior of the novel impregnated resin exhibits essentially the same properties as found for the analogous solvent extraction system employing TT14C4 and HDDNS in toluene. This is the first demonstration of synergism in a solvent-impregnated resin involving a functionalized support.

---

1. Chemistry Division, ORNL (Retired).
2. Graduate Student, Department of Chemistry, University of Tennessee, Knoxville, TN.
3. Department of Chemistry, University of Tennessee, Knoxville, TN.
4. B. A. Moyer, G. N. Case, A. A. Kriger, and S. D. Alexandratos, Anal. Chem. (submitted).
5. A. A. Kriger, M. S. Thesis, University of Tennessee, Knoxville, TN.

9. SURFACE SCIENCE RELATED TO HETEROGENEOUS CATALYSIS

The purpose of this research program is to study fundamentals of surface reactivity by experimental and computational examination of atomic and molecular interactions at well-characterized solid surfaces. The goal is to obtain mechanistic details about how chemical reactions occur at catalytically active surfaces. Such information could have significant impact upon many technologies. Particular emphasis is placed upon understanding mechanisms of desulfurization chemistry, and the effect of the reactant and product species on the surfaces of metals and alloys. Details of surface reaction pathways, as affected by temperature and coverage, are extracted. The effects of the adsorbate, its decomposition products, or other associated species on the substrate structure and component distribution are determined. Conversely the effect of substrate structure on the adsorbate, for example its bonding site and desorption energy, is also investigated. The approach is largely experimental and is embodied in the application of various techniques including electron spectroscopies (high resolution energy loss, diffraction, x-ray and soft x-ray photoemission, Auger emission), ion scattering spectroscopy, quantitative chemical dosing, and temperature programmed reaction to monitor and control surface processes. Computational work has the dual goals of modeling surface reactions and increasing understanding of the fundamentals of analytical probes.

REACTIONS OF ORGANIC AND ORGANOSULFUR MOLECULES ON MODEL CATALYTIC SURFACES

Patterns of Reactivity for Ni(110) With Organosulfur Compounds

D. R. Huntley

Over the past few years a wide variety of adsorbates have been studied on Ni(110) resulting in the identification of general reactivity patterns of nickel metal centers toward various functional groups in organic and organosulfur molecules. The adsorbates studied included H_2S, alkyl thiols (methanethiol, ethanethiol), aryl thiols (benzenethiol, *p*-methyl benzenethiol, *m*-methyl benzenethiol), polyfunctional thiols (mercaptoethanol, ethanedithiol), and other organic compounds (ethanol, benzene, ethylene, ethyl iodide). The overall reaction selectivity of the Ni(110) surface is briefly summarized below.

Thiols chemisorb on Ni(110) at 100 K with dissociation of the sulfhydryl bond. The thiolate species formed upon adsorption is generally stable to about 200 K when C-S bond scission commences. The temperature of C-S bond scission shows some correlation with gas phase C-S bond dissociation energy for the alkyl thiols, but the aryl thiols (with significantly stronger C-S bonds) do not follow the correlation. Ni(110) is inactive with respect to C-O bond scission.

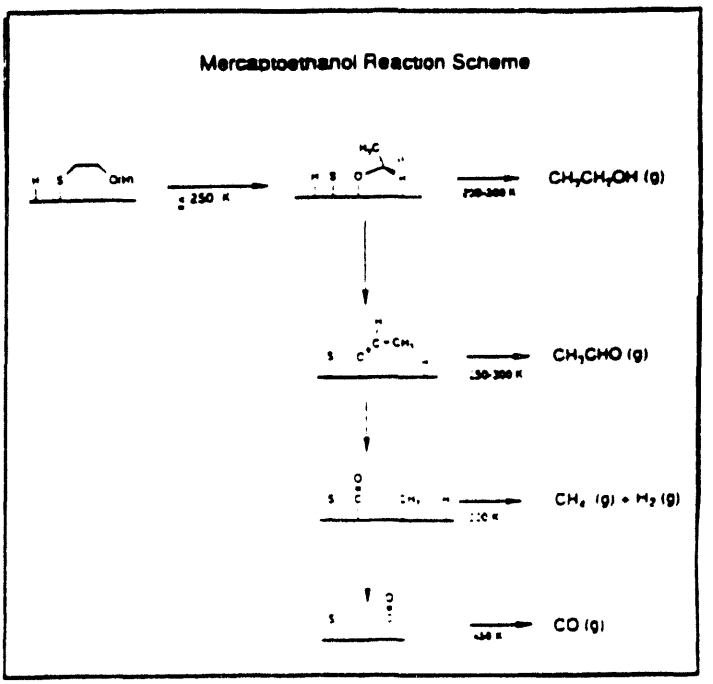
Reactions of C_2 thiols (ethanethiol, ethanedithiol and mercaptoethanol) indicate that C-S bond scission occurs preferentially to C-C bond scission. However, C-C bond scission does occur in ethoxide, an intermediate formed from both ethanol and mercaptoethanol.

Ni(110) is quite reactive toward both C-H bond scission and formation. Both reactions occur at relatively low temperature for alkyl species (< 300 K). However, cleavage of aromatic C-H bonds occurs above 300 K. Carbon-oxygen bond formation only occurs from recombination of surface carbon and oxygen to form CO. Carbon-sulfur bond formation is never observed. Oxygen-hydrogen bond formation is observed in several cases including recombination of ethoxide and surface hydrogen and reaction of surface oxygen with S-H groups. Carbon-carbon bond formation is not a major reaction step in these systems.

Reactions of Polyfunctional Thiols

D. R. Huntley

Reactions of ethanedithiol and mercaptoethanol were studied with the goal of determining the reaction selectivity in these compounds. Ethanedithiol and mercaptoethanol are structurally similar molecules, yet the chemistry they undergo is quite different. Mercaptoethanol reacts with Ni(110) to form ethanol, acetaldehyde, methane, CO and hydrogen. Ethanedithiol produces ethylene with very high selectivity. The mechanistic details of the mercaptoethanol reaction have been elucidated. Mercaptoethanol reactivity is dominated by thiolate formation. It is difficult to determine how much interaction there is between the hydroxyl functionality and the surface prior to C-S bond scission. However, near 200-250 K, the C-S bond cleaves, as in the simple thiols, with the evolution of ethanol and formation of surface ethoxide. The ethoxide dehydrogenates to form acetaldehyde, some of



which is observed as a TPD product. Dehydrogenation at the α carbon continues, resulting in the formation of CO. Methane is also observed as a desorption product, and presumably is formed from the β carbon in the ethoxide (the carbon initially bonded to S). Ethanedithiol adsorbs in a bidentate fashion, resulting in a dithiolate which selectively splits out ethylene and produces surface sulfur. The difference in the reactivity of ethanedithiol and mercaptoethanol is understood in terms of the inactivity of the Ni(110) surface towards C-O bond scission, presumably because of the stronger C-O bonds compared with C-S bonds. The mechanism of ethanethiol reaction on Ni(110) is summarized in the above figure.

Selectivity of Ethane and Ethylene Formation

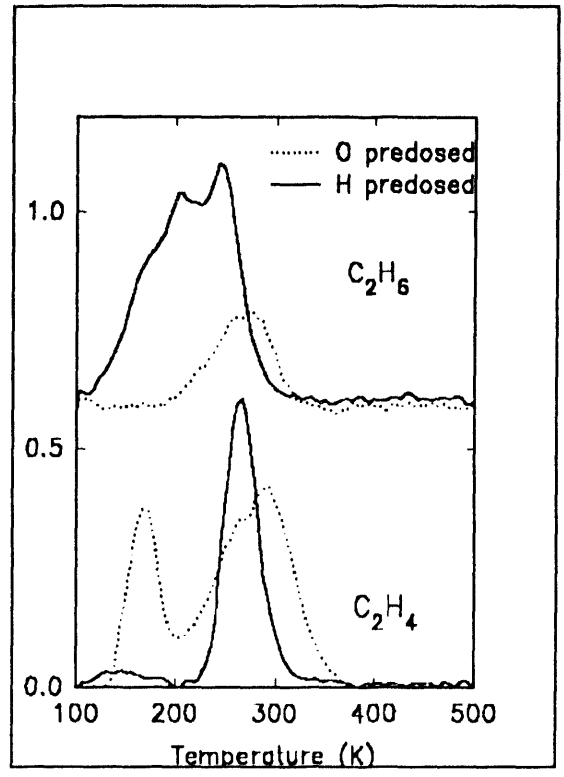
D. R. Huntley

Temperature programmed reaction studies of ethanethiol adsorbed at 100 K indicate several reaction products. A competition occurs between decomposition to form surface carbon, sulfur and hydrogen (which desorbs as H_2) and hydrocarbon formation. Within the hydrocarbon formation channel, both ethane and ethylene are formed. In this study, the selectivity for ethylene formation was examined and found to be determined by several factors, including ethanethiol exposure, and surface pretreatment.

Regardless of pretreatment, the selectivity to ethylene was found to be a function of ethanethiol exposure. For low thiol coverages, ethylene formation is preferred. However, at coverages near 0.5 ML, the selectivity is about 60% on the clean surface. The result of predosing the surface in hydrogen is a decrease in selectivity to ethylene at low

thiol coverage. Conversely, oxygen causes an increase in the ethylene selectivity at high thiol coverage.

In addition to changes in overall selectivity, the coadsorption of hydrogen or oxygen results in dramatically different desorption profiles for both ethane and ethylene as shown in the figure. Oxygen promotes low temperature ethylene desorption while hydrogen promotes low temperature ethane desorption. These results can be understood in terms of altering the available hydrogen coverage. Predosing the surface with oxygen causes a decrease in the reactive hydrogen coverage because oxygen tends to scavenge hydrogen to form hydroxyl species and water. In the absence of surface hydrogen, the dehydrogenation channel is preferred, resulting in higher selectivity to ethylene. Modification of the ethylene bonding by oxygen results in the low temperature desorption channel. Predosing the surface with hydrogen results in hydrogenation of C_2 species at low temperatures and a greater selectivity to ethane formation.



Effects of C-X Bond Energies on Reaction Pathways

D. R. Huntley, F. A. Grimm[1]

A fundamental understanding of the relationship between reaction selectivities and gas phase bond dissociation energies would be useful in predicting reaction pathways in complex reaction mixtures. This relationship has been explored computationally using various methods including BOC-MP and quantum chemical methods. The reactions of several heteroatom containing organic compounds have been studied to address the issue of how the the gas phase energy of the carbon-heteroatom bond affects the reaction pathways and kinetics.

Correlations between C-S bond energy and desulfurization kinetics have been suggested previously in the literature. In addition, the differences in reactivity between alcohols and thiols is generally attributed to differences in the C-S *vs* C-O bond energies. The reactions chosen in this study are ethanethiol, methanethiol, benzenethiol, ethanol, ethyl iodide and ethanedithiol on Ni(110). These compounds have a range of C-X bond energies ranging from 53.4 to 86 kcal/mole for ethyl iodide and benzenethiol, respectively.

A comparison of ethanethiol, methanethiol and benzenethiol reactions on Ni(110) indicate that despite the stronger bond energy in benzenethiol, the phenylthiolate undergoes C-S bond scission at a lower temperature than ethanethiol and methanethiol. Methylthiolate is slightly more stable that ethylthiolate, as indicated by the desorption of methane at slightly higher temperatures than ethane. Cleavage of the weak C-I bond occurs at low temperature (<150 K) while cleavage of the C-O bond is not observed.

For R-X compounds (R=methyl, ethyl), there does seem to be a general trend that the stronger the C-X bond in the gas phase compound, the more difficult the C-X bond scission is on the Ni surface. However, benzenethiol is an anomoly since it undergoes relatively facile C-S bond scission, yet has the highest C-S bond energy. In fact, the C-S bond energy in benzenethiol is comparable to the C-O bond energy in ethanol, yet the Ni surface is inactive for cleaving C-O bonds while very easily cleaving aryl C-S bonds. The difference is not in the stablility of the Ni-X bond, since Ni-O and Ni-S bonds are energetically comparable. Ethanedithiol undergoes C-S bond scission at a significantly higher temperature than either ethanethiol or mercaptoethanol, despite the similarity in the C-S bond energies. The situation is clearly complex, and will be studied more quantitatively in the future.

---

1. Chemistry Department, University of Tennessee, Knoxville

Adsorption and Reaction of Methanethiol, CH_3SH, on W(001) and Ru(0001).

D. R. Mullins, P. F. Lyman[1]

The adsorption and reaction of CH_3SH on W(001) and Ru(0001) have been studied. The high resolution and sensitivity provided by the soft x-ray excited S 2p photoemission allows quantitative monitoring of decomposition as a function of coverage and temperature. This provides a sensitive measure of changes occurring near the sulfur atom in the molecule. The general reaction pathways are found to be similar to Ni(110). The methanethiol adsorbs through the sulfur atom, losing the sulfhydryl hydrogen at temperatures below 100 K. At low coverages the molecule fully decomposes into atomic sulfur, atomic carbon and gaseous hydrogen. At higher coverages a competing reaction pathway results in the production of atomic sulfur and gaseous methane. Two sulfur containing intermediates can be detected in the S 2p spectra on both surfaces. These intermediates are identified as methyl thiolate species, CH_3S-, adsorbed in different bonding sites. Adsorption in two different sites is not surprising on W(001) since multiple bonding sites for atomic sulfur were previously observed on this surface. Two adsorption states is more unexpected on Ru(0001) since on this surface atomic sulfur exists in only one adsorption state regardless of coverage or the presence of other coadsorbed species.

The details of the decomposition of methanethiol differ significantly on W(001) and Ru(0001). The C-S bond is much less stable on Ru(0001) than on W(001). At low coverages atomic sulfur can be observed at 150 K on Ru(0001) whereas the thiolate intermediates are stable to higher temperatures on W(001). The two intermediate states are populated sequentially on Ru(0001) but are populated concurrently on W(001). One state is distinctly more stable on W(001) however, while both states decompose at about the same rate on Ru(0001). These characteristics can be related to the chemical and structural properties of the surfaces. In general, chemical activity for a variety of reactions has been observed to increase as one progresses across the second and third row transition series. Predictions of such periodic trends have appeared in the literature which predict a higher activity for C-S bond cleavage on Ru than on W, in agreement with these measurements. Bond activation is thought to result from the back donation of substrate electron density

into the adsorbate antibonding orbitals. This transfer is facilitated by bringing the adsorbate into closer proximity with the surface. On W(001) there is a large difference in the adsorbate "height" for an adsorbate in a four-fold site compared to one in a bridge or top site. This difference between a three-fold site and a lower coordination site is much smaller on Ru(0001). Hence one would expect a greater difference in the reactivity of intermediates adsorbed in different sites on W(001) compared to Ru(0001) as observed experimentally.

---

1. NSLS, Brookhaven National Laboratory, Upton, NY

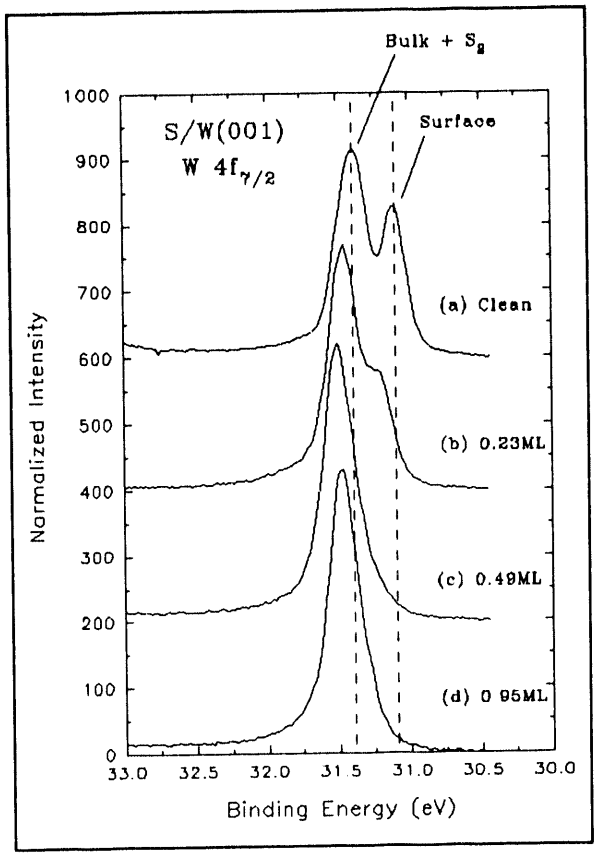
STRUCTURAL STUDIES OF SURFACES BY SXPS AND ION SCATTERING

Chemisorption Studied by Core Level Spectroscopy From the Substrate

D. R. Mullins, P. F. Lyman[1]

In order to better understand the adsorption process, photoemission from the substrate surface atoms provides an ideal complement to the photoemission from the adsorbate. Unfortunately, the signal from the surface atoms is overwhelmed by the large signal from the bulk substrate atoms. Tunable synchrotron radiation provides the means of selecting the kinetic energy of the detected photoelectron in order to minimize the escape depth and thereby optimize the surface sensitivity. In addition, for a number of third row transition metals, and in particular tungsten, the 4f core level photoemission from the surface atoms is shifted in energy and therefore distinguishable from the bulk atoms. The W $4f_{7/2}$ photoemission from W(001) covered with S, C, O and Ni have been obtained as a function of coverage and temperature and the results provide insight for understanding the influence of adsorbates on the substrate photoemission.

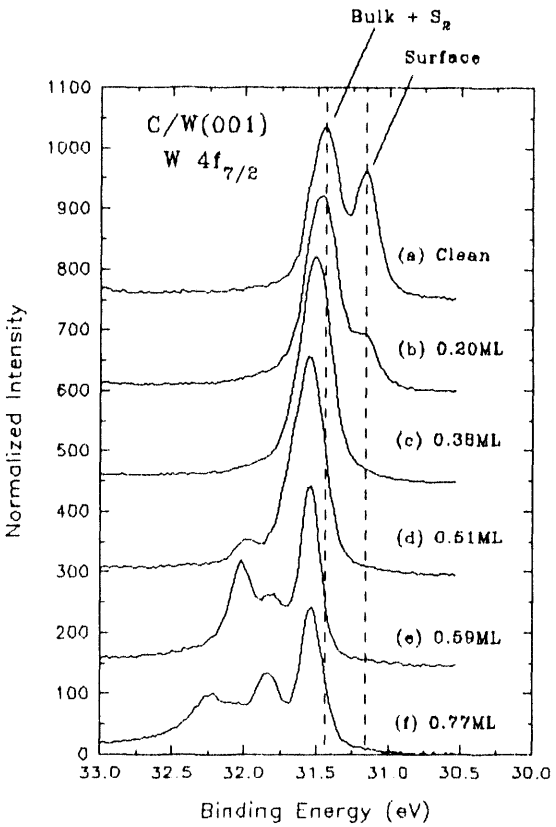
S on W(100). The W $4f_{7/2}$ spectrum from a clean W(001) surface consists of peaks from the bulk and first layer W atoms separated by 0.35eV as shown in the figure below. A third, unresolved peak believed to originate from second layer atoms is present between the two main features. When sulfur is adsorbed, the signal from the top layer is rapidly attenuated and disappears by 0.25 ML of S. Two new, incom-



pletely resolved features appear at higher binding energies. One peak occurs between the surface and bulk peaks. This peak intensity maximizes at 0.25 ML of S and then disappears at 0.5 ML. The other new peak is at a binding energy slightly greater than the bulk peak giving rise to the apparent shift of that peak. The intensity of this peak grows nearly linearly with S coverage. The peak position and the coverage dependance of the sulfur induced features can be correlated with proposed structural and chemical properties of sulfur on W(001). The binding energies are related to the number of sulfur atoms bonded to a given first layer W atom; the more sulfur atoms the higher the binding energy. The first sulfur induced peak maximizes when each surface W atom is bonded to one S atom. It then declines as additional S bonds to the surface. The effect of sulfur apparently saturates when two S atoms are bonded to each surface atom. Above 0.5 ML of S no additional features are observed. The amount of the shift correlates with the electronegativity of S relative to other adsorbates. H induces a smaller shift while O produces a larger one.

C on W(001). In the early stages of adsorption, C produces the same qualitative effect as S. The clean surface peak is rapidly attenuated and the bulk peak appears to shift to higher binding energy as seen in the figure. No new peaks occur between the surface and bulk peaks. Above 0.5 ML of C, at least four new peaks emerge as a function of coverage. There are several differences between the adsorption of C and the adsorption of S which may be related to the more dramatic effect C has on the W 4f photoemission. It was previously demonstrated by ion

scattering that C adsorption is restricted to the four-fold sites. Because of carbon's smaller size, it can pack more closely together than S permitting up to four C atoms to be bonded to a single surface W atom. The small size also allows the C atom to interact more directly with the second layer W atoms. It isn't clear why C induces a greater binding energy shift than S. The initial indication is that a C adatom is more electronegative than a S adatom.



Ni on W(001). SXPS studies of the adsorption of Ni/W(001) have been undertaken to characterize the evolution of surface structure and electronic properties as the metal adsorbate deposits and interacts with the substrate. This is of interest as a preliminary to understanding how reactivity (specifically towards organo-sulfur molcules) varies between Ni and W surfaces. Previous ion scattering studies from this group indicate that strong interaction occurs between the Ni and the W adsorbate. Portions of several synchrotron runs have been expended in an attempt to characterize this system by W core level photoemission, but have been thwarted by problems with impurites (oxygen and metallic), insufficient resolution, or time constraints. Recently, a high quality and extensive data set has finally been obtained. The results exhibit behavior which differs from that observed for oxygen, carbon and sulfur adsorbates. The first monolayer of Ni causes an attenuation of the surface peak in a manner observed for other adsorbates. However, at coverages near and above 2 ML a new feature is resolvable and remains at all higher coverages examined. This feature may be associated with an interface state, associated with W atoms located at the boundary between the substrate and overlying Ni. Interestingly this interface state is

not evident at 1 ML, possibly because the (001) surface is low coordinate. Annealing the room temperature deposited surface to 1000 K, a process known from ion scattering to cause mixing in the interface layer has only subtle effects on the peak shape above 1 ML. Work is in progress to compare these results with published accounts of similar studies and to establish their theoretical basis.

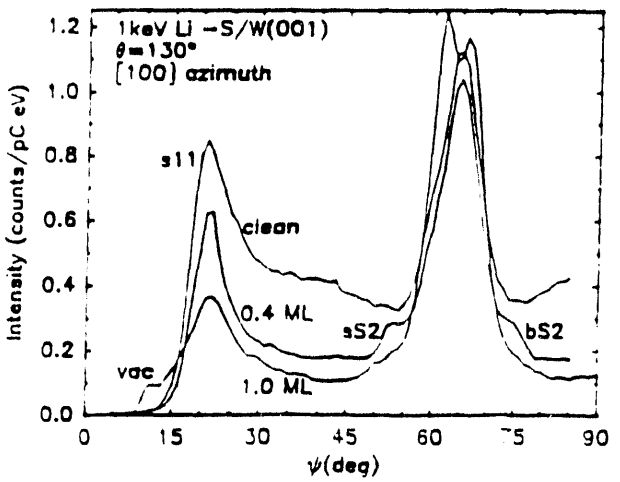
---

1. NSLS, Brookhaven National Laboratory, Upton, NY

Chemisorption and Bi-Metallic Surfaces Studied by Ion Scattering

S. H. Overbury, R.J.A. van den Oetelaar,[1] D. M. Zehner[2]

S on W(001). Ion scattering studies were carried out to investigate the adsorption on and interaction of S with a W(001) surface. This study was motivated by previous ion scattering studies of sulfidation of Ni and Mo surfaces, but more directly by synchrotron based studies of the S 2p SXPS of S on W completed by this group previously. In that study clear evidence was found for two chemically distinct types of sulfur atoms co-existing on the surface at certain coverages and annealing temperatures. The structural nature of the S types and their effect on the substrate structure were not unambiguously determined.



Preliminary ion scattering studies indicate that, for coverages below about 0.4 ML S, the substrate is largely unaffected by S atoms. The shadowing and blocking features from the clean surface are largely unchanged (see the figure) and new features associated with shadowing and blocking by S atoms in four-fold hollows appear. There is evidence for slight relaxation of W atoms in response to the S atoms from the off-azimuth shape of the shadow cone. Above 0.4 ML, larger movements in the surface W atoms occur as indicated in a broadening of a shadowing

edge, especially evident for surfaces annealed to elevated temperatures as seen in the figure. A shadowing feature indicative of significant numbers of surface vacancies or a rippling of the W surface is also apparent near S saturation coverages. This type of movement has now been seen for many adsorbates on W(001) by ion scattering and has been proposed by others from x-ray scattering for O on Mo(001). This behavior is apparently common on (001) faces of Mo, W and their alloys (e.g., Mo-Re). Scattering from S atoms is characterized by two poorly defined critical edges which could be associated with nearest neighbor and next nearest neighbor separations. However, the possibility of two different S heights, perhaps associated with substrate relaxation, has not been eliminated. Work on this problem will continue to clarify several points, and to identify the S types observed by SXPS.

Clean Mo-Re alloy surface. The structure and composition of a clean $Mo_{0.75}Re_{0.25}$(001) alloy surface was analyzed by low energy alkali ion scattering. This problem was investigated first because it is important to achieve a basic understanding of how structure and composition of alloy surfaces are related to chemistry occurring at alloy surfaces and secondly because this particular surface alloy had been previously examined by detailed LEED studies within the ORNL Solid State division. The current state of surface analysis and knowledge of alloy surfaces is such that it is still important to compare experimental techniques in test cases to obtain good experimental corroboration of atomic scale structural parameters such as first and second layer compositions and surface relaxations.

Li^+ ion scattering was performed as a function of incident ion energy, incident polar and azimuthal angles, and laboratory scattering angles. The locations of observed shadowing and blocking edges were fully consistent with the bulk termination structure predicted by the p(1x1) LEED pattern. Incident angles were identified where scattering near the kinematic single scattering energy predominantly originates from the first layer or from first and second layers in comparable amounts. A model was developed to take into account possible contributions from deeper layers. Data from different incident energies and lab angles were collected to vary in a predictable way the relative contri-

butions of deeper layers and differences in scattering cross sections of the Mo and Re atoms. All data were compiled and used to solve the model equations for first and second layer compositions. The critical angles associated with the onset of second layer scattering angles were measured to determine the first-second interlayer spacing of the alloy surface. Variation of incident energy and laboratory scattering angle were also used in these measurements to characterize and eliminate various systematic errors. The results are shown in the following table and compared with LEED results. It is found that Mo is

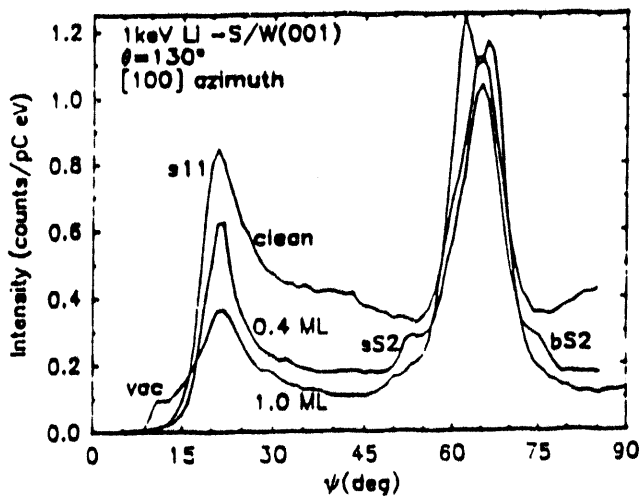
	ISS	LEED
x_1(Re)	.04 ± .01	.04
x_2	.52 ± .05	.47
Δd_{12}(%)	-9 ± 5	-11

strongly surface active, being present in excess at the first layer, but a reversal occurs in the second layer where Re is present in excess compared to bulk composition. There is remarkably good agreement between the ion scattering and LEED techniques, and such close agreement between two independent studies using techniques based on completely different physics provides further credibility to the results. This system now provides a reliable experimental basis for theoretical studies of equilibrium alloy surfaces.

Oxidized $Mo_{0.75}Re_{0.25}$(001) Alloy Surface. The effects of adsorbed oxygen on the structure and composition of a single crystal Mo-Re alloy surface has been studied by low energy alkali ion scattering. The goal of this work is to use a well-characterized model surface to study how adsorbates affect the structure and composition of alloy surfaces and how the adsorbate bonding sites are affected by coverage and first layer structural changes.

Adsorption of oxygen on the $Mo_{0.75}Re_{0.25}$(001) surface is found to alter the structure of the substrate. The p(1x1) LEED pattern associated with the clean surface is rapidly attenuated and poorly defined diffuse features appear with increasing oxygen coverage. Only one sharp LEED

pattern, a p(2x1), is observed and this is obtained over a small range of coverages determined to be near 1.0 ML. The structure associated with this pattern is obtained only for annealing temperatures sufficiently high to allow diffusion of substrate atoms, but not so high as to reduce the oxygen coverage. Detailed ion scattering studies of the p(2x1) surface indicate that this surface has a large number of substrate vacancies, presumably ordered into an alternate missing row structure to yield the LEED pattern. The vacancy formation is clearly indicated by an increase in ion scattering yield at grazing incidence. The location of oxygen atoms atop second layer atoms is indicated by characteristic shadowing features induced by the oxygen. A ball model highlighting the structural features present on the surface is shown in the figure. Analysis of the angle dependence of Re scattering intensity indicates that the low first layer concentration does not increase upon oxygen adsorption and the second layer Re composition decreases. This behavior is rationalized partly by the higher stability of oxides of Mo compared to Re. However the vacancy formation suggests another previously unanticipated factor. Creation of vacancies reduces the coordination of second layer atoms, favoring occupation by the more surface active Mo. This case clearly demonstrates the interplay between structure and composition of alloy surfaces.



---

1. Eindhoven University of Technology, Amsterdam, The Netherlands
2. Solid State Division, ORNL

WORK FUNCTION DEPENDENCE IN RELAXATION OF MULTI-CHARGED IONS

S. H. Overbury, F. W. Meyer,[1] L. Folkerts,[1] I. G. Hughes,[1] D. M. Zehner[2]

Experiments were undertaken to examine the effect of work function

on rate of electronic relaxation of multi-charged ions scattering from metal surfaces. These studies of the interaction of multi-charged ions with metal surfaces have been done at ORNL's ECR ion source in collaboration with members of the Physics and Solid State Divisions at ORNL. Cs dosing of a Au(110) surface was used to vary the surface work function, a modification predicted to affect the critical distance above the surface at which conduction band electrons can neutralize incoming multicharged ions. The predicted enhancement in K-shell Auger relaxation rates of incident N^{6+} was observed for the first time. Theoretical efforts to model the complex ion relaxation process and the effect of surface electronic properties are in progress in the Physics Division and by collaborators at the University of Tennessee. It is hoped that such understanding may lead to the use of these exotic ions as probes of surface or surface adsorbate electronic properties.

---

1. Physics Division, ORNL
2. Solid State Division, ORNL

IMPROVED SURFACE ANALYSIS SYSTEM

D. R. Huntley

During this period, a new high resolution electron energy loss spectrometer was purchased and delivered, and a new ultrahigh vacuum system was custom designed and purchased to house the new spectrometer. A new specimen manipulator was also required and purchased. The new spectrometer has improved resolution and signal intensity and lower background levels than the previous HREELS system. This improvement in performance should provide a tremendous enhancement in identification of intermediates in surface reaction pathways.

In addition, the new UHV system was designed with provisions for having multiple dosers for various kinds of organic compounds. There are currently two conductance limited directed dosers of different design, one for compounds with high vapor pressures such as methanethiol or ethanethiol and one for low vapor pressure compounds such as mercaptoethanol and benzenethiol. Recently, a new method for cleanly dosing

reactive compounds with room temperature vapor pressures less than 1 atm was developed. This method has significantly improved both the cleanliness and ease of dosing compounds such as benzenethiol and mercaptoethanol, both of which are extremely difficult to work with and reactive.

10. PHOTOLYTIC TRANSFORMATIONS OF HAZARDOUS ORGANICS

This research program constitutes a fundamental investigation of the photochemistry of aromatic hydrocarbons (ArH) and polynuclear aromatic hydrocarbons (PAHs) both in heterogeneous and aqueous media by product analysis and *in situ* spectroscopic techniques. Work in this laboratory has demonstrated the dramatic effect which a highly polar surface, such as that of SiO_2, can have on the photochemistry of weakly interacting organics, as typified by unsubstituted ArHs and PAHs. The surface has been demonstrated to influence the kinetics of photodecomposition and the subsequent fate of the initially formed photoproducts. Current research into the heterogeneous photochemistry of PAHs includes (1) the study of a series of substituted naphthalenes at an SiO_2/air interface; and (2) the study of acenaphthylene photochemistry at an SiO_2/air interface. The photochemistry of ArHs and PAHs in aqueous media, though of notable environmental concern, has not been well studied. Initial studies performed in this laboratory revealed photoproducts arising from a previously postulated cation radical pathway. Current research into the aqueous photochemistry of PAHs focuses on naphthalene and acenaphthyelene. These studies are designed to enhance our basic understanding of photochemical processes occurring in aqueous solutions and at industrially and environmentally important interfaces. Among other benefits to be derived from this research is a better understanding of those factors which control the environmental fate and residence times of anthropogenic materials which are generated through the consumption of fossil fuels.

HETEROGENEOUS PHOTOCHEMISTRY

R. T. Dabestani, M. E. Sigman, J. T. Barbas,[1] E. A. Chevis[2]

The influence which solid/air and solid/liquid interfaces have on photochemical events of environmental or industrial relevence continue to be investigated. Typically, the PAH to be studied is adsorbed onto the surface of a solid support from solution in a low boiling organic solvent which is subsequently removed. The solid supports investigated in this work are all highly polar, non-semiconducting, materials such as silicas and aluminas. These materials are ubiquitous in the environment and constitute a series of supports for modeling photochemical events in natural settings. The interaction of the PAH with the surface is investigated by determining isotherms for the adsorption process and through spectroscopic investigations utilizing reflectance and emission

spectra as well as excited state lifetime determinations. Photoproducts are removed from the support and analyzed by GC, GC-MS, and HPLC.

Photolysis of Substituted Naphthalenes at an SiO_2/air Interface

Substituted naphthalenes are known to be photooxidized in TiO_2/CH_3CN slurries to give the corresponding substituted phthalates. This is well studied chemistry involving excitation of the semiconductor, TiO_2, and subsequent oxidation of the naphthalene by electron transfer to the positive center in the valence band of TiO_2. Research in our laboratory has shown that similar photoproducts can be derived from the photolysis of substituted naphthalenes at highly polar, yet insulating, interfaces. Photooxidation on insulating surfaces is initiated by direct electronic excitation of the substituted naphthalene.

Photolysis of naphthalene at an SiO_2/air interface proceeds to give phthalic acid, 49% yield, as the only isolable photoproduct. Similarly, photolysis of naphthalene at an Al_2O_3/air interface proceeds to give phthalic acid in 31% yield. Photolysis on both solids also produces an intractable colored material which could not be further characterized. The photolysis of 1-methylnaphthalene at an SiO_2/air interface leads to the formation of 2-acetylbenzoic acid, 35% yield, and 1-naphthaldehyde, 6% yield. Photolysis of 1-cyanonaphthalene under similar conditions does not lead to observable photodecomposition on extended irradiation. Photolysis of a series of substituted naphthalenes has been carried out at two surface loadings, 2.5×10^{-5} mol/g and 2.5×10^{-6} mol/g. These surface loadings correspond to less than 3% of a monolayer. The photodecomposition is observed to occur more slowly by a factor of approximately two at the higher surface loadings. The decreased rate at the higher surface coverage is not attributable to an excimer emission pathway which would result in an inefficient use of excitation energy. The faster rate at lower surface coverage is postulated to arise from stronger interactions of the adsorbate and the surface which enhances the stabilization of polar intermediates formed in the reaction. This thesis is supported by the observed Freundlich adsorption isotherm for the adsorption of the substituted naphthalenes onto the SiO_2 from a cyclohexane solution.

Two oxidation mechanisms are thought to be operative in these photoreactions. One mechanism involves the transfer of an electron from an excited state of the substituted naphthalene to oxygen, generating a cation radical-superoxide pair. The superoxide formed from the photolysis of unsubstituted naphthalene on SiO_2 has been observed by electron spin resonance spectroscopy. The possible involvement of singlet oxygen is currently being investigated. Singlet oxygen can be generated by in situ photolysis of coadsorbed methylene blue. The methylene blue is irradiated at 650 nm, far to the red of the lowest energy electronic transitions associated with the substituted naphthalenes. Singlet oxygen prepared in this fashion readily reacts with good acceptors. 1-Methoxynaphthalene, for example, reacts with singlet oxygen at an SiO_2/O_2 interface to produce 4-methoxy-1,2-naphthoquinone and 1,4-naphthoquinone. Direct photolysis of 1-methoxynaphthalene on SiO_2 generates 1,4-naphthoquinone, 32%, 4-methoxy-1,2-naphthoquinone, 23%, and phthalic acid and mono-methylphthalate in combined yield of 20%. Furthermore, the two quinones are formed in the same ratio in both the direct photolysis and the singlet oxygen sensitized reaction.

Photodecomposition of Acenaphthylene on the Surface of SiO_2

Previous work on photolysis of acenaphthylene adsorbed on the surface of SiO_2 claimed photodimerization to *cis* and *trans* dimer as a major path to acenaphthylene decomposition; however, the presence of photooxidation products was not indicated. The ratio of *cis/trans* dimer was shown to vary as a function of surface loading and was found to be about 0.6 at the lowest coverage, approximately 1.4% of a monolayer. We have re-examined the photolysis of acenaphthylene at an SiO_2/air interface. The research has revealed that acenaphthylene undergoes photooxidation as well as dimerization when photolyzed at low surface coverage (2.5×10^{-5} moles/g, 3.7% of a monolayer) on SiO_2. The same oxidation products are observed when singlet oxygen was generated in situ by irradiation of coadsorbed methylene blue. This result suggests that oxidation is mediated by the addition of singlet oxygen ($^1O_2$) to ground state acenaphthylene. Although photooxidation of acenaphthylene accounts for a significant portion of its loss, our recent results have shown that photodimer yield increases as the surface coverage is

increased. We observed formation of both *trans* and *cis* dimer in a ratio of *cis/trans* = 13 (surface loading 2.5 x 10^{-5} moles/g) under aerated conditions. These observations suggest that at low surface coverage dimerization in the presence of oxygen takes place from both the singlet and the triplet manifolds. This conclusion follows from the fact that trans dimer can only form from the interaction of acenaphthylene triplet with ground state acenaphthylene. When photolysis of acenaphthylene was carried out in the presence of a singlet oxygen trap such as 2,5-dimethylfuran or N,N-dimethylaniline co-adsorbed on the surface, the only products observed were acenaphthylene dimers and oxidized trap. The absence of oxidation products derived from acenaphthylene under these conditions clearly confirms the role of singlet molecular oxygen in this process. Accordingly, no photodimers were observed when photolysis was carried out in the presence of methylene blue as a sensitizer. In contrast to the photolysis of naphthalene at an SiO_2/air interface, photolysis of acenaphthylene under these conditions did not produce any superoxide which could be detected by electron spin resonance spectroscopy.

Our photoproduct studies of photolyzed acenaphthylene on SiO_2 under a variety of conditions have revealed that oxidation products of acenaphthylene are formed by the addition of singlet molecular oxygen to ground state acenaphthylene. The observed oxidation products are: 2-hydroxy-1-acenaphthenone (3%), 1,2-acenaphthenedione (4%), 1,8-naphthalenedicarboxaldehyde (50%) and 1,8-naphthalic anhydride (3%). Dimerization which accounts for about 40% of acenaphthylene loss, on the other hand, appears to be primarily singlet derived. Thus, photodecomposition of acenaphthylene adsorbed in low surface coverage at an SiO_2/air interface is an efficient process which proceeds to give oxidation products in about 60%. This is a process which has not been reported previously. The remainder of the material balance is accounted for as dimer, about 40%, deriving primarily from the singlet manifold.

AQUEOUS PHOTOCHEMISTRY

M. E. Sigman, E. A. Chevis[2]

Research into the fates of PAHs in aqueous solutions under photolytic conditions continues in this laboratory. Previous investigation

by other researchers into the aqueous photochemistry of unsubstituted PAHs have focused primarily on determination of the quantum yields for the photodepletion of these materials. The PAHs studied in this program are dissolved in water without the aid of an organic co-solvent. This approach eliminates any concerns of selective solvation and limits the upper working concentration of each PAH to it's aqueous saturation solubility. Isolation, identification and quantitation of the products of PAH photodecomposition in water constitute a major portion of this work. Analysis and spectroscopic techniques similar to those used in the heterogeneous photochemistry program are also utilized in this work.

Photolysis of Naphthalene and Acenaphthylene in Water

The photodepletion of naphthalene in water has been found to approximate first-order kinetics through the first three half-lives. The reaction is not strictly first order, as demonstrated by the observed concentration-dependent quantum yield for photolysis. An analysis of the initial rate data indicates that the reaction proceeds with an overall kinetic order of approximately 1.3. The quantum yield data becomes concentration-independent, quantum yield approximately 5×10^{-3}, at concentrations below 5×10^{-6} M. At higher concentrations, the quantum yield is concentration-dependent. Previous investigations of the photophysics of naphthalene by S. Steenken has shown that the cation radical is formed in water upon excitation. The formation of the cation radical was determined to be a two photon process based on laser power-dependence of the transient intensity in a series of absorption experiments. Two photon processes are not possible under the low light flux conditions of our experiments, and we have shown that the photodecomposition is indeed monophotonic at both high and low concentrations of naphthalene. Previous work by other researchers reports that singlet oxygen addition to naphthalene is very inefficient. Furthermore, changes in the absorption spectrum of naphthalene during photolysis indicates a complex mechanism based on the absence of an isosbestic point. Further mechanistic and product studies on the aqueous photochemistry of naphthalene are currently underway.

Initial results from a study of the aqueous photochemistry of acenaphthylene indicate a unique mix of photooxidation and photodimeri-

zation. Photolysis of an 8 x 10^{-5} M solution of acenaphthylene in water resulted in the formation of 1,8-naphthalenedicarboxaldehyde, acenaphthone, 1-acenaphthenol, acenaphthenone, 2-hydroxy-1-acenaphthenone, 1,8-naphthalic anhydride, and both *cis* and *trans* dimers. In the aqueous photolysis the yields of the two dimers, *cis* and *trans*, are approximately equal at low conversions. Dimerization from the S_1 state leads only to the *cis* dimer, whereas dimerization from the T_1 state is reported to lead to both the *cis* and *trans* dimers in comparable yields. The quantum yield for photolysis of acenaphthylene in water is directly proportional to the concentration, and the reaction is strongly inhibited by oxygen. The observed ratio of *cis/trans* dimer formed upon photolysis in water, and the quenching of the reaction by oxygen indicate that the T_1 state plays an important role in dimer formation. Work is underway to quantitate the products formed from the photolysis of acenaphthylene in water and to further delineate the mechanism of photodecomposition.

---

1. Valdosta State University, Valdosta, GA.
2. Oak Ridge Research Institute, Oak Ridge, TN.

11. DNA SEQUENCING AND MAPPING

The Human Genome Program is an ambitious effort with the goal of initially constructing a high resolution genetic map and later locating and sequencing the estimated 100,000 genes found within the 23 human chromosome pairs. Some of the objectives of the program are to complete a physical map of the chromosomes by 1995 and completely sequence the genome within 15 years. If this task is to be accomplished in this period of time, faster, less expensive, and less labor intensive methods of DNA sequencing and mapping must be developed. One method of achieving greater speed in DNA sequencing and mapping is to employ multiple, unique labels in a process called multiplex analysis. We have focused on metal-centered organic compounds and a variety of detection methods as a strategy for devising more efficient DNA labeling methods. Mass labels using iron, tin, and the lanthanide elements, electrochemically detectable ferrocene derivatives, and luminescent complexes of the lanthanides have been prepared and tested. Other work has focused on the chemical modification of surfaces so that DNA can be attached to these surfaces for imaging by scanning probe microscopy.

STABLE ISOTOPE LABELS

G. M. Brown, M. J. Doktycz,[1] J. E. Elbert,[2] M. L. Garrity,[2] K. B. Jacobson,[3] R. A. Sachleben, F. V. Sloop[3]

The metallic elements we employ are not natural constituents of DNA and each isotope of these elements can serve as a unique label. Resonance ionization spectroscopy-mass spectrometry (RIS/MS) is a highly specific, very sensitive, laser-based analytical technique that affords selectivity by element and isotope and thus is ideal when dealing with discrete mass labels. Associating the detected isotope with one of the four bases of DNA in a sequencing reaction for which it was used then permits the positive identification of the sample fragment. Elements that are readily ionized by the laser based RIS method and have four or more stable isotopes are potential candidates for DNA sequencing labels.

Triethylstannylpropanoic Acid Labels

Considerable effort has been directed toward the development of tin isotopes as labels for DNA. Tin forms stable organometallic compounds and has ten isotopes, eight of which are commercially available. The

organotin compound triethyl-stannyl propanoic acid (TESPA) was selected as a likely carrier molecule for tin isotopes and its NHS ester (N-hydroxysuccinimidyl triethylstannylpropanoate) could be readily reacted with an oligomer's 5'-terminal amine for the covalent attachment of the carrier. Adapta-tions of literature synthetic methods resulted in a seven-step synthesis (Figure 11.1, Scheme A) for the production of NHS-TESPA, with a 20-25% overall yield from tin oxide.[4] Subsequent efforts to improve the synthesis of this compound resulted in a five-step scheme (Figure 11.1, Scheme B) that relied on one less chromatographic procedure, avoided a troublesome side reaction, and increased the overall yield by 60%.[5]

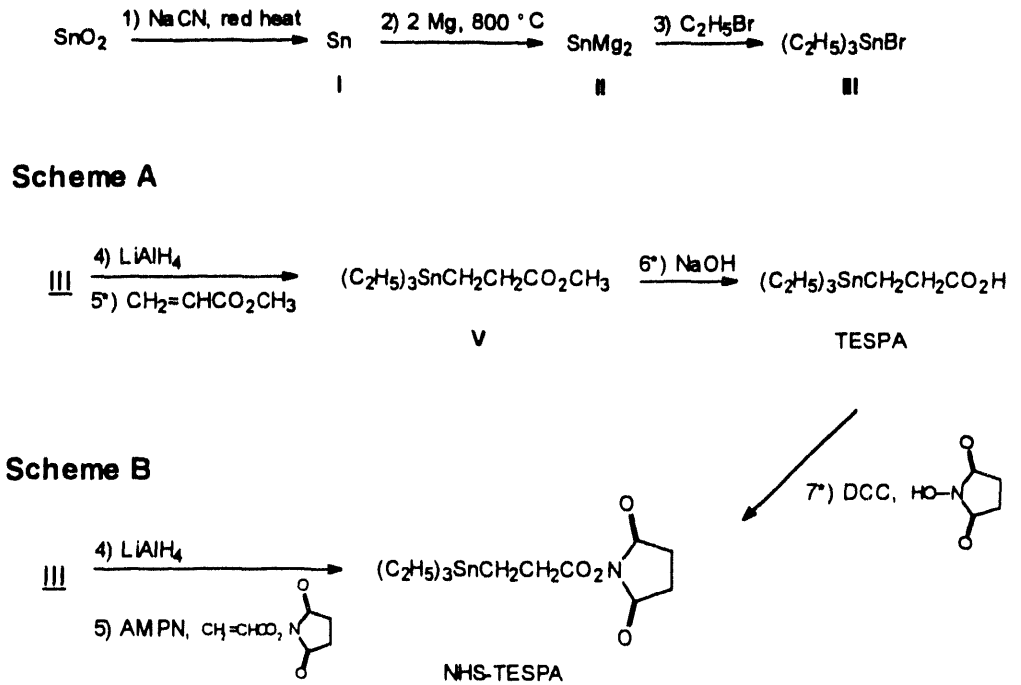


Figure 11.1 Synthesis of NHS-TESPA. Tin oxide (SnO_2), enriched in a given isotope, was the source of tin. Reactions 1-4, leading to triethylstannane (IV), were common to both the previously described synthetic route (Scheme A) and the improved synthetic route (Scheme B).

The improvement in the TESPA synthesis (Figure 11.1, Scheme B) came after the production of triethylstannane. This product was reacted with N-acryloxysuccinimide in the presence of the free radical initiator

2,2'-azobis(2-methylpropionitrile) (AMPN) to yield NHS-TESPA. This synthetic route resulted in a higher final product yield with fewer synthetic steps. The final product, NHS-TESPA, was later attached, through an amide linkage, to oligodeoxynucleotide primers for use in Sanger sequencing and polymerase chain reactions (PCR).

All eight commercially available stable isotopes of tin (^{112}Sn, ^{116}Sn, ^{117}Sn, ^{118}Sn, ^{119}Sn, ^{120}Sn, ^{122}Sn, ^{124}Sn) have been incorporated in TESPA carriers for use as DNA labels. The usefulness of TESPA as a DNA reporter has been demonstrated in a number of practical applications. The label has been shown to be stable in the standard molecular biology procedures involved in Sanger dideoxy sequencing and PCR operations, and it readily survives the electrophoretic separation process. Tin-labeled DNA fragments, arising from both PCR and Sanger sequencing reactions, have been successfully detected by RIS/MS in the gels in which they were electrophoretically separated.

Lanthanide Ion Labels

There are 50 stable isotopes of the elements in the lanthanide series (elements with atomic number 57 to 71) having an abundance of 0.1% or greater. When bound by a ligand system which attaches the Ln(III) ion to DNA, the electrophoretic mobility of all the lanthanide elements should be practically identical, creating an attractive system for multiplex analysis with mass labels. A derivative of the macrocyclic chelating agent, 1,4,7,10-tetraazacyclododecane--1,4,7,10-tetraacetic acid (DOTA) was used to attach lanthanide ions to oligonucleotides.

A high-yield, general synthetic route was developed for the synthesis of derivatives of DOTA with an aryl substituent at one of the ethylene carbon atoms. Benzyl and 2-naphthylmethyl derivatives have been prepared by this pathway. The methyl ester of the aryl substituted alanine is the starting material for the synthesis of substituted DOTA ligands. Tosyl protection of the amine followed by reaction with ethylenediamine, further protection, and reduction yield the tosyl protected diethylenetriamine with an aryl substituent. Ring formation was accomplished by treatment with cesium carbonate and 2,2'-(tosyl-

imino)bisethyl ditosylate (Richman-Atkins conditions). Deprotection was accomplished by reduction with lithium tetrahydroaluminate and the acetate arms were attached by treatment with the t-butylester of bromoacetic acid. Acid hydrolysis of the t-butyl groups yielded the tetraacetic acid of the aryl substituted tetraazacyclododecane.

Nitration of a benzyl substituent provided a point of attachment of the ligand to DNA. Nitration of the phenyl group was accomplished at the tetraazacyclododecane intermediate and gave primarily the desired para-isomer. The acetate arms were added to the nitro-substituted macrocycle with t-butylbromoacetate as previously outlined. Our procedure for preparation of p-nitrobenzyl-DOTA is a considerable improvement over the previously reported procedures both in terms of the yield and the ease of purification of the intermediates and final product. The nitro group was reduced to an amine with hydrogen over a Pd catalyst and reacted with thiophosgene to produce the benzylisothiocyanate derivative of DOTA. The reaction of the isothiocyanobenzyl-DOTA with the 5'-hexylamine linker arm of a synthetic primer covalently attaches the ligand to the oligomer. The HPLC-purified ligand-primer complex was reacted with an excess of aquated $EuCl_3$ followed by separation of the Eu-oligonucleotide adduct from excess Eu(III) by a final HPLC purification step.

Adding the isothiocyano-DOTA reagent to the hexylamine oligonucleotide while it is still attached to the controlled pore glass (CPG) column on which it was synthesized allowed us to eliminate several time-consuming HPLC purification steps. The CPG column was removed from the automated synthesis machine, and isothiocyano-DOTA was added to the amine group of a CPG support-bound 17-mer sequencing primer. The DNA-DOTA ligand adduct was then reacted with a large excess of $EuCl_3$, the CPG was washed well to remove uncomplexed Eu(III), and the Eu(III)-labeled oligonucleotide was cleaved from the CPG support and purified by HPLC.

Preliminary experiments using Eu(III) complexed by isothiocyanobenzyl-DOTA as a DNA label have been quite promising. The M13-Eu(DOTA) primer was tested in the Sanger sequencing procedure against an underivatized primer, and the ^{32}P-radiolabeled reaction products compared

following slab gel electrophoresis. Autoradiographic results indicate that the presence of the label did not interfere with the enzymatic synthesis of DNA and that the label was stable to the conditions of electrophoresis.

---

1. Postdoctoral Research Fellow, ORNL Biology Division.
2. Postdoctoral Research Fellow.
3. ORNLBiology Division.
4. R. A. Sachleben, G. M. Brown, F. V. Sloop, H. F. Arlinghaus, M. W. England, R. S. Foote, F. W. Larimer, R. P. Woychik, N. Thonnard, and K. B. Jacobson, *Genet. Anal. Tech. Appl.* **1991**, *8*, 167-170.
5. F. V. Sloop, G. M. Brown, R. S. Foote, K. B. Jacobson, K. B., and R. A. Sachleben, *Bioconjugate Chem.* (in press).

LUMINESCENT LANTHANIDE IONS AS LABELS FOR DNA

G. M. Brown, J. E. Elbert,[1] M. L. Garrity,[1] R. A. Sachleben, T. J. Sworski[2]

Fluorescent reporters are preferable to the traditionally used radioactive labels for DNA since they permit the multiplexing of samples, although the organic dyes which have been used to date have broad emission maxima which seriously limit the number of simultaneously employed dyes. The lanthanide ions Sm(III), Eu(III), Tb(III), and Dy(III) have luminescent excited states in fluid solution which are long-lived, metal centered f-f states. A different detection approach, utilizing pulsed-excitation and time-gated emission analysis, can take advantage of these long lifetimes for enhanced background or impurity fluorescence rejection. The bandwidths are quite narrow, even at room temperature, which allows multiple probes to be detected simultaneously with little overlap of emission. The f-f transitions of the lanthanide elements have very low oscillator strengths, and the emission intensity at fixed excitation intensity can be greatly enhanced if the excitation is ligand localized to a conjugated π-system (high extinction coefficient) having an energetic triplet state. Energy transfer from a ligand-based state to the emitting state of a lanthanide ion has been demonstrated to occur with high efficiency. Naphthalene is one group which has a lowest triplet energy state appropriate to transfer energy to Sm, Eu, Tb, or Dy. The organic moiety thus acts as an antenna to

efficiently direct excitation energy to the Ln(III) ion and allows the use of a single excitation wavelength for all Ln(III) ions.

Efficient energy transfer from an organic triplet state to the Ln(III) ions in amine-carboxylate ligands was previously demonstrated in a naphthyl substituted derivative of the non-cyclic ligand diethylene-triaminepentaacetic acid (NapDTPA). We have also prepared the ligand 2-(2-naphthylmethyl)-DOTA by the methods outlined in the previous section, and Ln(III) complexes with this ligand were generated. Emission spectra were obtained for the Eu(III), Tb(III), and Sm(III) complexes by excitation of the naphthalene group. Sharp bands characteristic of the emission from f-f states of Ln(III) ions were observed. Strong lines were observed at 545 nm, 598 nm, and 615 nm for the Tb(III), Sm(III), and Eu(III) complexes, respectively. The Dy(III) complex is expected to have a strong line at 575 nm.

The time dependence of emission at 615 nm from Eu(NapDOTA) reflects rate limiting transfer of excitation energy from the naphthalene triplet to the emitting Eu(III) excited state. The fitted rate constant for intramolecular energy transfer is 1.2×10^5 s^{-1}, and this value compares well with the rate of energy transfer from excited naphthalene to Eu(III) in Eu(NapDTPA) (1.0×10^5 sec^{-1}). Energy transfer from the triplet state of naphthalene to the Ln(III) center in Tb(III) complexes is more complicated than the behavior observed for the analogous Eu(III) complexes. The photophysics of the complex Tb(NapDTPA) were studied in detail by initial excitation of both the naphthalene and Tb(III) centers followed by studies of the time dependence of the emission from the Tb(III) center at 545 nm. Flash photolysis, with detection of the triplet state of naphthalene by transient absorbance measurement, was investigated following excitation of the naphthalene center at 308 nm. The results of these studies, when considered in reference to an energy level diagram of the Tb(NapDTPA) complex, suggest that energy transfer from T_1 of naphthalene to Tb is a reversible process. The energies of the naphthyl excited state and the Tb(III) excited states are roughly equal, and energy transfer can also occur from the Tb(III) based state to the naphthyl group. The following reaction scheme appears to account for the observations:

$$\begin{array}{ccccc} {}^{*}\text{Nap-Tb} & \rightleftharpoons & \text{Nap-}{}^{*}\text{Tb} & & k_1,\ k_2 \\ k_4 \ \llcorner\text{--->} & \text{Nap-Tb} & \text{<---}\lrcorner\ k_3 & & \end{array}$$

where * indicates the electronically excited species. Equations have been solved to describe the time dependence of the concentrations for the general reaction scheme describing this process. However the observed "rate constants" are a complex function of the rate constants for the individual steps in the reaction scheme. The value of k_3 is taken to be 4 X 10^2 sec^{-1}, the rate constant for decay of *Tb(DTPA). The rate of decay of Gd(*NapDTPA), as observed by transient absorption spectroscopy, is 1.0 X 10^5 sec^{-1}, and this value is an approximation to k_4. The calculated values of k_1 and k_2 are 3.3 X 10^5 sec^{-1} and 1.3 X 10^4 sec^{-1}, respectively.

Work is in progress to create a DOTA ligand which has the antenna molecule more intimately attached to the Ln(III) ion. Reversible energy transfer between the excited naphthyl antenna and Tb(III) leads to a loss of emission intensity. Greater lanthanide luminescence intensities can be achieved by using sensitizers of higher triplet energy, greater absorption extinction coefficients, and larger intersystem crossing yields. The acetophenones have triplet energies several kcals/mol greater than the metal excited state and intersystem crossing yields near 100%. The placement of the sensitizer in an arm position will enhance the energy transfer by increasing the orbital overlap of the sensitizer and metal. A tetraazacyclododecane with three acetate arms (DO3A) will be made by a literature procedure, and the fourth nitrogen will be alkylated with 2-bromoacetophenone.

---

1. Postdoctoral Research Fellow.

2. ORNL Chemistry Division, Retired.

ELECTROCHEMICALLY ACTIVE FERROCENE DERIVATIVES AS LABELS FOR DNA

F. V. Sloop,[1] G. M. Brown, R. A. Sachleben

The use of ferrocene as a label for DNA was first demonstrated using this organometallic compound as a carrier for iron isotopes in the

stable isotopes program. The intrinsic electroactivity of ferrocene provides an alternative means for identifying DNA fragments derivatized with this compound. Amperometry of electroactive species has demonstrated sensitivity levels in the femtomole and attomole range. Since electrochemical detection has the required sensitivity and the ferrocenecarboxylamide group functions as a primer for both the Sanger sequencing procedure and PCR amplification of DNA, a new project was begun to take advantage of these properties to create new reporters for DNA sequencing and mapping. We intend to combine amperometric detection and capillary gel electrophoresis into a powerful integrated analytical system. The half-wave potential of the Fe(II)/Fe(III) couple in ferrocene derivatives varies with the substituent conjugated to the cyclopentadienyl ring. This makes possible a series of unique labels, in the form of different ferrocenecarboxylic acid derivatives. Efforts are currently underway to synthesize a number of ferrocene derivatives (in the form of NHS esters) for attachment to DNA primers.

Amperometric analyses of electroactive substances, undergoing capillary electrophoretic separations, requires that those analytes be transported to an electrochemical cell that is outside (off-column) of the high voltage separation field to limit interference with the electrochemical analysis cell. The electroendosmotic flow of solution within the capillary during capillary zone electrophoresis (CZE) provides a means for transport of species from the column. However, capillary gel electrophoresis (CGE) must be used to separate oligonucleotides since the gel introduces the necessary frictional component required to successfully discriminate DNA fragments by size. Electroendosmotic flow is suppressed during CGE, and an alternative method, such as the use of the sheath flow cuvette, is required to transport labeled DNA fragments to the off-column analytical cell. The simplest cell consists of a working electrode with a fixed potential relative to a reference electrode. DNA fragments, tagged with electroactive ferrocene derivatives, are directed to this cell and detected by the anodic current. Design features for an analytical cell suitable for integration into a capillary gel electrophoresis system are currently under consideration. Efforts are being directed toward the design of

both a simple, single working electrode system, and a multiple working electrode system capable of detecting several electroactive species concurrently.

---

1. ORNL Biology Division.

CHEMICAL MODIFICATION OF SURFACES FOR THE IMMOBILIZATION OF DNA

D. P. Allison,[1] L. A. Bottomley,[2] G. M. Brown, K. B. Jacobson,[3] J. J. Schrick,[3] T. Thundat,[1] R. J. Warmack,[1] R. P. Woychik[3]

The scanning tunneling microscope (STM) and the atomic force microscope (AFM) are relatively new and potentially powerful instruments for imaging biological materials. One major problem in imaging DNA is the instability of the DNA on its mounting surface to forces exerted by the scanning probe. A typical result is that most molecules are removed by tip forces, and only portions of the molecules trapped in adsorbate patches or in surface irregularities are imaged. We have found that surfaces can be chemically treated to attract DNA and these surfaces can be used routinely and reproducibly to image DNA by STM or AFM. Radioscintillography and autoradiography of ^{32}P-labeled DNA were found to be a quantitative measure of the binding of DNA to chemically modified surfaces. Chemically modified surfaces were compared to water treated surfaces for their ability to hold labeled DNA. This assay was found to be an effective screening method in identifying surface active reagents that should bind DNA tightly enough to resist translocation by the probe tip.

Alkanethiols and alkanedisulfides adsorb from solution onto gold surfaces to form strong Au-S-C bonds, and for long-chain alkane groups this adsorption results in a self-assembled, densely packed monolayer on the surface. The solution solid interface can be conveniently functionalized by changing the head group of the alkanethiol adsorbed on the gold surface. The affinity of DNA for gold surfaces modified by the adsorption of ethanethiol derivatives with carboxylic acid, alcohol, and amine groups was determined. DNA had a greater affinity for the surfaces modified with thiols having protonated amine groups (cystamine and 2-dimethylaminoethanethiol) than for the surface modified by 2-

mercaptoethanol. The affinity of DNA for the latter surface was approximately equal to that of a water-treated gold surface. Reproducible STM images of entire molecules of uncoated plasmid DNA were obtained using 2-dimethylaminoethanethiol to chemisorb the DNA to gold. However, most of the images show negative contrast, indicating the tip apparently moves down as it traverses a DNA strand. The STM functions by moving the piezoelectric transducer to keep the tunneling current constant, and these results are consistent with a greater tunneling barrier through the DNA molecule.

The AFM has the ability to obtain high resolution images on non-conducting as well as conducting surfaces, and like STM, it can be operated either in air or a liquid environment. Mica, an atomically flat insulator, is ideally suited for use with the AFM. Images of DNA on mica by AFM can be routinely obtained by simply drying a drop of a DNA containing-solution onto a freshly cleaved surface. These structures are probably stabilized by hydrogen bonding of Si-OH to DNA. However aggregation, network formation, and some degree of "super twisting" were observed in images of both linear and circular DNA on untreated mica. "Super twisting" of DNA is probably due to capillary forces acting on the molecule during the drying process. The surface of mica can be modified by substituting metal ions for the potassium of natural mica in an ion exchange process. DNA adsorbed on mica surfaces modified by substitution with Mg(II), Co(II), La(III), and Zr(IV) show excellent images of open circular DNA with little indication of "super twisting." The enhanced stability of DNA adsorption on chemically modified mica is probably due to increased electrostatic interaction between DNA and the surface. Unfortunately, this interaction was not strong enough to obtain satisfactory images under an aqueous buffer solution. The surface of mica was chemically modified with the silane reagents, 3-aminopropyltrimethoxysilane and trimethoxysilylpropyl-N,N',N"-trimethylammonium chloride, in an effort to create a positively charged surface for adsorption of DNA. These reagents react with the Si-OH groups to attach the amine or quaternary ammonium groups with an inert Si-O-Si linkage. Images of DNA on these modified surfaces were not persistent under solution. Work is in progress to modify the

surface of mica with a silyl-epoxy reagent so that a covalent bond can be formed between DNA and the surface.

---

1. ORNL Health and Safety Research Division.
2. Department of Chemistry and Biochemistry, Georgia Institute of Technology
3. ORNL Biology Division.

12. SPECIAL TOPICS

12.1 MICROEMULSION FUELS

A. L. Compere, W. L. Griffith, J. S. Johnson, Jr.,[1] V. Krishnan,[2] R. Triolo,[3] P. C. Ho

The challenge of meeting increasingly stringent emissions standards, coupled with the need to increase use of domestic fuel sources, is encouraging evaluation of new fuel and combustion technologies. Microemulsion technology can permit formulation of functional high-oxygenate middle distillate fuels for boilers, heating, power generation, or road use. Because the dispersed aggregate size is typically 3 to 8 nm, the current generation of microemulsion fuels is clear, stabilized by its own Brownian motion, and low in viscosity. Microemulsion techniques have been demonstrated to permit formulation of diesel fuels which have adequate ignition delay but which contain up to half oxygenates. Correlation of composition and physical solution structure using neutron scattering and phase studies has yielded some insights into the construction of stable, high-oxygenate fuels. In the last two fiscal years, correlations between surfactant composition and ignition delay have led to the ability to make a broad range of fuels which combine high concentrations of oxygenates with acceptable performance in conventional equipment. In early tests, the fuels have shown decreases in NO_x emissions under normal operating conditions. This technology could make a significant contribution to meeting the Clean Air Act.

Novel Fuel Systems

A. L. Compere, W. L. Griffith

Studies of microemulsion fuels with modified combustion properties are ongoing. Using this technology, it has been possible to modify fuel structure to incorporate liquid and solid emissions control compounds. The fuel systems currently under investigation substantially decrease the amount of NO_x emissions from both research and large stationary diesel engines. Combustion modeling to permit better understanding of these systems is ongoing. Collaborative experiments with the combustion

group at Princeton University are also under way. This research has benefited from cooperation with both engine developers and petroleum companies.

Since a broad range of functional fuel compositions is now available, the project is changing focus to explore the correlations between dispersed aggregate physical structure, combustion pattern, emissions, and bulk solution composition. Because combustion chemistry is extremely complicated, we intend to start with stationary and falling drop combustion of model compound systems. The results from these studies will be used to design flow reactor kinetic experiments. Throughout the process, combustion experiments with standard diesel fuels under normal operating conditions will be used as a check for potential applicability. The results are expected to be applicable to middle distillate fuels for boilers, road, and stationary diesel engines.

Alcohol Partition in Water-in-Oil Systems

W. L. Griffith, J. S. Johnson, Jr.,[1] R. Triolo[3]

Microemulsions for fuels typically are comprised of hydrocarbon, water, surfactant and alcohol. With collaborators at the University of Palermo, we have carried out small-angle neutron scattering (SANS) studies of a model system containing oleate surfactant, water, alcohol, and hexadecane.[4] Recent attention has been to the effect of size (1-pentanol to 1-octanol) and quantity of alcohol on the aggregates for two composition ranges, expressed as moles/mole of potassium oleate: $C_{16}H_{34}$ 5.5, D_2O 30; and $C_{16}H_{34}$ 15, D_2O 45. As in earlier studies, the fits to the patterns over all compositions were best by monodisperse oblate ellipsoids of axial ratios about 0.5. The conclusion is strengthened here by the use in polydisperse fits of an analytical integration of the Blum and Stell expressions for a gamma (Schulz) distribution,[5] rather than approximate methods used earlier. As before, particle size increases with increasing water/surfactant ratio, and the function of the alcohol as cosurfactant is reflected in decrease in aggregate dimensions with increase in alcohol content, ratios of other components being constant. The major axes varied from 50 to 130 Å over the compositional range.

From literature values of the areas at hydrocarbon-water interfaces occupied by carboxylate and alcohol hydroxyl groups, the distribution of alcohols between the hydrocarbon and aqueous phases can be estimated. Figure 12.1 summarizes the fraction of total alcohol in the particles as a function of moles alcohol/mole oleate for the high-D_2O set. It can be seen that for a given alcohol, the fraction decreases with increasing stoichiometric alcohol. In accord with the increasing hydrophobicity of higher alcohols, the fraction decreases with chain length.

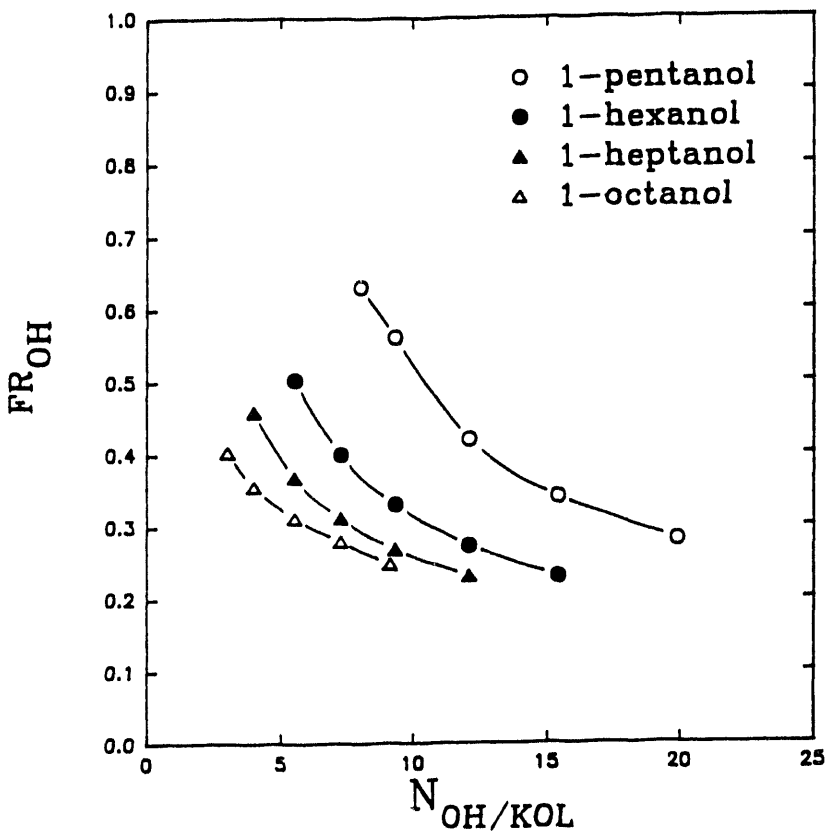


Figure 12.1. Fraction of the total alcohol in the shall as a function of the stoichiometric alcohols to surfactant molar ratio. (Molar ratios of all systems: hexadecane/oleate, 15.0; H_2O/oleate, 45.0)

Micelles of low-equivalent-weight amphiphiles

W. L. Griffith, P. C. Ho, J. S. Johnson, Jr.[1]

Low-molecular weight organic salts, such as sodium cymene sulfonate, have been shown to have solubilizing properties for hydrocarbons in water similar to surfactants. Lower members have been reported not to have critical micelle concentrations in water solutions, but SANS has

indicated that aggregation does occur, e.g., between 1 and 2 *M* for sodium toluene sulfonate. We have collected patterns for a number of examples. From preliminary analysis, numbers of monomers per aggregate range from about 8 for 2.6 *M* sodium *p*-toluene sulfonate to 30 for 0.75 *M* sodium 2,4,6 triisopropyl benzene sulfonate.

---

1. ORNL, retired.
2. University of Tennessee Department of Mechanical and Aerospace Engineering.
3. University of Palermo, Palermo, Italy.
4. E. Caponetti, A. Lizzio, R. Triolo, W. L. Griffith, and J. S. Johnson, Jr., "Alcohol Partition in a Water-in-Oil Microemulsion from Small-Angle Neutron Scattering," *Langmuir* **1992**, *8*(6), 1554.
5. W. L. Griffith, R. Triolo, and A. L. Compere, "Analytical Scattering Function of a Polydisperse Percus-Yevick Fluid with Schulz-(GAMMA-) Distributed Diameters," *Physical Review A* **1987**, *35*(5), 2200.

12.2 SEMICONDUCTOR-CATALYZED PHOTOOXIDATION OF ORGANIC CONTAMINANTS SEPARATED BY MEMBRANE-ASSISTED SOLVENT EXTRACTION

Yunfu Sun,[1] G. M. Brown, B. A. Moyer

Current waste treatment technologies have numerous drawbacks and are applicable only to certain specific types of wastes. Incineration, which is the most widely applied method in industry, is effective only for bulk organic wastes and often releases toxic byproducts into the environment. The treatment of dilute aqueous solutions containing organic compounds by TiO_2-mediated photooxidation has been demonstrated in a number of laboratories, but the application of this technology has been limited under real waste-treatment conditions. First, the photocatalyst separation from the treated streams is difficult, and attempts to immobilize TiO_2 can reduce its photoactivity. Second, other components (for example, inorganic species) of the waste stream adsorb onto the TiO_2 surface. The deactivating effect of the adsorbed species represents a key problem in the application of this technology. Significant to DOE needs, some adsorbing species (e.g., uranium) may also be radioactive, leading to the creation of a new radioactive waste with consequent drawbacks for treatment of mixed waste. In addition,

photolysis of very dilute solutions of contaminants is an inefficient use of light energy.

We have developed a two-stage separation-photooxidation process as a means of effectively decomposing hazardous organic compounds in aqueous waste streams in general and in mixed-waste streams in particular. In the two-stage process, an aqueous stream flows by a membrane that selectively extracts and concentrates the organic contaminants into a carrier stream containing a dispersed photocatalyst for closed-cycle flow to the photodestruction cell. This method overcomes many of the shortcomings of previously employed methods of remediating aqueous solutions containing hazardous organic compounds. In particular, with an appropriate membrane, the separator will be a barrier to radionuclides present in the aqueous stream or to other inorganic species which may deactivate the TiO_2 photocatalyst. Thus, the membrane separator allows the system to be forgiving of variations in the composition of the feed stream. Variations in ionic strength (or identity of ionic component), differences in the concentration of the contaminants, and the presence of colloidal or suspended solids in the feed stream can be handled without difficulty. Aqueous feed streams which only contain organic pollutants exit the treatment process as clean water, and a mixed-waste feed stream would emerge as simple radioactive waste. Since the TiO_2 photocatalyst is contained in a solvent system and never comes in contact with the feed stream, the separation of the photocatalyst from the feed stream is not a concern. Fluorocarbons were chosen for the photolysis solvent because of their extremely high chemical stability to oxidation, the increased oxygen solubility in fluorocarbons, and their ability to solubilize and concentrate organic contaminants.

The effectiveness of the process was demonstrated by the separation and photodestruction of trichloroethylene (TCE). The extraction of TCE from an aqueous solution into a fluorocarbon solvent (Galden HT110) occurs readily through a 25 μm thick membrane (Celgard 2500). The photodestruction of TCE was demonstrated by photolysis of a 1% solution of TCE in the fluorocarbon solvent irradiating with two 15W black-light fluorescent bulbs. The presence of water is necessary for the photocatalyzed mineralization of TCE as shown by the reaction in Eq. 12.1.

$$2C_2HCl_3 + 2H_2O + 3O_2 \text{ ---------> } 4CO_2 + 6HCl \qquad (12.1)$$

The photooxidation yielded dichloroacetic acid as a major intermediate, which is degraded slowly to carbon dioxide and hydrogen chloride as final products.

Experiments to elucidate the reaction mechanism have been initiated, and several lines of evidence are already revealing. A plot of the concentration of TCE vs the square of time is linear, indicating self catalysis, a radical chain reaction, or a combination of the two pathways. The quantum yield (ratio of molecules of TCE destroyed to photons absorbed) was observed to be very high and to increase with time during the first three quarters of the reaction. The highest quantum yield is 1.5, offering further evidence that a radical chain reaction is involved. By contrast, the photodegradation of toluene is much slower and simpler than the oxidation of TCE. A number of minor reaction intermediates are observed by GC, although none have been identified, and the reaction follows a simple first-order rate law. The initial quantum yield for toluene disappearance is 0.2, and although this value is smaller than that for TCE, it is nonetheless easily sufficient for this process to be an effective method of destroying toluene.

The process we have developed retains or even enhances all the virtues of TiO_2-mediated photodegradation. The process adds nothing to the waste stream being treated, it is nonselective, and it does not release toxic chemicals into the environment because the mineralization products are benign. While being able to accomplish treatments that the conventional aqueous slurry TiO_2 process can do, the process developed here also offers a number of improvements. The high concentration of TCE in the fluorocarbon, the high concentration of oxygen in the fluorocarbon phase, and interfacial effects on the chain length of radical reactions all may contribute to the efficiency of the photolysis. Analysis of the water for fluoride ion indicted photodecomposition of the fluorocarbon solvent was negligible. The presence of the membrane also prevents water-soluble inorganic species or colloidal solids in the waste stream that may deactivate or be harmful to TiO_2 photocatalyst from entering the photolysis solution. Hence, the process

should be useful to treat a variety of waste streams including mixed-waste streams, aqueous wastewater from the manufacture of munitions, or outdated and surplus chemical weapons agents.

---

1. Postdoctoral Research Fellow.

12.3 *IN SITU* SCANNING PROBE MICROSCOPY OF ACTIVELY CORRODING SURFACES

D. P. Allison,[1] G. M. Brown, T. G. Thundat,[1] R. J. Warmack[1]

Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) can be carried out on a sample immersed in an electrolyte solution and under potentiostatic control. These microscopies can provide atomic and even subatomic details of the topography of an electrode surface as it undergoes reaction. These details have previously been unavailable by any other method since most surface sensitive probes utilize electron or ion beams and are not suitable for work in the presence of a liquid. Electrochemistry with potentiostatic control of the solution-substrate interface allows the simulation of practical corrosion environments. We have begun a new program to utilize scanning probe microscopy in combination with electrochemistry to investigate localized corrosion phenomenon such as pitting and stress corrosion cracking, and to determine whether localized corrosion phenomena are initiated at grain boundaries or whether they are randomly initiated.

Titanium is the prototype of a metal whose corrosion resistance is provided by a protective oxide film. We have investigated the growth and dissolution of the protective TiO_2 film on a Ti electrode by *in situ* AFM and STM.[2] The specimen under investigation was polycrystalline material, and the presence of grain boundaries between individual crystallites was readily observed by AFM. Images were obtained under an aqueous solution containing 0.1 M oxalic acid with the substrate under potentiostatic control. In this way the surface could be maintained in either an active or a passive state. In these *in situ* experiments we found that both the rate of growth of oxide and the dissolution of the metal are dependent on the crystallographic face of the titanium. AFM and STM showed the growth of titanium (IV) oxide or hydrous oxide has the appearance of hemispherical domes that grow together to form peaks

on the surface. Dissolution of the metal in the active region begins in areas between the peaks where the oxide is thin, and later the oxide coverage of the small peaks appears to coalesce to a smaller number of large peaks. AFM showed more utility than STM for *in situ* imaging because of the streaking of the STM tip when titanium is in the active state. The streaks in the images appeared to occur after the STM tip passed over certain high features on the surface, and we speculate that the presence of nonconducting oxide on these features may interfere with the maintenance of a stable tunneling current.

We will develop a nonconventional scanning probe microscopy technique which will use the signal from localized electrochemical reactions to correlate localized current flow from dissolution sites with surface topographical features. A hybrid instrument will be constructed that combines the capabilities of scanning electrochemical microscopy, vibrating probe microscopy, and the AFM to obtain both the electrochemical map and the topographic map of the corroding surface. The proposed instrument will combine three novel techniques: electrochemical determination of corrosion products, potential gradient mapping of the surface, and surface topography imaging. This instrument will enable us to simultaneously study *in situ* the processes taking place during corrosion at three fundamental levels, i.e., chemical analysis, electrical potential distribution, and geometrical mapping.

---

1. Health and Safety Research Division, ORNL
2. G. M. Brown, T. Thundat, D. P. Allison, and R. J. Warmack, *J. Vac. Sci. Technol. A* **1992**, *10*, 3001.

12.4 STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAM

New Options for Crystalline Waste Forms; The Crystallochemistry of Lanthanide and Actinide Titanates

C. E. Bamberger, T. J. Haverlock,[1] S. S. Shoup,[2] O. C. Kopp,[3] N. D. Stump[4]

The objective of this work is to obtain basic data on stability, crystallography, aqueous solubility, and hydrolytic behavior of a class of cationic solid-solution titanates. This information is aimed at providing new options for crystalline waste forms in which actinide

elements alone or in combination with divalent elements such as Sr can be stabilized. The targeted materials may well have the properties required (e.g., stability toward radiation, very low solubility in aqueous environments, etc.) for geological disposal of actinides. The first titanate anion being studied is $(Ti_2O_7)^{6-}$, and the solid solutions include lanthanide (Ln), actinide (An), and divalent cations such as Sr (M), in the combinations $[An(III)_x\ Ln(III)_{2-x}]\ Ti_2O_7$ or $[An(IV)_{x/2}\ M(II)_{x/2}\ Ln(III)_{2-x}]\ Ti_2O_7$. Because cerium is a good stand-in for plutonium, based on their similar redox potential, ionic radii, and crystallochemical behavior, exploratory synthesis and characterization studies were made with cerium. Trivalent cerium dititanate was synthesized by reaction of CeO_2 and TiO_2, with TiN as the reducing agent; similar reactions were used to prepare solid solutions of the type $Ln_{2-x}Ce_xTi_2O_7$ in which Ln = Gd, Er, or Lu. The red-brown coloration of the Ce^{3+}-compounds obtained absorbed effectively visible light and prevented us from recording useful Raman spectra. Thus, the solid solutions were studied only by x-ray diffraction (XRD). This allowed us to infer when a solid solution was saturated with Ce^{3+} by showing the presence of monoclinic $Ce_2Ti_2O_7$ as an additional phase, and by indicating the attainment of constancy of the lattice parameter of the cubic solid solution as the cationic fraction of Ce^{3+} increased. The results obtained for Gd-Ce, Er-Ce, and Lu-Ce are, respectively, 20, 25, and 30% Ce^{3+}. The reaction of CeO_2 with TiO_2 under an argon atmosphere at temperatures above 1000°C leads to the formation of Ce^{3+}-Ce^{4+} titanate (IV). Attempts to synthesize various titanates containing Ce^{3+} and Ce^{4+} indicated that less than 25% of the Ce^{3+} in $Ce_2Ti_2O_7$ and about 11% of the Ce^{3+} in $Ce_2O_3 \cdot 4\ TiO_2$ could be replaced by Ce^{4+}. To be able to stabilize higher amounts of Ce^{4+} is, very likely, possible but will require atmospheres with higher oxidation potentials, e.g., CO/CO_2. It was also found that under argon at temperatures above about 1100°C, some Ce^{3+} titanates spontaneously reduce further, forming Ti^{3+}/Ti^{4+} compounds. Argon-4% hydrogen was used to perform faster reductions on a series of preparations $Ce_2O_3 \cdot n\ TiO_{2-x}$. It was found, surprisingly, that little changes were observed in XRD patterns even when "n" was widely varied, e.g., from 3 to 7. The value of x in the compounds was determined from

weight changes upon their oxidation in air; it varied relatively little, 0.10-0.17. A closer examination of the compounds by XRD is currently under way.

The study of Ce^{4+}/Ce^{3+}-titanium compounds has resulted in some unexpected chemical behavior. This information will make predictions regarding the behavior of plutonium much easier.

---

1. Subcontractor employee.
2. Graduate student, Department of Chemistry, The University of Tennessee.
3. Consultant, Department of Geological Sciences, The University of Tennessee.
4. Postdoctoral guest.

12.5 SINGLE CRYSTAL NEUTRON DIFFRACTION INSTRUMENT

C. K. Johnson

The 4-circle Huber diffractometer previously used for structural chemistry research was reinstalled at the Oak Ridge High Flux Isotope Reactor (HFIR) and made operational for single-crystal neutron diffraction as part of the expanded ORNL research program in structural biology.

The current computer control instrumentation based on a PDP-11 computer and SmartStep controller is being updated. A DEC 3000 Model 400 Alpha AXP workstation with 32 MB memory, 16" color monitor, 1.05 GB disk, CDROM, and a 525MB QIC tape drive was chosen as the new control computer because of its suitability for possible future upgrades to large-scale area detection of neutrons. The workstation ethernet will connect to a modern commercial diffractometer controller through a terminal server with eight ports. The workstation ethernet also will be connected by a bridge to the HFIR ethernet, which in turn connects to the Oak Ridge broadband network.

The commercial diffractometer control software will operate under VMS on the alpha AXP workstation. The control system provides motor motion, zero-degree marker sensing at integral degree values, and limit-switch collision protection for the 2-θ, ω, χ, and ϕ drives of the Huber diffractometer. The controller also interfaces with eight single channel analyzers to accept and process continuous streams of count

pulses originating from one stationary input neutron beam monitor proportional counter, and seven diffraction neutron beam proportional counters. A custom designed Helium-3 counter tube two inches in diameter with seven internal chambers arranged hexagonally will be used as the detection counter. The center chamber of the array measures the Bragg diffraction, while the surrounding six chambers measure the diffuse scattering around the Bragg peak.

The diffuse intensity data will be used in combination with the Bragg data to analyze dynamical motion effects in biologically interesting small and macromolecules. New mathematical techniques will be worked out to accomplish the joint analysis of static structure and dynamical motion using Bragg and diffuse scattering data simultaneously in the refinement.

Neutron data sets on several small organic structures were collected during the shakedown period accompanying the recommission of the PDP-11 based instrument.

12.6 TOPOLOGY OF CRYSTALLOGRAPHIC SPACE GROUPS AND CRYSTAL-STRUCTURE ELECTRON-DENSITY FUNCTIONS

C. K. Johnson

Critical point networks in crystals provide a unique global topological characterization of crystal structure electron density functions that are useful in interpreting physical, chemical, and crystallographic properties. A point in the density map is critical if the first derivatives of the density function with respect to x, y, and z are zero. A critical point is called a peak, pass, pale, or pit if the signs of the second derivative matrix eigenvalues are (-, -, -), (-, -, +), (-, +, -), (+, +, +), respectively.

In the asymmetric unit of the electron density in a unit cell, the number of pits plus passes equals the number of pales plus peaks. We found that the simplest basic arrangements for critical points in a crystal is the simple-cubic-packing critical point network (1, 3, 3, 1) with 1 peak, 3 passes, 3 pales, and 1 pit. Other one atom per asymmetric unit networks include the (1, 2, 2, 1), (1, 4, 6, 3), (1, 6, 8, 3),

and (1, 3, 5, 3) arrangements characteristic of diamond, body-centered cubic, face-centered cubic, and hexagonal closest packing, respectively.

In a crystal structure, all fixed-point special positions of the crystal's space group must contain critical points. Thus, it is necessary to understand the singular set (i.e., special position) topology of the space groups. A convenient method for visualizing the singular set topology of fundamental domains in space groups involves the use of orbifold singular-set diagrams.[1-3]

Orbifolds are generalizations of manifolds. An n-orbifold is a topological n-space locally modeled on the quotient: (an open set in n-dimensional real space R^n)/(a finite group action). A manifold is regarded as an orbifold whose local group on each point is the identity operator. There are eight different orbifold geometries[4], but the ones of interest here are the euclidean 2-orbifolds, which correspond to the two-dimensional crystallographic plane groups, and the spherical 3-orbifolds which correspond to the three-dimensional crystallographic point groups.[1,3]

The euclidean 2-orbifold corresponding to a 2-dimensional projection of a space group serves as a base orbifold which can be lifted into a Seifert fiber space whose exceptional fibers trace the singular sets of the three-dimensional fundamental domain.[1,2] Individual lines and intersections of the singular set diagram represent spherical 3-orbifolds corresponding to special-position point groups with one and zero degrees of freedom, respectively. The resulting network may be characterized mathermatically as bridged links and tangles,[5] giving a concise representation of the space group's fundamental-domain special-position topology.

Fibered orbifold geometries also provide a mathematical framework for formulating analytical crystallographic functions in terms of the fundamental domain rather than the unit cell. This substitutes increased topological space complexity for decreased space group symmetry complexity. Various surfaces such as the torus, Klein bottle, annulus and mobius band, plus real-projective and lens spaces are needed, depending on the particular crystallographic group involved.

The methods described above will be used in an attempt to find a topological solution to the crystallographic direct methods phasing problem for macromolecules. This problem requires a joint analysis of critical point topology in both crystal and Fourier transformed space.

---

1. F. Bonahon and L. Siebenmann, "Seifert 3-Orbifolds and Their Role as Natural Crystalline Parts of Arbitrary Compact Irreducible 3-Orbifolds," unpublished preprint, **1983**.
2. W. D. Dunbar, "Fibered Orbifolds and Crystallographic Groups," Thesis, Princeton University, **1981**.
3. J. M. Montesinos, *Classical Tessellations and Three-Manifolds* **1987**, Springer, New York.
4. P. Scott, "The Geometries of 3-Manifolds," *Bull. London Math. Soc.* **1983**, *15*, 401.
5. D. Rolfsen, *Knots and Links* **1976**, Publish or Perish, Berkeley.

12.7 BACTERIA MONITORING BASED ON AUTOMATED OPTICAL MICROSCOPY

C. K. Johnson, R. L. Tyndall,[1] S. J. Kennel,[2] M. Smallwood,[3] W. Gabbard[3]

Our development of machine inspection devices for the examination of currency and postage stamps for printing flaws led to other applications for machine vision, including automated video microscopy. Optical microscopy is labor intensive and requires considerable operator skill to recognize key morphological characteristics in the complex microscopic images under examination. Biological, metallurgical, particulate aerosol, and forensic sciences all use optical microscopy extensively. Physical properties including absorption, fluorescence, radioactivity, and light scattering also can be measured in the microscope using spectroscopic or densitometry methods to complement morphological characteristics such as size and shape.

Commercial video microscopy equipment is becoming considerably less expensive as the number of equipment and software suppliers increases. A general purpose instrument is being assembled using a Leitz epi-fluorescence microscope, an Optimus machine vision software package, a Prior automated stage and focus, and a software controlled integrating solid state camera made by Image Technology.

Optical microscopy provides one of the fundamental analytical tools for identifying aerosol particles in the 0.5 to 30 micron size range including airborne pollen and pathogenic bacteria and fungi. Detection

of pathogenic microorganisms (e.g., bacteria and fungi) and toxic biological products (e.g., bacterial and fungal toxins and allergens) is of concern in reconnaissance for military biological agents, health and safety monitoring of indoor environments, and water quality monitoring. A collection and detection monitor utilizing fluorescence video microscopy combined with antibody biotechnology, automated image analysis video microscopy, and microprocess automation is being assembled.

The monitoring design, which is illustrated schematically in Figure 12.2, utilizes a cascade system of nucleopore filters to concentrate airborne or waterborne particles into minute circular racetracks. Microbes and other particles in the 0.5 to 5.0 micron size range are then circulated around the lanes of the racetrack for a half-hour period in a solution which includes a fluorescent vital dye which selectively stains living (respiring) microbes. Colloidal magnetic particles driven by a rotating magnetic field maintain the circulation. Patches of many different immobilized antibodies located in sectors around the lanes selectively capture specific microbes, and particles with specific antigenic toxins attached. Research is under way to characterize the affinity constants between various monoclonal antibodies and nonpathogenic bacteria.

The surface containing the circular arrays of antibody patches with fluorescent particles attached is then scanned by the automated video epifluoresence microscope to determine size, shape, fluorescent amplitude, and number of absorbed particles on each antibody patch. The antibody patch particle attachment data are then correlated with morphology and distribution data obtained previously from pure samples to identify the microbes and toxins present.

Particles in other size ranges may be selected by changing the filter characteristics. The larger allergenic pollen spores, for example, have complex shapes which allow more detailed morphological classification.

---

1. ORNL Health and Safety Division.
2. ORNL Biology Division.
3. ORAU Research Participant.

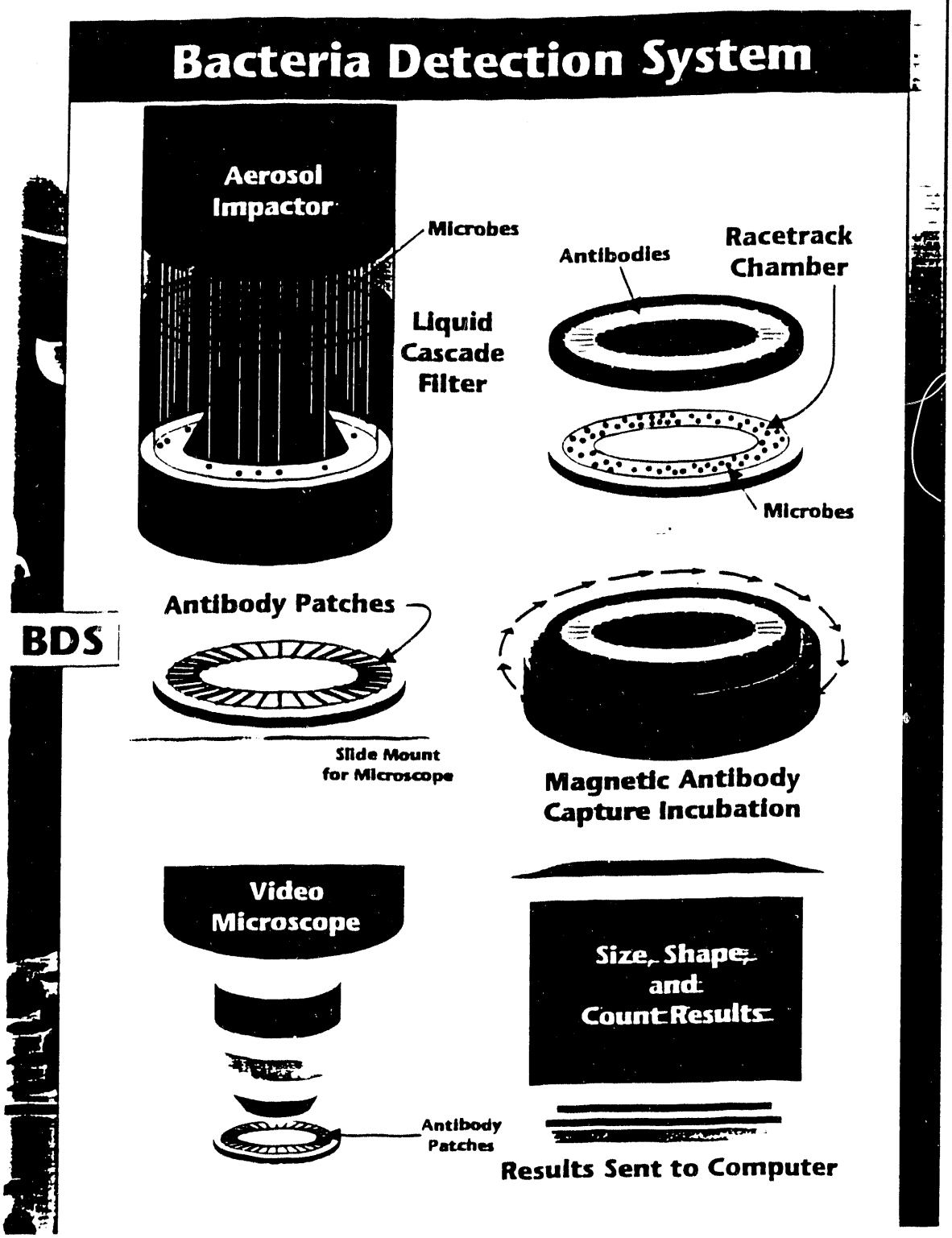

Bacteria Detection System
Aerosol Impactor
Microbes
Liquid Cascade Filter
Antibodies
Racetrack Chamber
Microbes
BDS
Antibody Patches
Slide Mount for Microscope
Magnetic Antibody Capture Incubation
Video Microscope
Size, Shape, and Count Results
Antibody Patches
Results Sent to Computer

Figure 12.2.

PUBLICATIONS, PRESENTATIONS, AND PATENTS

COAL CHEMISTRY

PUBLICATIONS

P. F. Britt, A. C. Buchanan, III, E. A. Malcolm[1], and C. A. Biggs, "Effect of Cross-Linking on the Pyrolysis of Diphenylalkanes," *J. Anal. Appl. Pyrolysis* (in press).

P. F. Britt and A. C. Buchanan, III, "The Effect of Cross-linking on the Thermal Decomposition of Diphenylalkanes," Preprints, *Div. Fuel Chem., Am. Chem. Soc.*, **1992**, *37(2)*, 914.

P. F. Britt and A. C. Buchanan,III, "Thermolysis of Surface-attached 1,4-Diphenylbutane: The Role of Hydrogen-Transfer Reactions on the Surface in Determining the Product Distribution," *J. Org. Chem.* **1991**, *56*, 6132.

P. F. Britt, A. C. Buchanan, III, and V. M. Hitsman,[2] "Thermolysis of Surface-Immobilized Phenethyl Phenyl Ether," Proceedings, *International Conference on Coal Science*, Butterworth-Heinemann, Ltd., **1991**, 207.

A. C. Buchanan, III, P. F. Britt, K. B. Thomas, and C. A. Biggs, "A Surface-Immobilized Model Compound Investigation of Catalytic Reactions in Dispersed Solids," *Energy & Fuels* (in press).

A. C. Buchanan, III, P. F. Britt, and C. A. Biggs, "Dispersed Catalysts: Evidence for a Role for Solid-State Interactions," *Energy & Fuels* **1992**, *5*, 110.

A. C. Buchanan, III, and P. F. Britt, "Hydrogen Transfer Pathways Under Restricted Diffusion", Preprints, *Div. Fuel Chem., Am. Chem. Soc.*, **1992**, *37(2)*, 954.

A. C. Buchanan, III, P. F. Britt, and C. A. Biggs, "Role of Solid-State Interactions in the Acid-Catalyzed Thermolysis of Surface-Attached Diphenylalkanes," Proceedings, *International Conference on Coal Science*, Butterworth-Heinemann, Ltd., **1991**, 162.

J. H. Burns and E. W. Hagaman, "Three Monofluorinated Small Molecules: *Ortho*-Fluorophenylglycine, Methyl-4-fluorocarbonylbenzoate, and 16-α-Fluoro-α-estradiol-3-methyl Ether", *Acta Crystallographica* (in press).

J. E. Coffield[3], G. Mamantov[3], S. P. Zingg, G. P. Smith, and A. C. Buchanan, III, "Reduction of Aromatic Compounds in Organic Chloro-aluminate Melts: II. Perylene," *J. Electrochem. Soc.*, **1992**, *139*, 355.

E. W. Hagaman, "^{13}C–^{19}F Dipolar Dephasing in Monofluorinated Organic Substances: Characterization by ^{1}H–^{13}C–^{19}F Triple Resonance ^{13}C CP/MAS and ^{19}F MAS NMR", *J. Magn. Reson.* (in press).

E. W. Hagaman and J. H. Burns, "The Determination of Local Structure in Organofluorides Using Fluorine-19 Carbon-13 Dipolar Coupling", *Fuel* (in press).

E. W. Hagaman and S. K. Lee[4], "Selective Fluorination of Coals: Structure at Reactive Sites by High Resolution Triple Resonance Solid State NMR", Preprints, *Div. Fuel Chem., Am. Chem. Soc.*, **1992**, *37(3)*, 1166.

E. W. Hagaman, "Coal Structure Determination Using ^{19}F as a Chemical Label and NMR Probe", *International Conference on Coal Science*, Butterworth-Heinemann, Ltd., **1991**, 76.

S. C. Mitchell,[5] C. J. Lafferty,[5] R. Garcia,[5] C. E. Snape,[5] A. C. Buchanan, III, P. F. Britt, and E. Klavetter,[6] "Silica-Immobilized Compounds as Models for Probing Coal Pyrolysis and Hydropyrolysis Phenomena," *Energy & Fuels*, **1993**, *7*, 331.

S. C. Mitchell,[5] C. J. Lafferty,[5] R. Garcia,[5] K. Ismail,[5] C. E. Snape,[5] A. C. Buchanan, III, P. F. Britt, and E. Klavetter,[6] "Pyrolysis and Hydropyrolysis of Diphenylmethane and Sulfur-Containing Compounds Immobilized on Silica", Preprints, *Div. Fuel Chem., Am. Chem. Soc.*, **1992**, *37(4)*, 1691.

PRESENTATIONS

P. F. Britt, A. C. Buchanan, III, and E. A. Malcolm[1], "Model Compound Studies of the Thermolysis of Lignin", American Chemical Society National Meeting, Denver, CO, March 28-April 2, 1993.

P. F. Britt, "Thermal Decomposition of Model Compounds for Coal. Impact of Restricted Diffusion on Free-Radical Reactions", Chemistry Department, James Madison University, October 30, 1992 (invited).

P. F. Britt, A. C. Buchanan, III, E. A. Malcolm[1], and C. A. Biggs, "Pyrolysis of Surface-Immobilized Model Compounds. Effect of Cross-linking on the Pyrolysis of Diphenylalkanes", The 10th International Conference of Fundamental Aspects, Processes and Applications on Pyrolysis, Hamburg, Germany, September 28-October 2, 1992.

P. F. Britt and A. C. Buchanan, III, "Modeling the Thermolysis of Ether Linkages in Low Rank Coal", 5th DOE Coal Chemistry Conference and Workshop, Rockford, IL, June 7-10, 1992.

P. F. Britt, A. C. Buchanan, III, E. A. Malcolm[1], C. A. Biggs, "The Effect of Cross-linking on the Thermal Decomposition of Diphenyl-alkanes", American Chemical Society National Meeting, San Francisco, CA, April 5-10, 1992.

P. F. Britt, A. C. Buchanan, III, and V. M. Hitsman,[2] "Thermolysis of Surface-Immobilized Phenethyl Phenyl Ether," 1991 International Conference on Coal Science, Newcastle, United Kingdom, September 16-20, 1991.

P. F. Britt, A. C. Buchanan, III, and V. M. Hitsman[2], "Thermolysis of Surface-Immobilized Phenethyl Phenyl Ether," American Chemical Society National Meeting, Atlanta, GA, April 14-19, 1991.

A. C. Buchanan, III and P. F. Britt, "Exploration of High Temperature, Organic Reactions on Surfaces," Department of Chemistry, University of Tennessee, Knoxville, TN, April 15, 1993 (Invited).

A. C. Buchanan, III and P. F. Britt, "Influence of Hydrogen Donors on High Temperature Free-Radical Chain Reactions on Surfaces", American Chemical Society National Meeting, Washington, DC, August 23-28, 1992.

A. C. Buchanan, III, and P. F. Britt, "Impact of Restricted Mass Transport on Hydrogen Transfer Pathways Relevant to Coal Processing", 5th DOE Coal Chemistry Conference and Workshop, Rockford, IL, June 7-10, 1992.

A. C. Buchanan, III and P. F. Britt, "Hydrogen Transfer Pathways Under Restricted Diffusion", American Chemical Society National Meeting, San Francisco, CA, April 5-10, 1992.

A. C. Buchanan, III, P. F. Britt, and C. A. Biggs, "Role of Solid-State Interactions in the Acid-Catalyzed Thermolysis of Surface-Attached Diphenylalkanes", 1991 International Conference on Coal Science, Newcastle, United Kingdom, September 16-20, 1991.

A. C. Buchanan, III, P. F. Britt, and C. A. Biggs, "Acid-Catalyzed Cracking of Surface-Immobilized 1,3-Diphenylpropane in Dispersed Solids," American Chemical Society National Meeting, Atlanta, GA, April 14-19, 1991 (Invited).

E. W. Hagaman, "Triple Resonance CP/MAS ^{13}C NMR Spectra of Organo-fluorides: Prescience of Fluorocoal", 33rd Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado, July 28-August 1, 1991.

E. W. Hagaman, "The Determination of Local Structure in Organofluorides Using Fluorine-19 Carbon-13 Dipolar Coupling", American Chemical Society National Meeting, New York, August 25-30, 1991.

E. W. Hagaman, "Coal Structure Determination Using ^{19}F as a Chemical Label and NMR Probe", 1991 International Conference on Coal Science, Newcastle, United Kingdom, September 16-20, 1991.

E. W. Hagaman and S. K. Lee[4], "Selective Fluorination of Coals: Structure at Reactive Sites by High Resolution Triple Resonance Solid State NMR", Am. Chem. Soc. National Meeting, Washington, D.C., August 23-28, 1992.

E. W. Hagaman and S. K. Lee[4], "A Chemical and Solid State ^{19}F NMR Study of the Fluorination of Poly(methacrylic acid) and Poly(4-vinylbenzoic acid)", ACS Eleventh Winter Fluorine Conference, St. Petersburg, Florida, January 25-30, 1993.

S. C. Mitchell,[5] C. J. Lafferty,[5] R. Garcia,[5] K. Ismail,[5] C. E. Snape,[5] A. C. Buchanan, III, P. F. Britt, and E. Klavetter,[6] "Pyrolysis and Hydropyrolysis of Diphenylmethane and Sulfur Containing Compounds Immobilized on Silica", American Chemical Society National Meeting, Washington, DC, August 23–28, 1992.

---

1. Oak Ridge Research Institute, Oak Ridge, TN.
2. Alma College, Alma, MI.
3. University of Tennessee, Knoxville, TN.
4. ORNL Postdoctoral Fellow.
5. University of Strathclyde, Glasgow, United Kingdom.
6. Sandia National Laboratories, Albuquerque, NM.

AQUEOUS CHEMISTRY AT HIGH TEMPERATURES AND PRESSURES

PUBLICATIONS

G. M. Anderson,[1] S. Castet,[2] J. Schott,[2] and R. E. Mesmer, "The Density Model for Estimation of Thermodynamic Parameters of Reactions at High Temperatures and Pressures," *Geochim. Cosmochim. Acta* **1991**, *57*, 1769.

J. L. S. Bell[3] and D. A. Palmer, "Acetate in Hydrothermal Solutions: Decomposition Kinetics and Metal Complexation," in *Water-Rock Interaction*, **1992**, Proceedings: 7th International Water-Rock Symposium, Y. K. Kharaka and A. S. Maest, eds., A. A. Balkema, 185.

J. L. S. Bell,[3] D. A. Palmer, and H. L. Barnes,[4] "Acetate in Hydrothermal Solutions: Decomposition Kinetics and Metal Complexation," in *Water-Rock Interaction*, **1992**, Y. K. Kharaka and A. S. Maest, eds., A. A. Balkema, 307.

J .L. S. Bell,[3] D. J. Wesolowski, and D. A. Palmer, "The Dissociation Quotients of Formic Acid in Sodium Chloride Solutions to 200°C," *J. Solution. Chem.* **1993**, *22*, 125.

J. L. S. Bell[3] and D. A. Palmer, "Experimental Studies of Decomposition of Organic Acid Anions," in *The Role of Organic Acids in Geological Processes*, M. D. Lewan and E. D. Pittman, eds., Springer-Verlag, Chapt. 8 (in press).

J. L. S. Bell,[3] D. A. Palmer, H. L. Barnes,[4] and S. F. Drummond,[5] "The Thermal Decomposition of Acetate. Part III. Catalysis of Mineral Surfaces," *Geochim. Cosmochim. Acta* (in press).

P. T. Cummings,[6] H. D. Cochran,[7] J. M. Simonson, R. E. Mesmer, and S. Karaborni,[8] "Molecular Dynamics Simulation of Supercritical SPC (Spherical Point Charge) Water and of Supercritical Aqueous Solutions", *J. Chem. Phys.* **1991**, *94*, 5606.

P. T. Cummings,[6] H. D. Cochran,[7] J. M. Simonson, R. E. Mesmer, and S. Karaborni,[8] "Simulation of Supercritical Water and of Supercritical Aqueous Solutions," *Proceedings: 2nd International Symposium of Chemistry in High Temperature Aqueous Solutions*, EPRI Report [extended abstract] (in press).

P. C. Ho, "Sorption of Cesium, Strontium, and Technetium onto Organic-extracted Shales," *Radiochimica Acta* **1992**, *56*, 159.

H. F. Holmes and R. E. Mesmer, "Mixing Effects in Aqueous Solutions at Elevated Temperatures," *J. Solution Chem.* **1992**, *21*, 713.

H. F. Holmes and R. E. Mesmer, "Isopiestic Studies of Aqueous Solutions At Elevated Temperatures. XI. $(1-y)CaCl_2+yBaCl_2(aq)$," *J. Chem. Thermodynamics* **1992**, *24*, 829.

H. F. Holmes and R. E. Mesmer, "Isopiestic Studies of $H_2SO_4(aq)$ at Elevated Temperatures. Thermodynamic Properties," *J. Chem. Thermodynamics* **1992** *24*, 317.

H. F. Holmes and R. E. Mesmer, "Isopiestic Studies of $NaHSO_4(aq)$ at Elevated Temperatures. Thermodynamic Properties," *J. Chem. Thermodynamics* **1993**, *25*, 99.

H. F. Holmes and R. E. Mesmer, "Mixing Effects in Aqueous Solutions at Elevated Temperatures," *Proceedings: 2nd International Symposium on Chemistry in High Temperature Aqueous Solutions*, EPRI Report (in press).

R. M. Kettler,[9] D. A. Palmer, and D. J. Wesolowski, "Dissociation Quotients of Oxalic Acid in Aqueous Sodium Chloride Media to 175°C," *J. Solution. Chem.* **1991**, *20*, 905.

R. M. Kettler,[9] D. J. Wesolowski, and D. A. Palmer, "Dissociation Quotients of Malonic Acid in Aqueous Sodium Chloride Media to 100°C," *J. Solution. Chem.* **1992**, *21*, 883.

R. M. Kettler,[9] D. J. Wesolowski, and D. A. Palmer, "Dissociation Quotients of Malonic Acid in Aqueous Sodium Chloride Media to 100°C," *EPRI Report*, (in press).

W. L. Marshall[10] and J. M. Simonson, "The Liquid-Vapor Critical Temperature Curve for $\{xD_2O + (1-x)H_2O\}$", *J. Chem. Thermodynamics* **1991**, *23*, 613.

W. L. Marshall,[10] "Volume, Electrostriction, and Solvation Relations Along the Liquid-Vapor Critical Curve of Aqueous Sodium Chloride Solutions," *J. Solution Chemistry*, (in press).

R. E. Mesmer, "A New Approach to Measuring pH in Brines and Other Concentrated Electrolytes," *Geochim. Cosmochim. Acta* **1991**, *55*, 1175.

R. E. Mesmer, D. A. Palmer, and J. M. Simonson, "Ion Association at High Temperatures and Pressures," *Activity Coefficients in Electrolyte Solutions*, **1991**, K. S. Pitzer, ed., 2nd Edition, CRC Press, Chapt. 8.

R. E. Mesmer and H. F. Holmes, "pH, Definition and Measurement at High Temperatures," *J. Solution Chem.* **1992**, *21*, 725.

R. E. Mesmer, "Needs for Research in Aqueous Chemistry at High Temperatures and Pressures," *Proceedings: 2nd International Symposium on Aqueous Chemistry in High Temperature Aqueous Solutions*, EPRI Report (in press).

R. E. Mesmer and H. F. Holmes, "pH, Definition and Measurement at High Temperatures and Pressures," *Proceedings: 2nd International Symposium on Chemistry in High Temperature Aqueous Solutions*, EPRI Report (in press).

C. Nguyen-Trung,[11] G. M. Begun,[10] and D. A. Palmer, "Aqueous Uranium Complexes. Part II. Raman Spectroscopic Study of the Complex Formation of Dioxouranium(VI) Ion with a Variety of Inorganic and Organic Ligands," *Inorg. Chem.* **1992**, *31*, 5280.

C. S. Oakes,[12] J. M. Simonson, and R. J. Bodnar,[12] "Apparent Molar Volumes of $CaCl_2$(aq) to 250°C, 400 bars, and from 0.242 to 6.150 mol•kg^{-1}," J. Solution Chem. (in press).

D. A. Palmer and J. M. Simonson, "Experimental Studies of the Volatility of Ammonium Chloride," in *Proceedings: International Conference on Fossil Plant Cycle Chemistry*, **1991**, R. B. Dooley, ed., Baltimore, 1991. *EPRI TR-100195*, 2.

D. A. Palmer and D. J. Wesolowski, "Aluminum Speciation and Equilibria in Aqueous Solution. II. The Solubility of Gibbsite in Acidic Sodium Chloride Solutions from 30 to 70°C." *Geochim. Cosmochim. Acta* **1992**, *56*, 1093.

D. A. Palmer and K. E. Hyde,[13] "Ferrous Chloride and Acetate Complexation in Aqueous Solutions at High Temperatures." *Geochim. Cosmochim. Acta* **1993**, *57*, 1393.

D. A. Palmer and S. E. Drummond,[5] "An Experimental Study of the Solubility of Magnetite in Sodium Acetate Solutions," *Proceedings: Interaction of Iron-Based Materials with Water and Steam*, Heidelberg, Germany, June 3-5, 1992 (in press).

D. A. Palmer and J. M. Simonson, "Experimental Studies of the Volatility of Ammonium Chloride," *Proceedings: Third Fossil Plant Cycle Chemistry Conference*, *EPRI Report* (in press).

D. A. Palmer and J. M. Simonson, "The Volatility of Ammonium Chloride over Aqueous Solutions to High Temperatures," *J. Chem. Eng. Data* (in press).

D. A. Palmer and J. M. Simonson, "Behavior of Ammonium Salts in Steam Cycles," *EPRI Final Report RP-8000-55*, Electric Power Research Institute, Palo Alto, CA (in press).

Donald A. Palmer and David J. Wesolowski, "Aluminum Speciation and Equilibria in Aqueous Solution. Part III. Potentiometric Determination of the First Hydrolysis Constant of Aluminum(III) in Sodium Chloride Solutions to 125°C," *Geochim. Cosmochim. Acta* (in press).

D. A. Palmer, G. M. Begun,[10] and F. H. Ward,[10] "A Micro-Raman Cell for Studying Aqueous Solutions at High Temperatures and Pressures," *Rev. Sci. Instrum.* (in press).

J. M. Simonson and D. A. Palmer, "An Experimental Study of the Volatility of Ammonium Chloride from Aqueous Solutions to High Temperatures", in *Proceedings: International Water Conference*, **1992**, Engineers' Society of Western Pennsylvania, Pittsburgh, Oct. 21-23, 1991, IWC-91-32, 253.

J. M. Simonson and D. A. Palmer, "Author's Closure -- "An Experimental Study of the Volatility of Ammonium Chloride from Aqueous Solutions to High Temperatures", in *Proceedings: International Water Conference*, **1992**, Engineers' Society of Western Pennsylvania, Pittsburgh, Oct. 21-23, 1991, IWC-91-32, 260.

J. M. Simonson and D. A. Palmer, "Liquid-Vapor Partitioning of HCl(aq) to 350°C," *Geochim. Cosmochim. Acta* **1993**, *57*, 1.

J. M. Simonson and D. A. Palmer, "Distribution of Ammonium Salts between Liquid and Steam at High Temperatures," *Proceedings: Interaction of Iron-Based Materials with Water and Steam*, Heidelberg, Germany, June 3-5, 1992 (in press).

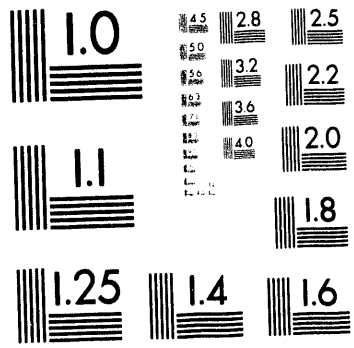
J. M. Simonson and R. E. Mesmer, "Calorimetry of Electrolyte Solutions at High Temperatures and Pressures," Chapter in *Experimental Chemical Thermodynamics*, *2*, Solution Chemistry (in press).

J. M. Simonson and D. A. Palmer, "A Speciated Model for the Distribution of HCl(aq) Between Liquid and Vapor Phases to the Solvent Critical Conditions," *Geochimica Cosmochimica Acta* (in press).

J. M. Simonson, C. S. Oakes,[12] and R. J. Bodnar,[12] "Densities of NaCl(aq) to 523 K and 40 MPa Measured With A New Vibrating-tube Densimeter," *J. Chemical Thermodynamics* (in press).

R. van Eldik,[14] W. Gaedé,[14] S. Wieland,[14] J. Kraft,[14] M. Spitzer,[14] and D. A. Palmer, "Spectrophotometer Stopped-Flow Apparatus Suitable for High Pressure Experiments to 200MPa," *Rev. Sci. Instrum.* (in press).

D. J. Wesolowski and D. A. Palmer, "Experimental Studies of Aluminum Solubility and Speciation in Brines," in *Water-Rock Interaction*, **1992**, eds., Y. K. Kharaka and A. S. Maest, Proceedings of the 7th


1.0
2.8
2.5
3.2
2.2
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

3 of 3

International Symposium on Water-Rock Interaction, A. A. Balkema, Rotterdam, 185.

PRESENTATIONS

J. L. S. Bell,[3] D. A. Palmer, S. E. Drummond,[5] and H. L. Barnes,[4] "The Kinetics of Heterogeneously-Catalyzed, Thermal Decomposition of Acetate in Aqueous Solutions," American Chemical Society National Meeting, Atlanta, GA, April 14-19, 1991.

J. L. S. Bell,[3] D. A. Palmer, and H. L. Barnes,[4] "Acetate In Hydrothermal Solutions: Decomposition Kinetics and Metal Complexation," The 7th International Symposium on Water-Rock Interaction, Park City, UT, July 13-18, 1992.

J. L. S. Bell,[3] D. A. Palmer, S. E. Drummond,[5] and H. L. Barnes,[4] "Decomposition of Acetic Acid on Iron Oxide Surfaces," The 205th American Chemical Society National Meeting, Denver, CO, March 28-April 2, 1993.

P. C. Ho and D. A. Palmer, "Electrical Conductivity Measurements of Aqueous Electrolyte Solutions to High Temperatures," Joint Meeting of The 12th IUPAC Conference on Chemical Thermodynamics and The 47th Calorimetry Conference, Snowbird, UT, August 16-21, 1992.

H. F. Holmes and R. E. Mesmer, "Thermodynamics in Sulfate-Bisulfate Systems to 225°C," 46th Calorimetry Conference, DeKalb, IL, July 28-August 1, 1991.

H. F. Holmes and R. E. Mesmer, "Mixing Effects in Aqueous Solutions at Elevated Temperatures," 2nd International Symposium on Chemistry in High Temperature Aqueous Solutions, Provo, UT, August 19-22, 1991.

H. F. Holmes, R. H. Busey,[10] J. M. Simonson, and R. E. Mesmer, "Thermodynamics of $CaCl_2$(aq) at Elevated Temperatures and Pressures," 12th IUPAC Conference on Chemical Thermodynamics and 47th Calorimetry Conference (joint), Snowbird, UT, August 16-21, 1992.

R. M. Kettler,[9] D. A. Palmer, and D. J. Wesolowski, "A Potentiometric Study of the Dissociation Constants of Oxalic Acid in 0-5 Molal NaCl Brines to 200°C," Second International Symposium on Chemistry in High Temperature Water, Provo, UT, August 20-22, 1991.

R. M. Kettler,[9] D. A. Palmer, and D. J. Wesolowski, "The Dissociation Quotients of Oxalic Acid in Aqueous Sodium Chloride Media to 175°C," 15th Meeting of the European Association of Organic Geochemists, Manchester, UK, September 16-20, 1991.

R. E. Mesmer, "Needs for Research in Aqueous Chemistry at High Temperatures and Pressures," 2nd International Symposium on Aqueous Chemistry in High Temperature Aqueous Solutions, Provo, UT, August, 1991.

R. E. Mesmer, D. A. Palmer, and J. M. Simonson, "Ion Association at High Temperatures and Pressures," 12th IUPAC Conference on Chemical Thermodynamics and 47th Calorimetry Conference, Snowbird, UT, August, 1991.

R. E. Mesmer and H. F. Holmes, "pH, Its Definition and Measurement at High Temperatures," 2nd International Symposium on Aqueous Chemistry in High Temperature Aqueous Solutions," Provo, UT, August, 1991.

R. E. Mesmer and H. F. Holmes, "pH, Its Definition and Measurement," 46th Calorimetry Conference, DeKalb, IL, August, 1991.

R. E. Mesmer, "Aqueous Chemistry at High Temperatures and Pressures," Executive Committee, Oak Ridge National Laboratory, June, 1992.

R. E. Mesmer, D. A. Palmer, and J. M. Simonson, "Ion Association at High Temperatures," Joint Meeting of The 12th IUPAC Conference on Chemical Thermodynamics and The 47th Calorimetry Conference, Snowbird, UT, August 16-21, 1992.

C. S. Oakes,[12] R. J. Bodnar,[12] and J. M. Simonson, "P-V-T Properties for the System $NaCl-CaCl_2-H_2O$ to 700°C and 5 kbars," Geological Society of America, 1991 Annual Meeting, San Diego, CA, October 20-24, 1991.

D. A. Palmer and J. M. Simonson, "Experimental Studies of the Volatility of Ammonium Chloride," International Conference on Fossil Plant Cycle Chemistry, Baltimore, MD, June 4-6, 1991 .

D. A. Palmer, K. E. Hyde,[12] and C. Nguyen-Trung,[11] "Experimental Measurements of Metal Complex Formation Equilibria to High Temperatures," Second International Symposium on Chemistry in High Temperature Water, Provo, UT, August 20-22, 1991.

D. A. Palmer, "The Formation of Aqueous Metal Chloride Complexes to High Temperatures," The 202nd American Chemical Society National Meeting, New York, NY, August 26-30, 1991.

D. A. Palmer and J. M. Simonson, "The Volatility of Aqueous Ammonium Chloride to High Temperatures," Symposium on The Chemistry of Water and Steam in Power Plants, at the IAPWS Annual Meeting, Tokyo, Japan, September 15-21, 1991.

D. A. Palmer and S. E. Drummond,[5] "An Experimental Study of the Solubility of Magnetite in Sodium Acetate Solutions," International Conference of Interaction of Iron-Based Materials with Water and Steam, Heidelberg, Germany, June 3-5, 1992.

D. A. Palmer, D. J. Wesolowski, and J. L. S. Bell,[3] "Potentiometric Measurements Aluminum(III) Hydrolysis and Complexation with Acetate in Sodium Chloride Solution," Joint Meeting of The 12th IUPAC Conference on Chemical Thermodynamics and The 47th Calorimetry Conference, Snowbird, UT, August 16-21, 1992.

J. M. Simonson and D. A. Palmer, "An Experimental Study of the Volatility of Ammonium Chloride from Aqueous Solutions to High Temperatures," 52nd Annual Meeting, The International Water Conference, Pittsburgh, PA, October 21-23, 1991.

J. M. Simonson and D. A. Palmer, "Distribution of Ammonium Salts Between Liquid and Steam at High Temperatures," International Conference on Interaction of Iron Based Materials with Water and Steam, Heidelberg, Germany, June 3-5, 1992.

D. J. Wesolowski and D. A. Palmer, "Potentiometric Measurements of the Hydrolysis of Al^{3+} in 0-5 Molal Aqueous Sodium Chloride Solutions in the 0-150°C Range," Geological Society of America, Annual Meeting, San Diego, CA, October 21-24, 1991.

D. J. Wesolowski, D. A. Palmer, and R. E. Mesmer, "Use of Hydrogen-Electrode Potentiometric Cells for the Determination of the Equilibrium Quotients of Acid/Base, Metal Hydrolysis and Complexation Reactions in Aqueous Electrolyte Solutions in the 0-300°C Range," V. M. Goldschmidt Conference, Reston, VA, May 8-10, 1992.

D. J. Wesolowski and D. A. Palmer, "Experimental Studies of Aluminum Solubility and Speciation in Brines," The 7th International Symposium on Water-Rock Interaction, Park City, UT, July 13-18, 1992.

---

1. University of Toronto, Toronto, Canada.
2. University Paul Sabatier, Toulouse, France.
3. ORISE Postdoctorate.
4. Dept. of Geology, Penn State University, University Park, PA.
5. Formerly Chemistry Division.
6. Visiting Scientist, University of Virginia.
7. ORNL Chemical Technology Division.
8. University of Virginia, Charlottesville, VA.
9. Visiting Scientist, University of Nebraska, Lincoln, NE.
10. Retired ORNL Employee.
11. Visiting Scientist, CREGU, Vandoeuvre Les Nancy, France.
12. Guest from VA Polytechnic Institute & State University, Blacksburg, VA.
13. Visiting Scientist, Dept. of Chemistry, State University of NY, College at Oswego.
14. University of Witten/Herdecke, Germany.

GEOCHEMISTRY

PUBLICATIONS

G. M. Anderson,[1] S. Castet,[2] J. Schott,[2] and R. E. Mesmer, "The Density Model for Estimation of Thermodynamic Parameters of Reactions at High Temperatures and Pressures", *Geochimica et Cosmochimica Acta* **1991**, *55*, 1769.

J. L. S. Bell,[3] "Acetate Decomposition in Hydrothermal Solutions," *Ph.D. Thesis* **1991**, The Pennsylvania State University.

J. L. S. Bell[3] and D. A. Palmer, "Acetate in Hydrothermal Solutions: Decomposition Kinetics, Metals Complexing and Their Interrelated Roles in Basin Processes," *Proceedings of the 7th International Symposium on Water-Rock Interaction* **1992**, eds. Y. K. Kharaka and A. S. Maest, A. A. Balkema, 307.

J. L. S. Bell,[3] D. A. Palmer, H. L. Barnes,[4] and S. E. Drummond,[5] "Thermal Decomposition of Acetate. Part III. Catalysis by Mineral Surfaces," *Geochimica et Cosmochimica Acta* (in press).

J. L. S. Bell[3] and D. A. Palmer, "Experimental Studies of Organic Acid Decomposition," eds. M. D. Lewan and E. D. Pittman, *The Role of Organic Acids in Geological Processes 18*, Springer-Verlag (in press).

J. L. S. Bell,[3] D. J. Wesolowski, and D. A. Palmer, "The Dissociation of Quotients of Formic Acid in Sodium Chloride Solutions to 200°C," *Journal of Solution Chemistry* **1993**, *22*, 125.

J. G. Blencoe and S. M. Sterner,[6] "Volumetric Properties and Phase Relations for H_2O, CO_2, CH_4 and N_2 Calculated from Equations of State: Review and Analysis," Fourth Biennial Pan-American Conference on Research on Fluid Inclusions, *Program and Abstracts* **1992**, 100.

J. G. Blencoe, C. V. Guidotti,[7] F. P. Sassi,[8] "Numerical Geothermometers for Quasibinary Paragonite-Muscovite Pairs," *Geochimica et Cosmochimica Acta* (in press).

J. G. Blencoe, "A Two-Parameter Margules Method for Modelling the Thermodynamic Mixing Properties of Albite-Water Melts," *Trans. Royal Soc. Edinburgh Earth Sciences* **1992**, *83*, 423.

W. H. Christie,[9] L. R. Riciputi,[9] D. R. Cole, H. G. Machel,[10] and T. M. Rosseel,[9] "An Ion Microprobe Study of Small-Scale Chemical Variations that Occur in Certain Dolomitized Limestones," *Proceedings of the 40th ASMS Conference on Mass Spectrometry and Applied Topics* **1992**, 772.

D. R. Cole, "Possible Evidence for Fluid-Rock Oxygen Isotope Disequilibrium in Hydrothermal Systems," *Proceedings of the 7th International Symposium on Water-Rock Interaction* **1992**, eds. Y. K. Kharaka and A. S. Maest, A. A. Balkema, 995.

D. R. Cole, "Influence of Solution Composition and Pressure on the Rates of Oxygen Isotope Exchange in the System: Calcite-H_2O-NaCl at Elevated Temperatures," *Chemical Geology (Isotope Geoscience Section)* **1992**, *102*.

D. R. Cole, Hiroshi Ohmoto,[11] and Gary K. Jacobs,[12] "Isotopic Exchange in Mineral-Fluid Systems. III. Rates and Mechanisms of Oxygen Isotope Exchange in the System Granite-H_2O ± NaCl ± KCl at Hydrothermal Conditions," *Geochimica et Cosmochimica Acta* **1992**, *56*, 445.

D. R. Cole, L. R. Riciputi[9] and H. G. Machel,[10] "Ion Microprobe Studies of Diagenesis," 7th Meeting of the European Union of Geosciences, *Terra Abstracts* **1993**, *5*, 369.

D. R. Cole, "Evidence for Oxygen Isotope Disequilibrium in Selected Geothermal and Hydrothermal Ore Deposit Systems," *Chemical Geol. (Isotope Geoscience Sect.)* (in press).

D. R. Cole, L. R. Riciputi,[9] and H. G. Machel,[10] "An Ion Microprobe Study of Sulfur Isotope Variability in Pyrites from Devonian Carbonates, Western Canada Sedimentary Basin, Alberta, Canada," 7th Meeting of the European Union of Geosciences, *Terra Abstracts of the European Union of Geosciences* **1993**, *3*, 369.

D. R. Cole, D. J. Wesolowski and S. E. Drummond,[5] "The Solubility of Calcite and Dolomite to Temperatures of 300°C and Pressures of 1.3 Kbars," *V. M. Goldschmidt Conference, Program and Abstracts* **1992**, *A22*.

M. S. Drummond,[13] D. T. Allison,[13] and D. J. Wesolowski, "Igneous Petrogenesis and Tectonic Setting of the Elkahatchee Quartz Diorite, Alabama Appalachians: Implications for Penobscotian Magmatism in the Eastern Blue Ridge," *American Journal of Science* (in press).

N. W. Dunbar,[12] L. R. Riciputi,[9] G. K. Jacobs,[12] M. T. Naney,[5] and W. H. Christie,[9] "Generation of Rhyolitic Melt in a Man-Made Magma: Implications for Fractional Crystallization Processes in Natural Magmas," *Journal of Volcanology and Geothermal Resources* (in press).

P. G. Feiss,[14] R. K. Vance,[15] and D. J. Wesolowski, "Volcanic-Hosted Gold and Base Metal Mineralization Associated with Late Proterozoic-Early Paleozoic Back-Arc Extension in the Carolina Terrane, Southern Appalachian Piedmont," *Geology* **1993** (in press).

R. G. Gibson[16] and M. T. Naney,[5] "Magma Mixing and Textural Development of Silicic Volcanic Rocks from the Inyo Chain, Eastern California, USA," *Journal of Geophysical Research* **1992**, *97B*, 4541.

T. H. Giordano[17] and S. E. Drummond,[5] "The Potentiometric Determination of Stability Constants for Zinc Acetate Complexes in Aqueous Solutions to 295°C," *Geochimica et Cosmochimica Acta* **1991**, *55*, 2401.

A. P. Gize,[18] H. L. Barnes,[4] and J. L. S. Bell,[3] "A Critical Evaluation of Organic Processes in Mississippi Valley-Type Genesis," *Source, Transport and Deposition of Metals, Proceedings of 25 Years SGA Anniversary Meeting,"* **1992**, 527, eds. M. Dagel and J. L. Leroy, Balkema, Rotterdam, Nancy, France, September 1991.

C. V. Guidotti,[7] C. Mazzoli,[8] F. P. Sassi,[8] and J. G. Blencoe, "Compositional Controls on the Cell Dimensions of $2M_1$ Muscovite and Paragonite," *European Journal of Mineralogy* **1992**, *4*, 283.

C. V. Guidotti,[7] F. P. Sassi,[8] and J. G. Blencoe, "P-T-X Limits of the Binary Paragonite-Muscovite Solvus: Evidence from Natural Paragonite-Muscovite Pairs," *Geochimica et Cosmochimica Acta* (in press).

C. V. Guidotti,[7] F. P. Sassi,[8] and J. G. Blencoe, "The Effects of Ferromagnesian Components on the Paragonite-Muscovite Solvus: A Semi-quantitative Analysis Based on Geochemical Data for Natural Paragonite-Muscovite Pairs," *Mineralogy and Petrology* (in press).

J. Horita,[3] D. J. Wesolowski, and D. R. Cole, "The Effects of Dissolved Salts on Oxygen and Hydrogen Isotope Fractionation Between Water Vapor and Brines at 50-100°C," *Proceedings of the 7th International Symposium on Water-Rock Interaction* **1992**, eds. Y. K. Kharaka and A. S. Maest, A. A. Balkema, 999.

J. Horita,[3] D. R. Cole, and D. J. Wesolowski, "The Activity-Composition Relationship of Oxygen and Hydrogen Isotopes in Aqueous Salt Solutions. II: Vapor-liquid Water Equilibration of Mixed Salt Solutions from 50 to 100°C and Geochemical Implications," *Geochim. Cosmochim. Acta* (in press).

J. Horita,[3] D. J. Wesolowski, and D. R. Cole, "The Activity-Composition Relationship of Oxygen and Hydrogen Isotopes in Aqueous Salt Solutions. I: Vapor-Liquid Water Equilibration of Single Salt Solutions from 50 to 100°C," *Geochimica et Cosmochimica Acta* **1993**, *57* (in press).

J. Horita,[3] A. Weinberg,[19] N. Das,[19] and H. D. Holland,[19] "The Geochemistry of Brine Inclusions in Halite from the Middle Devonian Prairie Formation, Western Canada," *Journal of Sedimentary Petrology* (in press).

D. B. Joyce[3] and J. R. Holloway,[20] "An Experimental Determination of the Thermodynamic Properties of H_2O-CO_2-NaCl Fluids at High Pressures and Temperatures," *Geochimica et Cosmochimica Acta* **1993**, *57*, no. 3.

R. M. Kettler,[21] D. A. Palmer, and D. J. Wesolowski, "Dissociation Quotients of Oxalic Acid in Aqueous Sodium Chloride Media to 175°C", *Journal of Solution Chemistry* **1991**, *20*, 905.

R. M. Kettler,[21] D. A. Palmer, and D. J. Wesolowski, "Dissociation Quotients of Malonic Acid in Aqueous Sodium Chloride Media to 100°C," *Journal of Solution Chemistry* **1992**, *21*, 883.

G. H. Mack,[17] D. R. Cole, T. H. Giordano,[17] W. C. Schaal,[25] and J. H. Barcelos,[26] "Paleoclimatic Controls on Stable Oxygen and Carbon Isotopes in Caliche of the Abo Formation (Permian), South-Central New Mexico, U.S.A," *Journal of Sedimentary Petrology* **1991**, *61*, 458.

G. H. Mack,[17] D. R. Cole, W. C. James,[26] T. H. Giordano,[17] and S. Salyards,[27] "Stable Oxygen and Carbon Isotopes of Pedogenic Carbonate as Indicators of Plio-Pleistocene Paleoclimate in the Southern Rio Grande Rift, South-Central New Mexico," *American Journal of Science* (in press).

Leon Maya, David R. Cole, and Edward W. Hagaman, "Carbon-Nitrogen Pyrolyzates: Attempted Preparation of Carbon Nitride," *Journal of the American Ceramic Society* **1991**, *74*, 1686.

R. E. Mesmer, Comments on "A New Approach to Measuring pH in Brines and Other Concentrated Electrolytes by K. G. Knauss, T. J. Wolery and K. J. Jackson," *Geochimica et Cosmochimica Acta* **1991**, *55*, 1175.

N. Miljevic,[28] Z. Maksimovic,[29] J. Pezdic,[30] D. R. Cole, and W. A. Van Hook,[31] "Hydrogen and Oxygen Isotope Ratios in Praseopal and Crysoprase-Containing Hydrous Nickel Silicates," *Mineralium Deposita* (in press).

D. A. Palmer and D. J. Wesolowski, "Aluminum Speciation and Equilibria in Aqueous Solution. Part II. The Solubility of Gibbsite in Acidic Sodium Chloride Solutions from 30 to 70°C," *Geochimica et Cosmochimica Acta* **1992**, *56*, 1093.

D. A. Palmer and J. L. S. Bell,[3] "Aluminum Speciation and Equilibria in Aqueous Solution. Part IV. A Potentiometric Study of Aluminum Acetate Complexation in Acidic NaCl Brines to 150°C," *Geochimica et Cosmochimica Acta* (in press).

D. A. Palmer and S. E. Drummond,[5] "An Experimental Study of the Solubility of Magnetite in Sodium Acetate Solutions," *Proceedings of the International Conference on Interaction of Iron Based Materials with Water and Steam* (in press).

D. A. Palmer and D. J. Wesolowski, "Aluminum Speciation and Equilibria in Aqueous Solution. Part III. Potentiometric Determination of the First Hydrolysis Constant of Aluminum(III) in Sodium Chloride Solutions to 125°C," *Geochimica et Cosmochimica Acta* (in press).

J. D. Pasteris,[32] J. C. Seitz,[3] G. B. Morgan, VI,[32] and B. Wopenka,[32] "CH_4-Rich Inclusions from Quartz Veins in the Valley and Ridge Province and Anthracite Fields of the Pennsylvania Appalachians -- Discussions," *American Mineralogist* **1993**, *78*, 216.

L. R. Riciputi,[9] D. R. Cole, H. Machel,[10] W. H. Christie,[9] and T. M. Rosseel,[9] "Small-Scale Trace Element Zonations in Carbonates: An Ion Microprobe Study of Diagenesis in the Upper Devonian Nisku Formation, Western Canada Sedimentary Basin," *Water-Rock Interaction* **1992**, eds. Y. K. Kharaka and A. S. Maest, A. A. Balkema, 1197.

L. R. Riciputi,[9] W. H. Christie,[9] D. R. Cole, and T. M. Rosseel,[9] "Analysis of Rare Earth Elements in Silicates by Ion Microprobe Using Doubly-Charged Ions," *Analytical Chemistry* (in press).

L. R. Riciputi,[9] D. R. Cole and H. G. Machel,[10] "Ion Microprobe Studies of Diagenesis: I. Carbonates in the Devonian Nisku Formation of Alberta, Canada," *Journal of Sedimentary Petrology* (in press).

L. R. Riciputi,[9] W. H. Christie,[9] D. R. Cole, and T. M. Rosseel,[9] "Analysis of Rare Earth Elements in SIMS Using Doubly-Charged Ions," *Analytical Chemistry* (in press).

T. M. Rosseel,[9] L. R. Riciputi,[9] W. H. Christie,[9] and D. R. Cole, Digital-imaging and Analysis with the Secondary Ion Microprobe," *Fifth East Coast Workshop on Secondary Ion Mass Spectrometry* **1992**, *35*.

J. C. Seitz,[3] J. G. Blencoe, D. B. Joyce,[3] and R. J. Bodnar,[16] "Excess Molar Volumes for CO_2-CH_4-N_2 Mixtures," In: *Proceedings of the 7th International Symposium on Water-Rock Interaction* **1992**, eds., Y. K. Kharaka and A. S. Maest, A. A. Balkema, Rotterdam, 1025.

J. C. Seitz,[3] J. D. Pasteris,[32] and G. B. Morgan, VI,[32] "Quantitative Analysis of Mixed Volatile Fluids by Raman Microprobe Spectroscopy: A Cautionary Note on Spectral Resolution and Peak Shape," *Applied Spectroscopy* (in press).

J. C. Seitz,[3] J. D. Pasteris,[32] and I-M. Chou,[35] "Raman Spectroscopic Characterization of Gas Mixtures. I. Quantitative Composition and Pressure Determination of CH_4, N_2, and Their Mixtures," *American Journal of Science* **1993**, *293*, 297.

J. C. Seitz,[3] J. G. Blencoe, D. B. Joyce,[3] and R. J. Bodnar,[16] "Volumetric Properties of CO_2-CH_4-N_2 Fluids: Comparison of Equations of State and Experimental Data with Implications for Fluid Inclusions," *Geochimica et Cosmochimica Acta* (in press).

David J. Wesolowski, "Aluminum Speciation and Equilibria in Aqueous Solution. Part I. The Solubility of Gibbsite in the System Na-K-$Al(OH)_4$-OH-Cl from 0 to 100°C," *Geochimica et Cosmochimica Acta* **1992**, *56*, 1065.

D.J. Wesolowski, "Review of Stable Isotope Geochemistry: A Tribute to Samuel Epstein," eds. H. P. Taylor, J. R. O'Neil, and I. R. Kaplan, *Economic Geology* **1992**, *87*, no. 8, 2192.

D. J. Wesolowski and D. A. Palmer, "Experimental Studies of Aluminum Solubility and Speciation in Brines," In: *Proceedings of the 7th International Symposium on Water-Rock Interaction* **1992**, eds. Y. K. Kharaka and A. S. Maest, A. A. Balkema, 185.

PRESENTATIONS

J. G. Blencoe, "A Vibrating-Tube Technique for Measuring the P-V-T Properties of C-O-H Fluids at Elevated Pressures and Temperatures," Symposium on Chemical and Isotopic Composition of Deep Gases, Abstracts of Papers, 201st National Meeting, Amer. Chem. Soc. GEOC *57*, 1991.

J. G. Blencoe, "Calculated Thermodynamic Mixing Properties for Albite-Water Melts," EOS *72*, 304, 1991.

J. G. Blencoe, "Evaluation of Thermodynamic Models for Albite-Water Melts," Second Hutton Symposium on the Origin of Granites and Related Rocks, Canberra, Australia, 1991.

J. G. Blencoe, C. V. Guidotti,[7] and F. P. Sassi,[8] "Thermodynamic Analysis of Solvus Data for Synthetic, Binary Paragonite-Muscovite Micas," V. M. Goldschmidt Conference, *A-10*, May 8-10, 1992.

J. G. Blencoe, C. V. Guidotti,[7] and F. P. Sassi,[8] "An Improved Set of Solvus Data for Synthetic, Binary Paragonite-Muscovite Micas," EOS *73*, 327, 1992.

D. R. Cole, "Mechanisms and Rates of Oxygen Isotope Exchange in the System: Calcite-H_2O-NaCl at Elevated Pressure and Temperature," *Geol. Soc. Amer. Ann. Mtg. Abst. with Programs* **1991**.

D. R. Cole and T. E. Burch,[36] "The Influence of Fluid Composition on the Mechanisms and Rates of Stable Isotope Exchange in Mineral-Fluid System at Elevated Temperatures and Pressures," Alfred O. Nier Symposium on Inorganic Mass Spectrometry, *Abstract Volume 50*, **1991**.

D. R. Cole and D. J. Wesolowski, "The Solubility of Calcite and Dolomite to Temperatures of 300°C and Pressures to 1.3 Kbars," 2nd International Symposium on Chemistry in High Temperature Aqueous Solutions, *Programs, Abst., Bibliog.* 20, Provo, Utah, August 19-22, 1991.

D. R. Cole, "The Relationship Between Mineral Chemistry and Oxygen Isotope Exchange Rates at Elevated Temperatures and Pressures," Geol. Soc. Amer. Ann. Mtg., *Abstrs. with Programs 24*, no. 7, A171, **1992**.

D. R. Cole, D. J. Wesolowski, and S. E. Drummond,[5] "The Solubility of Calcite and Dolomite to Temperatures of 300°C and Pressures of 1.3 Kbars," A22, V. M. Goldschmidt Conference, *Program and Abstracts*, Reston, Virginia, May 8-10, 1992.

D. R. Cole, "Evidence for Isotopic Disequilibrium in Hydrothermal Rock-Water Systems," Seminar Series, Dept. of Geology, University of Tennessee, January 21, 1993.

D. R. Cole, L. R. Riciputi,[9] and H. G. Machel,[10] "An Ion Microprobe Study of Sulfur Isotope Variability in Pyrites from Devonian Carbonates, Western Canada Sedimentary Basin, Alberta, Canada," 7th Meeting of the European Union of Geosciences, *Terra Abst.* 5, 369, **1993**.

D. R. Cole, L. R. Riciputi,[9] and H. G. Machel,[10] "Ion Microprobe Studies of Diagenesis," 7th Meeting of the European Union of Geosciences, *Terra Abst. 5*, 369, **1993**.

H. D. Holland[19] and J. Horita,[3] "The Phanerozoic History of Seawater," *GSA Abstracts with Program 23*, A111, **1991**.

J. Horita,[3] D. J. Wesolowski, and D. R. Cole, "The Effects of Dissolved NaCl and KCl on Oxygen and Hydrogen Isotope Fractionation Between Water

Vapor and Brines at 50-100°C," *Geol. Soc. Amer. Ann. Mtg., Abstr. with Prog. 23*, no. 5, A320, **1991**.

J. Horita[3] and H. D. Holland,[19] "The Evolution of Seawater During the Phanerozoic," 3rd Goldschmidt Conference, A-52, **1992**.

D. B. Joyce[3] and J. R. Holloway,[20] "Experimentally Determined Activity-Combination Relations for H_2O in C-O-H-NaCl Fluids by the H_2 Fugacity Buffer Technique," *GSA Abstracts with Programs 23*, no. 5, A52, **1991**.

D. Joyce[3] and J. Holloway,[20] "An Empirical Equation of State for the Mixing Properties of H_2O-CO_2 Fluids (Abstr.)," EOS Trans. Am. Geophys. Union 1992, no. 14, *Spring Meeting Supplement 73*, 357, **1992**.

R. M. Kettler,[21] D. A. Palmer, and D. J. Wesolowski, "A Potenticmetric Study of the Dissociation Constants of Oxalic Acid in 0-5 molal NaCl Brines to 175°C, 2nd International Symposium on Chemistry in High-Temperature Water, Provo, Utah, August 19-22, 1991.

R. M. Kettler,[21] D. A. Palmer, and D. J. Wesolowski, "The Dissociation Quotients of Oxalic Acid in Aqueous Sodium Chloride Media to 175°C," 15th Meeting of the European Association of Organic Geochemists, Manchester, UK, September 16-20, 1991.

H. G. Machel,[10] R. H. Krouse,[22] E. A. Burton,[23] J. M. Foght,[24] L. R. Riciputi,[9] and D. R. Cole, "The Nisku Sour Gas Play: A Unique National Laboratory for the Study of Thermochemical Reduction," *AAPG Ann. Mtg.*, New Orleans, *Abstrs. with Programs 142*, **1993**.

M. McCurry,[37] E. Durfee,[37] G. L. Farmer,[38] P. Verplank,[38] S. A. Metzman,[39] and D. R. Cole, "Petrology of the Organ Needle Pluton: Implications for Open System Evolution of Large Volume Compositionally Zoned Magna Bodies," *EOS, Trans., Amer. Geophys. Union 74*, no. 16, 334, **1993**.

H. C. Monger,[17] D. R. Cole, and T. H. Giordano,[17] "Stable Isotopes in Pleistocene and Holocene Aridisols of Southern New Mexico," *Soil Sci. Soc. Amer. Ann. Mtg.* **1991**.

H. C. Monger,[17] D. R. Cole, and J. W. Gish,[40] "Late Quaternary Paleosols and Climate Change in Southern New Mexico," *Geol. Soc. Amer. Ann. Mtg., Abstrs. with Programs 24*, no. 7, A285, **1992**.

H. C. Monger,[17] D. R. Cole, and J. W. Gish,[40] "Evidence of Holocene Climate Change in New Mexico Based on Stable Isotopes and Fossil Pollen in Buried Soils," *Amer. Soc. Agronomy, Absts. with Program*, **1992**.

M. T. Naney,[5] N. W. Dunbar,[12] L. Riciputi,[9] and W. H. Christie,[9] "Generation of Rhyolitic Melt from a Basaltic Parent: Crystallization Processes Within a Man-made Magma Body," *EOS* **1992**, 358.

Donald A. Palmer, David J. Wesolowski, and Julie L. S. Bell,[3] "Potentiometric Measurements of Aluminum(III) Hydrolysis and Complexation with Acetate in Sodium Chloride Solutions," *Program and Abstracts*, 12th IUPAC

Conference on Chemical Thermodynamics-47th Calorimetry Conference Joint Meeting, Snowbird, Utah, August 16-21, 1992 (in press).

L. R. Riciputi,[9] D. R. Cole, H. Machel,[10] T. M. Rosseel,[9] and W. H. Christie,[9] "The Ion Microprobe for Trace Element Analysis in Carbonates: Diagenesis in the Upper Devonian Nisku Formation, Western Canada Basin," Geol. Soc. Amer. Ann Mtg., *Abstrs. with Programs 24*, no. 7, A60, **1992**.

J. C. Seitz,[3] J. G. Blencoe, D. B. Joyce,[3] and R. J. Bodnar,[16] "P-V-T-X Properties of CO_2-CH_4 Mixtures at 100°C and 400 to 1000 bars by Vibrating Tube Densimetry," EOS *72*, 522, **1991**.

J. C. Seitz,[3] J. G. Blencoe, D. B. Joyce,[3] and R. J. Bodnar,[16] "Volumetric Properties of CO_2-CH_4-N_2 Mixtures," Fourth Biennial Pan-American Conference on Research on Fluid Inclusions, *Program and Abstracts 133*, **1992**.

J. C. Seitz,[3] J. G. Blencoe, D. B. Joyce,[3] and R. J. Bodnar,[16] "Excess Molar Volumes for CO_2-CH_4-N_4 Mixtures," Seventh International Symposium on Water-Rock Interaction **1992**.

J. C. Seitz,[3] J. D. Pasteris,[32] and G. B. Morgan, VI,[32] "Cautionary Note on Analytical Methodology for Quantitative Analysis of Co_2-CH_4-N_2-H_2 Fluids by Microsampling Raman Spectroscopy," Fourth Biennial Pan-American Conference on Research on Fluid Inclusions, *Program and Abstracts 72*, **1992**.

D. Voigt[4] and D. Joyce,[3] "Depression of the Granite Minimum by the Addition of Sillimanite," EOS Trans. Am. Geophys. Union, *Spring Meeting Supplement 72*, no. 17, 304, **1991**.

David J. Wesolowski and Donald A. Palmer, "Potentiometric Measurements of the Hydrolysis of Al^{3+} in 0-5 molal Aqueous Sodium Chloride Solutions in the 0-150°C Range," Geol. Soc. Amer. Annual Meeting, *Abstr. w. Programs 23*, no. 5, A212, **1991**.

David J. Wesolowski, Donald A. Palmer, and Robert E. Mesmer, "Use of Hydrogen-Electrode Potentiometric Cells for the Determination of the Equilibrium Quotients of Acid/Base, Metal Hydrolysis and Complexation Reactions in Aqueous Electrolyte Solutions in the 0-300°C Range," *Program and Abstracts A120*, V. M. Goldschmidt Conference, Reston, Virginia, May 8-10, 1992.

D. J. Wesolowski, "Fluid-Rock Interactions in the Earth's Crust: Geochemistry Related to Energy Technologies," Oak Ridge National Laboratory, Showcase Series Lecture, Oak Ridge, Tennessee, January 15, 1993.

---

1. University of Toronto, Toronto, Canada.
2. University Paul Sabatier, Toulouse, France.
3. ORISE Postdoctorate.
4. Penn State University, University Park, PA.

5. Formerly Chemistry Division.
6. Bayerisches Geoinstut, Universitat Bayreuth, F.R.G.
7. University of Maine, Orono, MA.
8. Dept. of Min. & Pet., University of Padova, Padova, Italy.
9. Analytical Chemistry Division.
10. University of Alberta, Canada.
11. State University of Pennsylvania.
12. Environmental Sciences Division.
13. University of Alabama.
14. University of North Carolina.
15. North Carolina State University.
16. VA Polytechnic & State University, Blacksburg, VA.
17. New Mexico State University, Las Cruces, NM.
18. University of Manchester.
19. Harvard University, Cambridge, MA.
20. Arizona State University, Tempe, AZ.
21. Visiting Scientist, University of Nebraska, Lincoln, NE.
22. University of Calgary.
23. Northern Illinois University.
24. University of Alberta, Edmonton, Alberta, Canada.
25. Universidade Estodual Paulista, Sao Paulo, Brazil.
26. Ohio State University.
27. University of California, Los Angeles.
28. Boris Kidric Inst., Belgrade, Yugoslavia.
29. University of Belgrade, Yugoslavia.
30. Institute Josef Stefan, Ljubljana, Yugoslavia.
31. University of Tennessee.
32. Washington University, St. Louis, MO.
33. Washington State University
34. Engineering Physics Division
35. U. S. Geological Survey.
36. Yale University
37. Idaho State University, Pocatello, ID.
38. University of Colorado, Boulder, CO.
39. Franklin and Marshall College, Lancaster, MA.
40. Quaternary Polynology Research, Flagstaff, AZ.

CHEMISTRY OF ADVANCED INORGANIC MATERIALS

PUBLICATIONS

M. M. Abraham[1] and C. E. Bamberger, "EPR Spectroscopic Determination of Ti^{3+} in Several Titanium Phosphate Compounds," *J. Am. Ceram. Soc.* **1991**, *74(9)*, 2299.

K. G. Alexander,[2] D. M. Kroeger,[2] J. Bentley,[2], and J. Brynestad, "Grain Boundary Compositions in Stoichiometric and Off-Stoichiometric $YBa_2Cu_3O_{7-x}$," *Physica C* **1991**, *180*, 337.

K. B. Alexander,[2] R. K. Williams,[2] D. M. Kroeger,[2] and J. Brynestad, "The Structure and Chemistry of Grain Boundaries in Ceramic Superconduc-

tors," *Ceramic Transactions* **1991**, *18*, 365; Superconductivity and Ceramic Superconductors II," eds., K. M. Nair, U. Balachandran, V-M. Chang, and A. S. Bhall.

"C. E. Bamberger, C. S. MacDougall,[3] G. M. Begun,[4], and T. Hatmaker,[5] "Synthesis of Solid Phosphate Compounds of Ti(III,IV)," *J. Am. Ceram. Soc.* **1991**, *74(4)*, 837.

C. E. Bamberger, L. F. Allard,[2] D. W. Coffey,[2] and M. R. Bennett,[6] "Whiskers of TiN by Topochemical Reaction," *J. Cryst. Growth* **1991**, *112*, 47.

C. E. Bamberger and J. Brynestad, "Comments on 'Synthesis of Titanium Nitride whiskers from Potassium Fluorotitanate (IV)'," by M. Tabuchi, Y. Kaneko, and H. Iwasaki, *J. Ceram. Soc. Japan* **1991**, *99*, 1172.

C. E. Bamberger and G. M. Begun,[4] "The Formation of Crystalline Needles of Rutile by Flux Evaporation," *J. Matls. Sci. Letters* **1992**, *11(2)*, 79.

C. E. Bamberger and K. B. Alexander,[2] "The Pseudomorphic Conversion of Platelets of Cr_2O_3 into CrN and Cr_3C_2," *J. Cryst. Growth* **1993**, *126*, 525.

C. E. Bamberger and O. C. Kopp,[7] "Acicular Crystals of Sodium Tungsten Bronzes," *J. Cryst. Growth* (in press).

K. M. Doverspike,[2] C. R. Hubbard,[2] R. K. Williams,[2] K. B. Alexander,[2] J. Brynestad, and D. M. Kroeger,[2] "Anisotropic Thermal Expansion of the 1:2:4 Yttrium Barium Copper Oxide Superconductor," *Physica C* **1991**, *172*, 486.

D. M. Kroeger,[2] H. S. Hsu,[2] J. Brynestad, V. K. Sikka,[2] T. Ward,[8] and T. Kodas,[8] "Processing and Properties of Powder-in-Tube Conductors Containing Bi(Pb) 2223 Powder Prepared by Aerosol Pyrolysis," Proc. of the International Workshop on Superconductivity, Honolulu, Hawaii, June 23-26, 1992.

B. N. Lucas,[2] W. C. Oliver,[2] R. K. Williams,[2] J. Brynestad, and M. E. O'Hern,[9] "The Hardness and Young's Modulus of Bulk $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_4O_8$ (1:2:4) as Determined by Ultra Low Load Indentation," *J. Mater. Res.* **1991**, *6*, 2519.

L. Maya, D. R. Cole, and E. W. Hagaman, "Carbon-Nitrogen Pyrolyzates: Attempted Preparation of Carbon Nitride," *J. Am. Ceram. Soc.* **1991**, *74*, 1686.

L. Maya, "Nitrogen and Boron-Containing Polymers as Precursors of Ceramic Materials," *Polym. Prep. (Am. Chem. Soc. Div. Polym. Chem.)* **1991**, *32*, 552.

L. Maya, "Preparation of Tin Nitride via an Amide Imide Intermediate," *Inorg. Chem.* **1992**, *31*, 1958.

L. Maya, "Plasma-Enhanced Chemical Vapor Deposition of Boron Nitride Using Polymeric Cyanoborane as Source," *J. Am. Ceram. Soc.* **1992**, *75*, 1985.

L. Maya, "Covalent Nitrides for Maskless Laser Writing of Microscopic Metal Lines," *Mater. Res. Soc. Symp. Proc.* **1993**, *282*, 203.

L. Maya, "Deposition of Crystalline Binary Nitride Films of Tin, Copper, and Nickel by Reactive Sputtering," *J. Vac. Sci. & Technol.* (in press).

L. Maya, "Paracyanogen Reexamined," *J. Polym. Sci. Polym. Chem. Ed.* (in press).

J. R. Thompson,[1] D. K. Christen,[1] H. R. Kerchner,[1] L. A. Boatner,[1] B. C. Sales,[1] B. C. Chakoumakos,[1] H. Hsu,[2] J. Brynestad, D. M. Kroeger,[2] R. K. Williams,[2] Yang Ren Sun,[1] Y. C. Kim,[1] J. G. Ossandon,[1] A. P. Malozemoff,[10] L. Civale,[11] A. D. Marwick,[11] T. K. Worthington,[11] L. Krusin-Elbaum,[11] and F. Holtzberg[11], "Studies of 'Non-Ideal' Superconductors Using DC Magnetic Methods," Magnetic Susceptibility of Superconductors and Other Spin Systems, eds. R. A. Hein et al., Plenum Press, New York, **1992**.

C. E. Vallet, "Computer Simulations of the Semiconductor-Metal Transition in Ru/Ti and Ir/Ti Mixed Oxides," *J. Electrochem. Soc.* **1991**, *138*, 1234.

C. E. Vallet and C. W. White,[1] "Application of Ion Implantation to Electrochemical Studies," *Nucl. Instrum. Methods* **1991**, *B1*, 855.

C. E. Vallet, A. Choudhury,[2] P. E. Sobol,[12] and C. W. White,[1] "XPS Characterization of Anodic Layers Grown on Ir- and Rh-Implanted Titanium," *Electrochim. Acta* **1993** (in press).

T. L. Ward,[9] S. W. Lyons,[9] T. T. Kodas,[9] J. Brynestad, D. M. Kroeger,[2] and H. Hsu,[2] "Characteristics of Bi-Pb-Sr-Ca-Cu-O Powders Produced by Aerosol Decomposition and Their Rapid Conversion to the High-T_c Phase," *Physica C* **1992**, *200(1-2)*, 31.

R. K. Williams,[2] J. Brynestad, T. J. Henson,[2] and D. M. Kroeger,[2] "Preparation and Grain Boundary Chemistry of Dense Polycrystalline $YBa_2Cu_4O_{\sim 8}$," *J. Appl. Phys.* **1991**, *69*, 2426.

R. K. Williams,[2] K. B. Alexander,[2] J. Brynestad, T. J. Henson,[2] D. M. Kroeger,[2] T. B. Lindemer,[13] G. C. Marsh,[2] J. O. Scarbrough,[2] and E. D. Specht,[2] "Oxidation Induced Decomposition of $YBa_2Cu_3O_{7-x}$," *J. Appl. Phys.* **1991**, *70*, 906.

PRESENTATIONS

L. Maya, "Nitrogen and Boron-Containing Polymers as Precursors of Ceramic Materials," ACS Fall Meeting, New York, New York, August 1991.

L. Maya, "Covalent Nitrides for Maskless Laser Writing of Microscopic Metal Lines," MRS Fall Meeting, Boston, MA, December 1992.

C. E. Vallet, "Photoacoustic Spectroscopy and the In-situ Characterization of the Electrochemical Interface," ORAU Traveling Lecture, Chemistry Department, Oklahoma State University, Stillwater, OK, December 12, 1992.

C. E. Vallet, "Photoacoustic Spectroscopy and the In-situ Characterization of the Electrochemical Interface," ORAU-Traveling Lecture, Department of Chemistry, Howard University, Washington, DC, April 3, 1992.

PATENTS

C. E. Bamberger, "Process for Preparing Whiskers, Fibers, and Flakes of Transition Metal Compounds," U.S. Patent 5,118,488 (June 2, 1992).

L. Maya, "Low-Loss Binder for Hot Pressing Boron Nitride," U.S. Patent 5,010,045 (April 1991).

L. Maya, "Precursors in the Preparation of Transition Metal Nitrides and Transition Metal Carbonitrides and Their Reaction Intermediates," U.S. Patent 5,023,213 (June 1991).

---

1. ORNL Solid State Division.
2. ORNL Metals and Ceramics Division.
3. ORNL Analytical Chemistry Division.
4. Retired, ORNL Chemistry Division.
5. Applied Technology Organization, K-25 Plant, Oak Ridge, TN.
6. Deceased.
7. Consultant, Department of Geological Sciences, University of Tennessee, Knoxville, TN.
8. University of New Mexico, Albuquerque, NM.
9. University of Tennessee, Knoxville, TN.
10. American Superconductor Corporation, Watertown, MA.
11. IBM, Yorktown Heights, NY.
12. Physical Electronics Laboratory, Perkin Elmer, Eden Prairie, MN.
13. ORNL Chemical Technology Division.

STRUCTURE AND DYNAMICS OF ADVANCED POLYMERIC MATERIALS

PUBLICATIONS

B. K. Annis, J. S. Lin,[1] E. M. Scherr,[2] and A. G. MacDiarmid,[2] "Evidence for the Development of a One-Dimensional Array of Crystallites in Stretched Polyaniline and the Effect of Cl^- Doping," *Macromolecules* **1992**, *25*, 429.

B. K. Annis, D. W. Noid, B. G. Sumpter, J. R. Reffner,[3] and B. Wunderlich,[4] "Application of Atomic Force Microscopy (AFM) to a Block Copoly-

mer and an Extended Chain Polyethylene," *Makromol. Chem., Rapid Commun.* **1992**, *13*, 169.

B. K. Annis, J. R. Reffner,[3] and B. Wunderlich,[4] "Atomic Force Microscopy of Extended Chain Crystals of Polyethylene," *J. Polymer Sci., Part B. Polymer Phys.* **1993**, *31*, 93.

B. K. Annis, D. W. Schwark,[5] J. R. Reffner,[3] E. L. Thomas,[5] and B. Wunderlich,[4] "Determination of Surface Morphology of Diblock Copolymers of Styrene and Butadiene by Atomic Force Microscopy," *Makromolekulare Chemie* **1992**, *193*, 2589.

B. K. Annis, E. D. Specht,[6] N. Theophilou,[2] and A. G. MacDiarmid,[2] "Structural Aspects of Stretched Emeraldine as Determined by X-Ray Scattering," *Polymer* **1991**, *32*, 1160.

A. Boller,[7] Y. Jin,[7] J. Cheng,[7] and B. Wunderlich,[4] "Analysis of the Thermal Properties and Motion in Crystalline *trans*-1,4-Poly(butadiene)," *Thermochim. Acta* (in press).

J. Cheng,[7] Y. Jin,[7] G. Liang,[7] B. Wunderlich,[4] and H. G. Wiedemann,[8] "Condis Crystals of Small Molecules. V. Solid State ^{13}C NMR and Thermal Properties of N,N'-bis(4-*n*-Octyloxybenzal)-1,4-Phenylenediamine (OOBPD)," *Mol. Cryst, Liq. Cryst.* **1992**, *213*, 237.

J. Cheng,[7] Y. Jin,[7] B. Wunderlich,[4] S. Z. D. Cheng,[9] M. A. Yandrasits,[9] A. Zhang,[9] and V. Percec,[10] "Solid State ^{13}C NMR Studies of Molecular Motion in MBPE-9 and MBPE-5," *Macromolecules* **1992**, *25*, 5991.

J. Cheng,[7] A. Xenopoulos,[7] and B. Wunderlich,[4] "Two-dimensional NMR Studies of ^{13}C Chemical Shifts in tetraalkylammonium Halides, the Additivity Rules," *Magnetic Resonance in Chemistry* **1992**, *30*, 917.

J. Cheng,[7] A. Xenopoulos,[7] and B. Wunderlich,[4] "Mesophases of Alkylammonium Salts. II. Disorder and Motion in the Low Homologs: $[CH_3(CH_2)_n)]_4NX$, $n = 0,1,2$, and X = Br and I," *Mol. Cryst. Liq. Cryst.* **1992**, *220*, 105.

J. Cheng,[7] A. Xenopoulos,[7] and B. Wunderlich,[4] "Mesophases of Alkylammonium Salts. III. Disorder and Motion in the Intermediate Homologs $[CH_3(CH_2)_{n-1}]_4NX$; n = 4, 5, 6, and 7; X = Br and I," *Mol. Cryst. Liq. Cryst.* **1992**, *220*, 127.

J. Cheng,[7] A. Xenopoulos,[7] and B. Wunderlich,[4] "Mesophases of Alkylammonium Salts. IV. A Solid State ^{13}C NMR Study on Motion in the High Homologs $[CH_3(CH_2)_{n-1}]_4NBr$, n = 8, 10, 12 and 18; and $[CH_3(CH_2)_{11}]_4NI$," *Mol. Cryst. Liq. Cryst.* **1992**, *225*, 337.

S. Z. D. Cheng,[9] J. Chen,[9] X. Wu,[9] M. A. Yandrasits,[9] Q. Zhuo,[9] R. P. Quirk,[9] A. Habenschuss and P. R. Zschack,[6] "Nonintegral and Integral Folding Crystal Growth in Low Molecular Weight Poly(ethylene oxide) Fractions," in *Crystallization of Polymers: Theoretical and Experimental Aspects*, NATO ASI-C Series "Mathematical and Physical Sciences."

S. Z. D. Cheng,[9] A. Zhang,[9] J. Barley,[9] J. Chen,[9] A. Habenschuss, and P. R. Zschack,[6] "Isothermal Thickening and Thinning Processes in Low Molecular Weight Poly(ethylene oxide) Fractions: 1. From Nonintegral Folding to Integral Folding Chain Crystal Transitions," *Macromolecules* **1991**, *24*, 3937.

S. Z. D. Cheng,[9] A. Zhang,[9] J. Barley,[9] J. Chen,[9] A. Habenschuss, and P. R. Zschack,[6] "Isothermal Thickening and Thinning Processes in Low Molecular Weight Poly(ethylene oxide) Fractions Crystallized from the Melt. 2. Crystals Involving More Than One-fold," *Polymer* **1992**, *33*, 1140.

S. Z. D. Cheng,[9] J. Chen,[9] J. S. Barley,[9] A. Zhang,[9] A. Habenschuss, and P. R. Zschack,[6] "Isothermal Thickening and Thinning Processes in Low Molecular Weight Poly(ethylene oxide) Fractions Crystallized from the Melt. 3. Molecular Weight Dependence," *Macromolecules* **1992**, *25*, 1453.

J. G. Curro[11,44] and K. S. Schweizer,[12,44] "Integral Equation Theory for Compressible Polymer Alloys: Thermodynamics, Scattering, and Miscibility," *Macromolecules* (in press).

J. G. Curro,[11,44] A. Yethiraj,[12] K. S. Schweizer,[12,44] J. D. McCoy,[11] and K. G. Honnell,[13,44] "Microscopic Equation-of-State for Hydrocarbon Fluids: Effect of Attractions and Comparison with Polyethylene Experiments," *Macromolecules* (in press).

J. A. Darsey,[14] D. W. Noid, and B. R. Upadhyaya,[7] "Application of Neural Network Computing to the Solution for the Ground-State Eigenenergy of Two-Dimensional Harmonic Oscillators," *Chem. Phys. Lett.* **1991**, *177*, 189.

J. A. Darsey,[14] D. W. Noid, B. Wunderlich,[4] and L. Tsoukalas,[7] "Neural-Net Extrapolations of Heat Capacities of Polymers to Low Temperatures," *Makromol. Chem. Rapid Communications* **1991**, *12*, 325.

J. A. Darsey,[14] A. G. Soman,[14] D. W. Noid, and B. G. Sumpter, "Modeling of Polymeric Systems Using Artificial Neural Network Computing," *Polymer Preprints*.

J. A. Darsey,[14] B. G. Sumpter, C. Getino,[15] and D. W. Noid, "A Neural Network Approach for the Investigation of Chemical Phenomena," *Proceedings of the SIMTEC/WNN 1992*, 546 (1992).

L. J. Effler,[16] J. F. Fellers,[17] and B. K. Annis, "Scanning Tunneling Microscopy and X-ray Analyses on Mesophase Pitch-based Carbon Fibers," *Carbon* **1992**, *30*, 631.

Y. Fu,[7] W. R. Busing,[17] Y. Jin,[7] K. A. Affholter,[18] and B. Wunderlich,[4] "Poly(ethylene terephthalate) Fibers 1. Crystal Structure and Morphology Studies with Full-pattern X-ray Diffraction Refinement," *Macromolecules* (in press).

M. Gehlsen,[19] J. H. Rosedale,[19] F. S. Bates,[19] G. D. Wignall,[1] L. Hansen,[20] and K. Almdal,[20] "Molecular Weight Scaling in Critical Polymer Mixtures," *Phys. Rev. Lett.* **1992**, *68*, 2452.

J. Grebowicz,[21] M. Varma-Nair,[7] and B. Wunderlich,[4] "The Thermal Properties of Poly(pivalolactone)," *Polymers for Advanced Technology* **1992**, *3*, 51.

F. X. Hartmann,[22] D. W. Noid, and Y. Y. Sharon,[23] "Model of Nuclear Excitation by Electronic Motion in Intense Laser Fields," *Phys. Rev.* **1991**, *A44*, 3210.

D. M. Hembree, Jr.,[24] D. F. Pedraza,[6] G. R. Romanoski,[6] S. P. Withrow,[1] and B. K. Annis, "Raman Spectroscopy of C-irradiated Graphite," *Materials Research Society Symposium Proceedings* (in press).

K. G. Honnell,[13,44] J. D. McCoy,[11] J. G. Curro,[11,44] K. S. Schweizer,[12,44] A. H. Narten,[25] and A. Habenschuss, "Local Structure of Polyethylene Melts," *J. Chem. Phys.* **1991**, *94*, 4659.

G. E. Ice,[1] C. J. Sparks,[6] A. Habenschuss, and L. B. Shaffer,[26] "Anomalous X-ray Scattering Measurement of Near-Neighbor Individual Pair Displacements and Chemical Order in $Fe_{22.5}Ni_{77.5}$," *Phys. Rev. Lett.* **1992**, *68*, 863.

Y. Jin,[7] A. Boller,[7] B. Wunderlich,[4] and B. V. Lebedev,[27] "Heat Capacities and Transitions in *n*-Perfluoroalkanes and Polytetrafluoroethylene," *Thermochim. Acta* (in press).

Y. Jin,[7] J. Cheng,[7] M. Varma-Nair,[7] G. Liang,[7] Y. Fu,[7] B. Wunderlich,[4] X-D. Xiang,[28] R. Mostovoy,[28] and A. K. Zettl,[28] "Thermodynamic Characterization of C_{60} by Differential Scanning Calorimetry," *J. Phys. Chem.* **1992**, *96*, 5151.

Y. Jin,[7] Y. Fu,[7] M. Mucha,[29] and B. Wunderlich,[4] "Thermal Characterization of Poly(ethylene terephthalate)," *Proc. 21st NATAS Conf.*, Atlanta, GA, Sept. 13-16, 1992, pgs. 683-688.

Y. Jin,[7] Y. Fu,[7] M. Mucha,[29] and B. Wunderlich,[4] "Thermal Characterization of Poly(ethylene terephthalate)," *Proc. 21st NATAS Conf.*, Atlanta, GA, Sept. 13-16, 1992, pgs. 683-688, *Thermochim. Acta* (in press).

Y. Jin[7] and B. Wunderlich,[4] "The Heat Capacity of *n*-Paraffins and Polyethylene," *J. Phys. Chem.* **1991**, *95*, 9000.

Y. Jin[7] and B. Wunderlich,[4] "Single Run Heat Capacity Measurements. III. Data Analysis," *J. Thermal Analysis* **1992**, *38*, 2257-2272.

Y. Jin[7] and B. Wunderlich,[4] "Single Run Heat Capacity Measurement by DSC: Principle, Experimental Detail and Data Analysis," *Proc. 21st NATAS Conf.*, Atlanta, GA, Sept. 13-16, 1992, pgs. 151-156.

Y. Jin[7] and B. Wunderlich,[4] "Single Run Heat Capacity Measurement by DSC: Principle, Experimental Detail and Data Analysis," *Proc. 21st NATAS Conf.*, Atlanta, GA, Sept. 13-16, 1992, pgs. 151-156, *Thermochim. Acta* (in press).

S. Knudson,[30] B. G. Sumpter, and D. W. Noid, "Dynamics of Charged Polymers. I," *Macromolecules* **1992**, *25*, 331.

G. L. Liang,[7] D. W. Noid, B. G. Sumpter, and B. Wunderlich,[4] "Dynamics of a Paraffin Crystal," *Makromol. Chemie, Theory and Simulation* (in press).

J. D. McCoy,[11] K. G. Honnell,[13,44] J. G. Curro,[11,44] K. S. Schweizer,[12,44] and J. D. Honeycutt,[31] "Single-chain Structure in Model Polyethylene Melts," *Macromolecules* **1992**, *25*, 4905.

S. A. Meyer,[32] M. Morgenstern,[32] S. K. Knudson,[30] and D. W. Noid, "Novel Method for WKB Analysis of Multidimensional Systems," *Am. J. Phys.* **1991**, *59*, 145.

J. Müller,[7] J. Burgdörfer,[7] and D. W. Noid, "Semiclassical Eigenenergies in the Wake of Fast Ions in Solids," *Proc. of the Workshop on Quantum Chaos*, International Center for Theoretical Physics, Trieste, Italy, **1991**, *178*, 60.

J. Müller,[7] J. Burgdörfer,[7] and D. W. Noid, "Semiclassical Eigenenergies in the Wake Potential," *Chem. Phys. Lett.* **1991**, *178*, 60.

J. Müller,[7] J. Burgdörfer,[7] and D. W. Noid, "Torus Quantization of Symmetrically Excited Helium," *Phys. Rev.* **1992**, *A 45*, 1471.

A. H. Narten,[25] A. Habenschuss, K. G. Honnell,[13,4] J. D. McCoy,[11] J. G. Curro,[11,44] and K. S. Schweizer,[12,44] "Diffraction by Macromolecular Fluids," *Faraday Discuss. Chem. Soc.* **1992**, *88*, 1791.

A. H. Narten,[25] A. Habenschuss, and A. Xenopoulos,[7] "Diffraction Pattern and Structure of Amorphous and Crystalline Regions in Semicrystalline Nylon 6.6," *Polymer* **1991**, *32*, 1923.

D. W. Noid and J. A. Darsey,[14] "Neural Net Simulation of Polymer Dynamics," *Comp. Poly. Sci.* **1991**, *1*, 157.

D. W. Noid, J. A. Darsey,[14] and B. G. Sumpter, "Applications of Neural Networks in Polymer Simulations," *Proceedings of the Society of Plastics Engineers* (in press).

D. W. Noid and B. G. Sumpter, "The Existence of Nonlinear Resonances in Polyethylene," *Makromol. Chem. Theory Simul.* **1992**, *1*, 359.

D. W. Noid, B. G. Sumpter, and R. Cox,[33] "Methods for Molecular Dynamics Simulations of Crystalline Polymers: Numerical Integration Schemes," *J. Comp. Polymer Sci.* **1991**, *1*, 161.

D. W. Noid, B. G. Sumpter, J. A. Darsey,[14] B. Wunderlich,[4] and A. Xenopoulos,[7] "Recent Advances in Molecular Dynamics Simulations: Applications to Polymer Crystals," in J. Menon, Ed., *Trends in Chemical Physics*, Research Trends, Trivandrum, India, pgs. 207-238 (1991).

D. W. Noid, B. G. Sumpter, G. Liang,[7] and B. Wunderlich,[4] "Molecular Dynamics Simulation of Electric Field Induced Motion in Crystalline Polyethylene," *Plastics Shaping the Future, Proc. of the SPE 50th Annual Technical Conference and Exhibits*, Antec, 1992, pp. 1982.

D. W. Noid, B. G. Sumpter, and B. Wunderlich,[4] "Molecular Dynamics Simulation of Twist Motion in Polyethylene," *Macromolecules* **1991**, *24*, 4147.

D. W. Noid, M. Varma-Nair,[7] B. Wunderlich,[4] and J. A. Darsey,[14] "Neural Network Inversion of the Tarasov Function Used for the Computation of Polymer Heat Capacities," *J. Thermal Analysis* **1992**, *37*, 2295.

M. R. Nyden[34] and D. W. Noid, "Molecular Dynamics of Initial Events in the Thermal Degradation of Polymers," *J. Phys. Chem.* **1991**, *95*, 940.

G. A. Pfeffer,[35] B. G. Sumpter, and D. W. Noid, "Conformational Changes in a Polyethylene Model Under Tension and Compression," *J. Polym. Eng. Sci.* **1992**, *32*, 1278.

K. A. Roles[7] and B. Wunderlich,[4] "Heat Capacities of Solid Copoly(amino acid)s," *J. Polymer Sci., Part B. Polymer Phys.* **1993**, 31, 27.

K. A. Roles[7] and B. Wunderlich,[4] "Heat Capacities of Solid Poly(amino acid)s. I. Polyglycine, Poly-L-alanine, and Poly-L-valine," *Biopolymers* **1991**, *31*, 477.

K. A. Roles,[7] A. Xenopoulos,[7] and B. Wunderlich,[4] "Heat Capacities of Solid Poly(amino acid)s. II. The Remaining Polymers," *Biopolymers* (in press).

R. Roy,[36] B. G. Sumpter, G. A. Pfeffer,[35] S. K. Gray,[37] and D. W. Noid, "Novel Method for Spectral Analysis," *Comp. Phys. Reports* **1991**, 205, 109.

D. W. Schwark,[5] D. L. Vezie,[5] J. R. Reffner,[3] E. L. Thomas,[5] and B. K. Annis, "Characterization of the Surface Morphology of Diblock Copolymers Via Low-Voltage, High Resolution Scanning Electron Microscopy and Atomic Force Microscopy," *J. Mater. Sci. Lett.* **1992**, *11*, 358.

K. S. Schweizer,[12,44] K. G. Honnell,[13,44] and J. G. Curro,[11,44] "RISM Theory of Polymeric Liquids: Self-Consistent Formulation and Nonideality Effects in Dense Solutions and Melts," *J. Chem. Phys.* **1992**, *96*, 3211.

K. S. Schweizer[12,44] and A. Yethiraj,[12] "Polymer RISM Theory; New Molecular Closures for Phase Separating Fluids and Alloys," *J. Chem. Phys.* (in press).

R. O. Shelton,[38] J. A. Darsey,[14] B. G. Sumpter, and D. W. Noid, "Neural Network Error Correction for Solving Coupled Ordinary Differential Equations," *Proceedings of the IJNN* **1992**, 4, 457.

M. T. Spining,[7] J. A. Darsey,[14] B. G. Sumpter, and D. W. Noid, "Opening up the Black Box of Artificial Neural Networks," *J. Chem. Ed.* (in press).

B. G. Sumpter, C. Getino,[15] and D. W. Noid, "A Neural Network Approach to the Study of Internal Energy Flow in Molecular Systems," *J. Chem. Phys.* **1992**, *97*, 293.

B. G. Sumpter, C. Getino,[15] and D. W. Noid, "Neural Network Predictions of Energy Transfer in Macromolecules," *J. Phys. Chem.* **1992**, *96*, 574.

B. G. Sumpter, C. Getino,[15] and D. W. Noid, "Computational Studies of Submicron Probing of Polymer Surfaces: I," *J. Chem. Phys.* **1992**, *96*, 7072.

B. G. Sumpter, C. Getino,[15] D. W. Noid, and B. Wunderlich,[4] "Computer Simulations of Atomic Force Microscopy: Crystalline Polymers and the Effects of Surface Contaminants," *Makromol. Chem.* **1993**, *2*, 55.

B. G. Sumpter and D. W. Noid, "Potential Energy Surfaces for Macromolecules: A Neural Network Technique," *Chem. Phys. Lett.* **1992**, *192*, 455.

B. G. Sumpter and D. W. Noid, "Computational Experiments on the Intramolecular Energy Flow in Macromolecules," *Chem. Phys.* **1992**, *160*, 393.

B. G. Sumpter, D. W. Noid, and B. Wunderlich,[4] "Molecular Dynamics Computational Studies of Conformation Disorder in Crystals of Macromolecules," in "Atomistic Modelling of Physical Properties of Polymers," *Advances in Polymer Science*, Springer Verlag, Berlin (in press).

B. G. Sumpter, D. W. Noid, and B. Wunderlich,[4] "Infrared Laser Induced Ablation and Melting in Model Polymer Crystals," in *Laser Ablation Mechanisms and Applications*," eds. J. C. Miller and R. F. Haglund, pgs. 334-342 "Lecture Notes in Physics," *Proc. of the Workshop on Laser Ablation Mechanisms and Applications*, 1991, Springer Verlag, New York.

B. G. Sumpter, D. W. Noid, and B. Wunderlich,[4] "Molecular Dynamics Study of the Degradation of Polymer Surfaces: Collisional Energy Transfer and Laser Ablation," *Chim. Oggi* **1991**, *33*.

B. G. Sumpter, D. W. Noid, and B. Wunderlich,[4] "Computer Simulation and Modeling of Polymeric Crystals," *Trends in Polymer Science* **1993**.

B. G. Sumpter, D. W. Noid, and B. Wunderlich,[4] "Computational Experiments on the Motion and Generation of Defects in Polymer Crystals," *Macromolecules* **1992**, *25*, 7247.

M. Varma-Nair,[7] A. Habenschuss, and Bernhard Wunderlich,[4] "Phase Transitions in Poly(4-hydroxybenzoic acid), Poly(2,6-hydroxynaphthoic acid)

and Their Copolymers," *Proc. 21st NATAS Conf.*, Atlanta, GA, Sept. 13-16, 1992,pgs. 343-348.

M. Varma-Nair,[7] Y. Jin,[7] J. Cheng,[7] and B. Wunderlich,[4] "Thermal Analysis of Polysilylenes," *Macromolecules* **1991**, *24*, 5442.

M. Varma-Nair,[7] Y. Jin,[7] and B. Wunderlich,[4] "Heat Capacities of Aliphatic and Aromatic Polysulphones," *Polymer* **1992**, *33*, 5272.

M. Varma-Nair,[7] R. Pan,[39] and B. Wunderlich,[4] "Heat Capacities and Entropies of Linear, Aliphatic Polyesters," *J. Polymer Sci., Part B, Polymer Phys.* **1991**, *29*, 1107.

M. Varma-Nair[7] and B. Wunderlich,[4] "Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules. X. Update of the ATHAS 1980 Data Bank" *J. Phys. Chem., Ref. Data* **1991**, *20*, 349.

M. Varma-Nair,[7] B. Wunderlich,[4] J. Grebowicz,[21] and R. Bauer,[21] "Thermal Analysis of Epoxy Resins," *Proc. 21st NATAS Conf.*, Atlanta, GA, Sept. 13-16, 1992, pgs. 54-59, *Thermochim. Acta* (in press).

M. Varma-Nair,[7] B. Wunderlich,[4] J. Grebowicz,[21] and R. Bauer,[21] "Thermal Analysis of Epoxy Resins," *Proc. 21st NATAS Conf.*, Atlanta, GA, Sept. 13-16, 1992, pp. 54-59.

G. D. Wignall,[1] B. K. Annis, and R. Triolo,[40] "X-ray Scattering Studies of the Structure of Aqueous Hydroxypropylcellulose Solutions," *J. Poly. Sci. B: Poly. Phys.* **1991**, *24*, 349.

B. Wunderlich,[4] "Molecular Dynamics Simulation and Thermal Analysis of Macromolecular Crystals," *Proc. 13th Nordic Symposium on Thermal Analysis*, *Thermochim. Acta* **1993**, *214*, 103.

B. Wunderlich,[4] "Unsolved Problems of Crystallization of Flexible Macromolecules. Attempts at the Understanding of the Molecular Process by Experiments and Computer Simulation," *Proc. of the NATO Advanced Research Workshop on Crystallization of Polymers*, Mons, Sept. 7-11, 1992, NATO ASI Series, Plenum, Kluver, Springer (1993).

B. Wunderlich,[4] "Molecular Dynamics Simulation and Thermal Analysis of Macromolecular Crystals," in *Integration of Fundamental Polymer Science and Technology. V.*, eds. P. J. Lemstra and L. A. Kleinjiens, Elsevier, London, pgs. 111-120, (1991).

B. Wunderlich,[4] "The Basis of Thermal Analysis," in *Thermal Characterization of Polymeric Materials*, ed. E. Turi, Academic Press, New York, pgs. 91-234, (1981); revised 2nd ed.

B. Wunderlich,[4] "Heat Capacity of Solid Polymers," in *Thermal Analysis in Metallurgy*, eds. R. D. Shull and A. Joshi, *Proc. of the TMS Meeting*, Anaheim, CA, 1991, The Minerals, Metals and Materials Soc., p. 77 (1992).

B. Wunderlich,[4] "New Directions in Thermal Analysis," *Proc. 20th NATAS Meeting*, Minneapolis, Sept. 1991, *Thermochim. Acta* **1992**, *212*, 131.

B. Wunderlich[4] and H. S. Bu,[41] "The Computation of Heat Capacities of Solid Macromolecules from Vibrational Spectra," *Proc. of the Ulmer Kalorimetrietage* in 1987, *Thermochimica Acta* **1987**, *119*, 225. Extended and updated to: B. Wunderlich, "The Heat Capacity of Rigid Crystals and Amorphous Phase Macromolecules," *Am. Chem. Soc., Polymer Div. Preprints* **1990**, *31(1)*, 272); published in S. Sivaram, ed., *Polymer Science, Contemporary Themes*, Vol. 2, pg. 491, Tata McGraw-Hill Publ., New Delhi, (1991).

B. Wunderlich[4] and Y. Jin,[7] "Thermal Properties of the Three Allotropes of Carbon," *Proc. 21st NATAS Conf.*, Atlanta, GA, Sept. 13-16, 1992, pp. 278-383, *Thermochim. Acta* (in press).

B. Wunderlich[4] and Y. Jin,[7] "Thermal Properties of the Three Allotropes of Carbon," *Proc. 21st NATAS Conf.*, Atlanta, GA, Sept. 13-16, 1992, pgs. 278-283. Updated and published as "Thermal Properties of the Four Allotropes of Carbon," *Thermochim. Acta* (in press)).

B. Wunderlich,[4] B. G. Sumpter, D. W. Noid, and G. L. Liang,[7] "Computer Simulation of Macromolecular Crystals and Their Defects," *Ordering in Macromolecular Systems*, ed. Akio Teramoto, Springer Verlag, Berlin (in press).

B. Wunderlich,[4] A. Xenopoulos,[7] D. W. Noid and B. G. Sumpter, "Defect Generation and Motion in Polyethylene-like Crystals, Analyzed by Simulation with Supercomputers," *Defects in Materials*. eds. P. D. Bristowe, J. E. Epperson, J. E. Griffith, and Z. Lilienthal-Weber, *Proc. of the 1990 Fall Meeting of the Mat. Res. Soc.* **1991**, *209*, 147.

A. Xenopoulos,[7] J. Cheng,[7] M. Yasuniwa,[42] and B. Wunderlich,[4] "Mesophases of Alkylammonium Salts. I. First-order Transitions," *Mol. Cryst. Liq. Cryst.* **1992**, *214*, 63.

A. Xenopoulos,[7] J. Cheng,[7] and B. Wunderlich,[4] "Mesophases of Alkylammonium Salts. V. Heat Capacities of Symmetric Halides with Alkyl Chains Longer Than Ethyl," *Mol. Cryst. Liq. Cryst.* **1992**, *226*, 87.

A. Xenopoulos,[7] A. H. Narten,[25] J. Cheng,[7] and B. Wunderlich,[4] "Investigations of the Transitions of Some Tetraalkylammonium Halides by DSC, NMR, and X-Ray Diffraction," *J. Non-Cryst. Solids* **1991**, *131*, 113.

A. Xenopoulos,[7] K. A. Roles,[7] and B. Wunderlich,[4] "A Possible Glass Transition in Poly(L-methionine) and Poly(L-serine)," *Polymer* (in press).

A. Xenopoulos,[7] J. A. Subirana,[43] and B. Wunderlich,[4] "Thermal Properties of Nylons Related to Polyglycine," *European Polymer Journal* (in press).

A. Xenopoulos[7] and B. Wunderlich,[4] "Thermal Analysis of Alkylammonium Salts," *Proc. 21st NATAS Conf.*, Atlanta, GA, Sept. 13-16, 1992, p. 239.

A. Xenopoulos[7] and B. Wunderlich,[4] "Conformational Motion and Disorder in Aliphatic Nylons. The Case of Nylon 6.6," *Colloid and Polymer Sci.* **1991**, *269*, 375.

A. Xenopoulos,[7] B. Wunderlich,[4] and A. H. Narten,[25] "Proton Motion in Aliphatic Nylons from Neutron Scattering," *Macromolecules* (in press).

M. A. Yandrasits,[9] S. Z. D. Cheng,[9] A. Zhang,[9] J. Cheng,[7] B. Wunderlich,[4] and V. Percec,[10] "Mesophase Behavior in Thermotropic Polyethers based on the Semiflexible Mesogen 1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane," *Macromolecules* **1992**, *25*, 2112.

A. Yethiraj,[12] J. G. Curro,[11,44] K. S. Schweizer,[12,44] and J. D. McCoy,[11] "Microscopic Equations-of-State of Polyethylene: Hard-Chain Contribution to the Pressure," *J. Chem. Phys.* **1992**, *98*, 1635.

A. Yethiraj[12] and K. S. Schweizer,[12,44] "On the Scaling of the Critical Temperature with the Degree of Polymerization of Symmetric Polymer Blends," *J. Chem. Phys.* **1992**, *97*, 5927.

A. Yethiraj[12] and K. S. Schweizer,[12,44] "Integral Equation Theory of Polymer Blends; Numerical Investigation of Molecular Closure Approximations," *J. Chem. Phys.* (in press).

PRESENTATIONS

B. K. Annis, "Applications of Atomic Force Microscopy to Polymer Samples," Digital Instruments Users Conference, Santa Barbara, CA, June 1991.

B. K. Annis, Y. Fu,[7] Y. Jin,[7] W. Busing,[17] and B. Wunderlich,[4] "Full Pattern X-ray Diffraction and Thermal Analysis study of Pet Fibers," American Physical Society Meeting, Indianapolis, IN, March 1992.

B. K. Annis, D. M. Hembree, Jr.,[24] D. F. Pedraza,[6] G. R. Romanoski,[6] and S. P. Withrow,[1] "Raman Spectroscopy of C-irradiated Graphite," Materials Research Society Symposium, Boston, MA, November 1992.

B. K. Annis, D. W. Noid, B. G. Sumpter, J. Reffner,[3] and B. Wunderlich,[4] "Applications of Atomic Force Microscopy to Polymer Samples," American Physical Society National Meeting, Cincinnati, OH, March 1991. (Poster)

J. Cheng,[7] Y. Jin,[7] and B. Wunderlich,[4] "Solid State C-13 NMR Studies of Molecular Motion in MBPE-9 and MBPE-5," American Physical Society Meeting, Indianapolis, March 15-20, 1992. (Poster)

J. Cheng[7] and B. Wunderlich,[4] "Study of Molecular Motion in Tetra-*n*-alkyl Ammonium Halides by NMR," American Physical Society Meeting, Cincinnati, OH, March 18-21, 1991. (Poster)

J. Cheng,[7] A. Xenopoulos,[7] and B. Wunderlich,[4] "Solid State NMR Study of Orientational and Conformational Motion and Disorder in Tetra-*n*-Alkyl

ammonium Halides," American Physical Society Meeting, Indianapolis, IN, March 15-20, 1992. (Poster)

S. Z. D. Cheng,[9] Jianhua Chen,[9] Xiaoxin Wu,[9] Micheal A. Yandrasits,[9] Qizhuo Zhuo,[9] Roderic P. Quirk,[9] Anton Habenschuss, and Paul R. Zschack,[6] "Nonintegral and Integral Folding Crystal Growth in Low Molecular Weight Poly(ethylene oxide) Fractions," NATO Advanced Research Workshop on Crystallization of Polymers, Universite de Mons-Hainaut, Mons, Belgique, September 7-11, 1992.

S. Z. D. Cheng,[9] J.-H. Chen,[9] A-Q. Zhang,[9] J. S. Barley,[9] X. X. Wu,[9] A. Habenschuss and P. R. Zschack,[6] "End Group Effect in Different Molecular Weight Fractions of Poly(Ethylene Oxide)," American Physical Society Meeting, Indianapolis, IN, March 16-20, 1992.

S. Z. D. Cheng,[9] A-Q. Zhang,[9] J-H. Chen,[9] J. S. Barley,[9] A. Habenschuss, and P. R. Zschack,[6] "Molecular Weight Dependence of Nonintegral Folding Chain Crystals in Low MW PEO Fractions," American Physical Society Meeting, Cincinnati, OH, March 18-22, 1991.

J. A. Darsey[14] and D. W. Noid, "Conformational Analysis of Polymeric Systems Using Neural Network Computing," American Physical Society National Meeting, Cincinnati, OH, March 1991.

J. A. Darsey,[14] D. W. Noid, and B. G. Sumpter, "Neural Network Simulations of Statistical Properties of Polymeric Systems," American Physical Society National Meeting, Indianapolis, IN, March 1992.

J. A. Darsey,[14] A. G. Soman,[14] D. W. Noid, and B. G. Sumpter, "Modeling of Polymeric Systems Using Artificial Neural Network Computing," American Chemical Society National Meeting, Denver, CO, March 1993.

J. A. Darsey,[14] B. G. Sumpter, C. Getino,[15] and D. W. Noid, "A Neural Network Approach for the Investigation of Chemical Phenomena," SIMTEC '92, International Simulation Technology Conference, NASA Johnson Space Center, Houston, TX, November 1992.

L. Franco,[43] J. Puiggalí,[43] C. Peraire,[43] A. Xenopoulos,[7] and J. A. Subirana,[43] "Síntesis, caracterización y estudios de biocompatibilidad de copolímeros de glicina y ácido ε-aminocaproico," Reunión Nacional de Materiales y Polímeros, Valencia, Spain, June 24-27, 1991.

Y. Fu,[7] Y. Jin,[7] K. Affholter,[18] W. Busing,[17] and B. Wunderlich,[4] "Full-Pattern (Two-dimensional Rietveld) X-Ray Diffraction Studies of Poly(ethylene terephthalate) Fibers," 41st Annual Denver X-Ray Conference, Colorado Springs, CO, August 3-7, 1992.

Y. Fu,[7] Y. Jin,[7] W. Busing,[17] and B. Wunderlich,[4] "Full-pattern X-Ray Diffraction and Thermal Analysis Study of Poly(ethylene terephthalate) Fibers," American Physical Society Meeting, Indianapolis, IN, March 15-20, 1992. (Poster)

C. Getino,[15] B. G. Sumpter, D. W. Noid, and B. Wunderlich,[4] "Internal Energy Migration in Polymer Crystals: A Semiclassical Trajectory

Study," 201st National American Chemical Society Meeting, Atlanta, GA, April 1991.

R. A. Guenther,[35] D. W. Noid, and B. G. Sumpter, "Implications of Quantum Chaology for Heat Capacities and Thermal Conductivities of Solids," American Physical Society National Meeting, Seattle, WA, March 1993.

A. Habenschuss, M. Varma-Nair,[7] and B Wunderlich,[7] "X-ray Diffraction Study of Poly(oxybenzoic Acid), POB, Poly(oxynaphthoic Acid), PON, and Their Copolymers," American Physical Society Meeting, Indianapolis, IN, March 16-20 1992. (Poster)

A. Habenschuss, A. Xenopoulos,[7] and A. H. Narten,[25] "X-ray Diffraction Studies of Aliphatic Nylons," American Physical Society Meeting, Cincinnati, OH, March 18-22, 1991. (Poster)

A. Habenschuss, A. Xenopoulos,[7] A. H. Narten,[25] and B. Wunderlich,[4] "X-ray Studies of Symmetric tetra-n-alkylammonium Halides," American Physical Society Meeting, Seattle, WA, March 22-26, 1993.

A. Habenschuss, A. Xenopoulos,[7] and B. Wunderlich,[4] "Structural Changes During Mesophase Transitions of Tetra-n-alkylammonium Halides," American Physical Society Meeting, Indianapolis, IN, March 16-20, 1992. (Poster)

A. Habenschuss, P. R. Zschack,[6] S. Z. D. Cheng,[9] A-Q. Zhang,[9] J. S. Barley.[9] and J-H. Chen,[9] "Isothermal Thickening and Thinning Processes in Low MW PEO Fractions," American Physical Society Meeting, Cincinnati, OH, March 18-22 1991. (Poster)

F. X. Hartmann,[22] D. W. Noid, and Y. Y. Sharon,[23] "Model of Electron Dynamics and Nuclear Excitation in Intense Ultrashort Wavelength Laser Fields," American Physical Society National Meeting, Indianapolis, IN, March 1992.

K. G. Honnell,[13,44] J. D. McCoy,[11] J. G. Curro,[11,44] K. S. Schweizer,[12,44] A. H. Narten,[25] and A. Habenschuss, "Local Structure of n-Alkane Fluids," American Physical Society Meeting, Cincinnati, OH, March 18-22, 1991.

Y. Jin,[7] A. Boller,[7] and B. Wunderlich,[4] "Heat Capacities and Transitions in Perfluorinated Paraffins and Poly(tetrafluoethylene)," Pitcon '93, Atlanta, GA, March 8-11, 1993.

Y. Jin,[7] J. Cheng,[7] and B. Wunderlich,[4] "Thermodynamic Properties and Motion in MBPE Polymers," American Physical Society Meeting, Indianapolis, IN, March 15-20, 1992. (Poster)

Y. Jin,[7] Y. Fu,[7] M. Mucha,[29] and B. Wunderlich,[4] "Thermal Characterization of Poly(ethylene terephthalate)," Northamerican Thermal Analysis Society Conference, Atlanta, GA, September 13-16, 1992. (Poster)

Y. Jin[7] and B. Wunderlich,[4] "Single Run Heat Capacity Measurement by DSC: Principle, Experimental Detail and Data Analysis," Northamerican Thermal Analysis Society Conference, Atlanta, GA, September 13-16, 1992.

Y. Jin[7] and B. Wunderlich,[4] "Heat Capacity of *n*-Paraffins and Polyethylene," American Physical Society Meeting, Cincinnati, OH, March 18-21, 1991. (Poster)

S. K. Knudson,[30] B. G. Sumpter, and D. W. Noid, "Dynamics of Charged Polymers: Silanes," American Physical Society National Meeting, Cincinnati, OH, March 1991.

G. L. Liang,[7] D. W. Noid, B. G. Sumpter, and B. Wunderlich,[4] "Molecular Dynamics Simulation of Phase Transition in Polyethylene," American Physical Society National Meeting, Indianapolis, IN, March 1992.

G. L. Liang,[7] D. W. Noid, B. G. Sumpter, and B. Wunderlich,[4] "Molecular Dynamics Simulation of Electric Field Induced Defects in Polyethylene," American Physical Society National Meeting, Cincinnati, OH, March 1991.

J. D. Londono,[7] G. D. Wignall,[1] H. D. Cochran,[18] and A. H. Narten,[25] "The Single Chain Structure of C-36 Chains in the Intermediate Angle Region," Gordon Conference on Polymer Physics, Salve Regina University, Newport, RI, August 3-7 1992. (Poster)

S. A. Meyer,[32] D. W. Noid, B. G. Sumpter, and J. A. Darsey,[14] "Neural Network Simulations of Chemical Systems," 203rd American Chemical Society National Meeting, San Francisco, CA, April 1992.

J. Müller,[7] J. Burgdörfer,[7] and D. W. Noid, "Semiclassical Mechanics of H_2^+ Beyond the Born-Oppenheimer Approximation," American Physical Society National Meeting, Indianapolis, IN, March 1992.

A. H. Narten,[25] "Diffraction by Macromolecular Fluids", International Symposium on Frontiers of Liquid and Amorphous States, Argonne National Laboratory, Argonne IL, August 13-15, 1991. (Invited)

A. H. Narten,[25] "Diffraction by Molecular Fluids," ORNL Chemistry Division Advisory Committee Review Meeting, Oak Ridge, TN, October 19 1991.

A. H. Narten,[25] "Dynamic Corrections for Small-Angle Neutron Scattering from Hydrogenous Liquids," Gordon Conference on Water and Aqueous Solutions, Holderness School, Plymouth, NH, August 3-7 1992.

A. H. Narten[25] and A. Habenschuss, "Diffraction Pattern and Structure of Amorphous and Crystalline Regions in Semicrystalline Poly(dimethylsilylene)," American Physical Society Meeting, Indianapolis, IN, March 16-20 1992.

A. H. Narten,[25] A. Habenschuss, K. G. Honnell,[13,44] J. D. McCoy,[11] J. G. Curro,[11,44] and K. S. Schweizer,[12,44] "Diffraction by Macromolecular Fluids", The Royal Society of Chemistry Faraday Division Symposium 27 on

The Conformation of Flexible Molecules in Fluid Phases, University of Southampton, December 16-18, 1991. (Invited)

D. W. Noid, "Applications of Neural Networks in Chemistry," Department of Chemistry, University of Arkansas, Little Rock, AR, November 1991. (Invited)

D. W. Noid, "Applications of Neural Networks in Chemistry," Shell Development Company, Houston, TX, November 1991. (Invited)

D. W. Noid, J. A. Darsey,[14] and Bobby G. Sumpter, "Applications of Neural Networks in Polymer Simulations," Society of Plastics Engineers, May 1993.

D. W. Noid and B. G. Sumpter, "Computational Studies of Polymeric Materials," Department of Materials Research, The University of Tennessee, Knoxville, TN, January 1993. (Invited)

D. W. Noid and B. G. Sumpter, "Applications of Neural Networks in Chemistry," Department of Chemistry, The University of Tennessee, Knoxville, TN, April 1992. (Invited)

D. W. Noid, B. G. Sumpter, J. A. Darsey,[14] and B. Wunderlich,[4] "Molecular Dynamics Simulation of Crystalline Polymers," 201st National American Chemical Society Meeting, Atlanta, GA, April 1991.

D. W. Noid, B. G. Sumpter, J. A. Darsey,[14] and B. Wunderlich,[4] "Molecular Dynamics Simulation of Crystalline Polymers," American Physical Society National Meeting, Cincinnati, OH, March 1991.

D. W. Noid, B. G. Sumpter, G. Liang,[7] and B. Wunderlich,[4] "Molecular Dynamics Simulation of Crystalline Polymers," Symposium on Molecular Simulations, 43rd Southeast Regional American Chemical Society Meeting, Richmond, VA, November 1991. (Invited)

D. W. Noid, B. G. Sumpter, M. Varma-Nair,[7] and B. Wunderlich,[4] "Neural Network Simulations of Chemical Systems," American Physical Society National Meeting, Indianapolis, IN, March 1992.

G. A. Pfeffer,[35] B. G. Sumpter, G. Liang,[7] D. W. Noid, and B. Wunderlich,[4] "Chaotic Dynamics and Conformational Change in Ultraoriented Polyethylene," American Physical Society National Meeting, Indianapolis, IN, March 1992.

G. A. Pfeffer,[35] B. G. Sumpter, and D. W. Noid, "Kinetics of Conformational Change in Ultra Oriented Polyethylene under Mechanical Stress," American Physical Society National Meeting, Cincinnati, OH, March 1991.

G. A. Pfeffer,[35] B. G. Sumpter, D. W. Noid, and B. Wunderlich,[4] "Rate of Conformational Change in a Model of Stressed Polyethylene," 26th American Chemical Society Midwest Regional Meeting, Omaha, NE, November 1991.

G. A. Pfeffer,[35] B. G. Sumpter, D. W. Noid, and B. Wunderlich,[4] "Infrared Laser Induced Chaos and Conformational Disorder in Polymer Crystals," Workshop on Laser Ablation, Oak Ridge National Laboratory, Oak Ridge, TN, April 1991. (Poster)

J. Puiggalí,[43] J-E. Aceituno,[43] L. Franco,[43] A. Prieto,[43] X. Vidal, A. Xenopoulos,[7] J. M. Fernández-Santín,[43] and J. A. Subirana,[43] "Comparative Study of Isomeric Polyamides with Isolated Methylene groups: Nylons 1.6, 4.3 and 2.5," 23rd Europhysics Conference on Macromolecular Physics, Stockholm, Sweden, May 27-31, 1991.

K. A. Roles[7] and B. Wunderlich,[4] "Heat Capacities of Solid Poly(amino Acid)s," American Physical Society Meeting, Cincinnati, OH, March 18-21, 1991.

R. O. Shelton,[38] J. A. Darsey,[14] B. G. Sumpter, and D. W. Noid, "Neural Network Error Correction for Solving Coupled Ordinary Differential Equations," International Joint Conference on Neural Networks, Baltimore, MD, June 1992.

A. G. Soman,[14] J. A. Darsey,[14] and D. W. Noid, "Application of Artificial Intelligence to Chemical Systems," Southwest Theoretical Chemistry Conference, Texas A&M University, College Station, TX, November 1992.

B. G. Sumpter, "A Neural Network Approach to the Study of Physical and Chemical Properties of Polymeric Materials," Theory Center and Computational Chemistry Lectures, Cornell University, April 27, 1992. (Invited)

B. G. Sumpter, "Computational Studies of Macromolecular Systems," Carnegie Mellon, April 1992. (Invited)

B. G. Sumpter, C. Getino,[15] and D. W. Noid, "Computational Experiments on the Migration of Internal Energy in Macromolecular Crystals," 2nd International Discussion Meeting on Relaxations in Complex Systems, June 1993. (Poster)

B. G. Sumpter, C. Getino,[15] D. W. Noid, A. Xenopoulos,[7] and B. Wunderlich,[4] "Computational Studies of Submicron Probing of Polymer Surfaces," 201st National American Chemical Society Meeting, Atlanta, GA, April 1991.

B. G. Sumpter, R. E. Guenther,[35] C. Halloy,[7] C. Getino,[15] and D. W. Noid, "Neural Network Simulations on Massively Parallel Computers: Applications in Chemical Physics," International Workshop on Artificial Neural Networks (IWANN'93), June 1993.

B. G. Sumpter and D. W. Noid, "Nonlinear Resonances and Chaos in Polyethylene," American Chemical Society Joint Central-Great Lakes Regional Meeting, Indianapolis, IN, May 1991. (Invited)

B. G. Sumpter, D. W. Noid, G. L. Liang,[7] and B. Wunderlich,[4] "Molecular Dynamics Simulation of Electric Field Induced Motion in Crystalline Polyethylene," Session on Computer Modeling and Simulation of Polymers,

National Meeting of Society of Plastics Engineers, Detroit, MI, May 1992. (Invited)

B. G. Sumpter, D. W. Noid, and B. Wunderlich,[4] "Infrared Laser Induced Chaos and Conformational Disorder in Polymer Crystals," Workshop on Laser Ablation--Mechanisms and Applications, Oak Ridge, TN, April 1991.

M. Varma-Nair,[7] A. Habenschuss, and B Wunderlich,[4] "Phase Transitions in Poly(4-hydroxybenzoic acid), Poly(2,6-hydroxynaphthoic acid) and their Copolymers," Northamerican Thermal Analysis Society Meeting, Atlanta, GA, September 1992. Atlanta GA.

M. Varma-Nair,[7] D. W. Noid, and B. Wunderlich,[4] "Neural Network Prediction of Heat Capacities of Macromolecules," American Physical Society National Meeting, Indianapolis, IN, March 1992.

M. Varma-Nair[7] and B. Wunderlich,[4] "High Temperature Transitions in Poly(oxy-1,4-phenylenecarbonyl-*co*-oxy-2,6-naphthaloyl)," American Physical Society Meeting, Cincinnati, OH, March 18-21, 1991.

M. Varma-Nair[7] and B. Wunderlich,[4] "Thermal Analysis of Epoxy Resins," NATAS Conference, Atlanta, GA, September 13-16, 1992.

G. A. Voth,[2] B. G. Sumpter, and D. W. Noid, "Existence of Nonlinear Resonance in Polyethylene," American Physical Society National Meeting, Cincinnati, OH, March 1991.

C. E. Wozny,[15] B. G. Sumpter, D. W. Noid, and B. Wunderlich,[4] "Vibrational Analysis of Random Coil Polyethylene," American Physical Society National Meeting, Seattle, WA, March 1993.

B. Wunderlich,[4] "Defects in Polyethylene," American Physical Society Meeting, Cincinnati, OH, March 18-21, 1991.

B. Wunderlich,[4] "Molecular Dynamics Simulation and Thermal Analysis of Macromolecular Crystals," Meeting of the Midwest Thermal Analysis Forum, Minneapolis, MN, April 17, 1991. (Invited)

B. Wunderlich, The Basis of Thermal Analysis. Feature lecture in a course on Thermal Analysis by the Polytechnic University of New York, held in Park Ridge, NJ. April 29 to May 1, 1991.

B. Wunderlich, "A Review of Phase Transitions Involving Mesophases," Plenary lecture, 23rd Europhysics Conference on Macromolecular Physics, Stockholm, Sweden, May 26-31, 1991.

B. Wunderlich,[4] "Simulation der Molekulardynamic und Thermische Analyse bei Polymerkristallen," Seminar, Technical University of Berlin (Berliner Polymeren Colloquium), Germany, June 4, 1991.

B. Wunderlich,[4] "Molecular Dynamics Simulation and Thermal Analysis of Macromolecular Crystals," Bundesanstalt für Materialprüfung, Berlin, Germany, June 5, 1991. (Invited)

B. Wunderlich,[4] "Molecular Dynamics Simulation and Thermal Analysis of Macromolecular Crystals," Institutscolloquium at the Inst. Phys. Chem., Humboldt University, Berlin, Germany, June 6, 1991.

B. Wunderlich,[4] "News from ATHAS (Atomic Force Microscopy, Solid State NMR and Calorimetry in the Study of Macromolecular Crystals)," Colloquium at the Institut für Makromolekulare Chemie, University of Freiburg, Freiburg, Germany, June 12, 1991. (Invited)

B. Wunderlich,[7] "Molecular Dynamics Simulation and Thermal Analysis of Macromolecular Crystals," Physical and Analytical Division of Tennessee Eastman, Kingsport, TN, June 20, 1991. (Invited)

B. Wunderlich,[4] "New Directions in Thermal Analysis," Plenary lecture, Northamerican Thermal Analysis Society Meeting, Minneapolis, MN, September 23-26, 1991.

B. Wunderlich,[4] "New Directions in Thermal Analysis," Plenary lecture at the 25th Annual Meeting of the Thermal Analysis Workgroup of the Netherlands, Wageningen, The Netherlands, October 1-2, 1991.

B. Wunderlich,[7] "The *Athas* System at the University of Tennessee," 25th Annual Meeting of the Thermal Analysis Workgroup of the Netherlands, Wageningen, The Netherlands, October 1-2, 1991.

B. Wunderlich,[4] "Detection of Disorder by Thermal Analysis," Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, October 31, 1991.

B. Wunderlich,[7] "Differential Thermal Analysis: Instrumentation and Interpretation," Featured Lecture at Eastern Analytical Symposium, Somerset, NJ, November 11-15, 1991.

B. Wunderlich,[4] "Characterization of the Glass Transition by Thermal Analysis," Fifth Analytical Symposium of the Hercules Co., Wilmington, DE, January 22-23, 1992. (Invited)

B. Wunderlich,[4] "Thermodynamics of Fullerene," Chemistry Division, ORNL, Oak Ridge, TN, January 29, 1992.

B. Wunderlich,[4] "Thermodynamics of Macromolecular Crystals," Department of Chemistry, Western Kentucky University, Bowling Green, KY, February 7, 1992.

B. Wunderlich,[4] "Unfreezing of Large-Amplitude Motion in Polymers," Research Laboratory, Shell Development Co., Westhollow, TX, February 17, 1992. (Invited)

B. Wunderlich,[4] "Distinction between Liquid Crystals, Plastic Crystals, and Condis Crystals," Research Laboratory, Shell Development Co., Westhollow, TX., February 18, 1992. (Invited)

B. Wunderlich,[4] "The Basis of Thermal Analysis," Thermal Analysis Course, Polytechnic University of New York, Park Ridge, NJ, April 27-29, 1992. (Invited)

B. Wunderlich,[4] A course of seven lectures, 90 minutes each, covering the "The Condensed State of Linear Macromolecules." (Crystal Structure I; Crystal Structure II; Crystal Morphology; Defects in Polymers; Transitions; Mesophases; and Melts and Glasses). Kgl. Technical University, Stockholm, Sweden, June 1-5, 1992.

B. Wunderlich,[4] "Molecular Dynamics Simulation and Thermal Analysis of Macromolecular Crystals," Plenary Lecture, 13th Nordic Symposium on Thermal Analysis and Calorimetry, Stockholm, Sweden, June 9-11, 1992.

B. Wunderlich,[4] "Defects in Polyethylene," Research Laboratorium, BASF, Ludwigshafen, Germany, June 16, 1992. (Invited)

B. Wunderlich,[4] "Computer Simulation of Polymer Crystals," Gordon Conference on Polymers, Brewster Academy, Wolfeboro, NH, June 28-July 3, 1992. (Invited)

B. Wunderlich,[4] "Thermotropic Polymer Mesophases with Missing Entropies of Transition," Gordon Conference on Liquid Crystals of Polymers, Colby Sawyer College, New London, NH, July 5-10, 1992. (Invited)

B. Wunderlich,[4] "The Thermodynamic Functions of Poly(amino acid)s and Proteins," 12th IUPAC International Conference on Chemical Thermodynamics, Snowbird, UT, August 16-21, 1992. (Invited)

B. Wunderlich,[4] "Measurement of Changing Conformational Disorder in Solids Outside the Transition Region by Calorimetry," 12th IUPAC International Conference on Chemical Thermodynamics, Snowbird, UT, August 16-21, 1992. (Invited)

B. Wunderlich,[4] "Unsolved Problems of Crystallization of Flexible Macromolecules. Attempts at the Understanding of the Molecular Process by Experiments and Computer Simulation," NATO Workshop on Polymer Crystallization, Mons, Belgium, September 6-12, 1992. (Invited)

B. Wunderlich,[4] "Thermal Properties of the Three Allotropes of Carbon," Northamerican Thermal Analysis Society Conference, Atlanta, GA, September 13-16, 1992.

B. Wunderlich,[4] "The Presence and Future of Chemical Industry," Discussion at the Plastic Federation of South Africa, Johannesburg, SAR, October 26, 1992.

B. Wunderlich,[4] "Determination of Molecular Mass and Crystallinity of Polytetrafluoroethylene," Atomic Energy Corporation of SASA, Pretoria, SAR, October 30, 1992. (Invited)

B. Wunderlich,[4] "New Directions in Thermal Analysis," Plenary lecture, South African Thermal Analysis Society Meeting, Pretoria, SAR, November 2-3, 1992. (Invited)

B. Wunderlich,[4] "The Theory and Practice of Measurement of Heat Capacity; The Microscopic Link Between Thermal Properties and Molecular Structure; The Link Between Thermal Properties and Molecular Structure; The Measurement, Classification, Interpretation, and Prediction of Phase Transitions," (Four Lectures) South African Thermal Analysis Society Meeting, Pretoria, SAR, Werkswinkel oor warmtekapasiteitsbepalings en die termodinamiese belangrikheid daarvan, November 2-3, 1992. (Invited)

B. Wunderlich,[4] "The Basis of Thermal Analysis and the Advanced Thermal Analysis System," SASOL Research Facility, Sasol, SAR, November 4, 1992. (Invited)

B. Wunderlich,[4] "The Industrial Handling of Nylons," Discussion at the SA Nylon Spinners, Capetown, SAR, November 6, 1992.

B. Wunderlich,[4] "The Defect State of Macromolecules in Crystals and Mesophases as Analyzed by Calorimetry, Supercomputer Molecular Dynamics Simulation, and Solid State NMR," 4th International Meeting of the Society of Polymer Science of Japan, Yokohama, Japan, November 29-December 3, 1992. (Invited)

B. Wunderlich,[4] "Defects in Polyethylene," Gunma University, Kiryu City, Japan, December 4, 1992. (Invited)

B. Wunderlich,[4] G. Liang,[7] B. G. Sumpter, and D. W. Noid, "Analysis of the Hexagonal Phases of Polymers and Oligomers," American Physical Society National Meeting, Seattle, WA, March 1993.

B. Wunderlich,[4] D. W. Noid, and B. G. Sumpter, "Defects in Polyethylene," American Physical Society National Meeting, Indianapolis, IN, March 1992.

B. Wunderlich,[4] D. W. Noid, A. Xenopoulos,[7] and B. G. Sumpter, "Defects in Polyethylene," American Physical Society National Meeting, Cincinnati, OH, March 1991.

B. Wunderlich,[4] "Polymer Films and Their Analysis," Medtronics Co., San Diego, CA, January 29, 1993. (Invited)

B. Wunderlich,[4] "The Nature of the Glass Transition and Its Determination by Thermal Analysis," Opening lecture, American Society for Testing Metals Meeting on The Assignment of the Glass Transition, Atlanta, GA, March 3-5, 1993.

B. Wunderlich, [4] "Analysis of the Hexagonal Phases of Polymers and Oligomers," American Physical Society Meeting, Seattle, WA, March 22-26, 1992.

B. Wunderlich, [4] "The Basis of Thermal Analysis," 17th Symposium on Thermal Analysis of New York Polytech, Park Ridge, NJ, April 19-21, 1993. (Invited)

B. Wunderlich,[4] "Production of Single Molecule Phases in Microgravity," Workshop on Organic and Polymeric Materials, NASA, Huntsville, AL, April 27-28, 1993. (Invited)

A. Xenopoulos,[7] "Experimentos computacionales sobre la dinámica interna de polímeros cristalinos," VII Reunion of the Quantum Chemistry Group of Catalunya, Barcelona, Spain, May 30, 1991.

A. Xenopoulos,[7] "Análisis termica de poliamidas alifáticas," Department of Chemical Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain, April 26, 1991.

A. Xenopoulos,[7] "Simulaciones de dinámica molecular de cristales de polietileno," Department of Chemical Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain, May 16, 1991.

A. Xenopoulos,[7] "DSC, diffusion de neutrons et diffraction de rayons X dans les polyamides," Laboratoire de Physique des Solides, Université Paul Sabatier, Toulouse, France, June 7, 1991.

A. Xenopoulos,[7] "Thermal Analysis and Neutron Scattering Studies of Nylon 6 and Nylon 6.6," Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg, Freiburg, Germany, July 2, 1991.

A. Xenopoulos,[7] "Defects in Aliphatic Polyamides," Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, September 5, 1991.

A. Xenopoulos,[7] "Mesophase Transitions in Polyamides and Ionic Salts," Polymer Research Institute, Polytechnic University, Brooklyn, NY, February 6, 1992.

A. Xenopoulos,[7] "Studies of Mobility and Disorder in Semicrystalline Nylons," General Electric Plastics, Mount Vernon, IN, April 14, 1993.

A. Xenopoulos,[7] "Mesophase Transitions and Conformational Disorder in the Solid State," Department of Chemistry, University of Crete, Heraklion, Greece, April 26, 1993.

A. Xenopoulos,[7] "Physical Characterization of Advanced Materials," Millipore Corporation, Bedford, MA, May 18, 1993.

A. Xenopoulos,[7] J. Cheng,[7] A. Habenschuss and B. Wunderlich,[4] "Distinction Between Plastic and Condis Crystals of Tetra-n-alkylammonium Halides," American Physical Society Meeting, Indianapolis, IN, March 16-20, 1992.

A. Xenopoulos,[7] L. Franco,[43] J-E. Aceituno,[43] X. Vidal,[43] J. M. Fernández-Santín,[43] J. Puiggalí,[43] and J. A. Subirana,[43] "Thermal Properties of Aliphatic Polyamides Related to Polyglycine," American Physical Society Meeting, Indianapolis, IN, March 16-20, 1992.

A. Xenopoulos,[7] A. Habenschuss, and B. Wunderlich,[4] "X-ray Diffraction Studies of Mesophase Transitions in Homologous Series of Symmetrical

tetra-n-alkylammonium Halides," American Crystallographic Association Meeting, Albuquerque, NM, May 23-28, 1993.

A. Xenopoulos,[7] A. H. Narten,[25] and B. Wunderlich,[4] "Proton Motion in Semicrystalline Nylons from Neutron Scattering," American Physical Society Meeting, Cincinnati, OH, March18-21, 1991.

A. Xenopoulos[7] and B. Wunderlich,[4] "Thermal Analysis of Aliphatic Polyamides," Polytechnic University, Barcelona, Spain, April 26, 1991.

A. Xenopoulos[7] and B. Wunderlich,[4] "Simulation of the Dynamics of Crystals of Polyethylene," Department of Chemical Engineering, Polytechnic University of Catalonia, Barcelona, Spain, May 30, 1991.

A. Xenopoulos[7] and B. Wunderlich,[4] "X-Ray and Neutron Scattering of Polyamides," Laboratory of Solid State Physics, University Paul Sabatier, Toulouse France, June 7, 1991.

A. Xenopoulos[7] and B. Wunderlich,[4] "Thermal Analysis and Neutron Scattering of Nylon 6 and Nylon 6,6," Institut für Makromolekulare Chemie, University of Freiburg, Freiburg, Germany, July 2, 1991.

A. Xenopoulos[7] and B. Wunderlich,[4] "Defects in Aliphatic Polyamides," Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, September 5, 1991.

A. Xenopoulos[7] and B. Wunderlich,[7] "Thermal Analysis of Alkylammonium Salts," Northamerican Thermal Analysis Society Conference, Atlanta, GA, September 13-16, 1992.

A. Xenopoulos,[7] B. Wunderlich,[4] and A. H. Narten,[25] "Proton Motions in Semicrystalline Nylons from Neutron Scattering", American Physical Society Meeting, March 18-22 1991, Cincinnati, OH.

A. Xenopoulos,[7] Y. Jin,[7] M. Diak,[7] G. Guichon,[7] R. N. Compton,[44] and B. Wunderlich,[4] "Thermodynamic Properties of C70," American Physical Society Meeting, Seattle, WA, March 22-26, 1993.

A. Xenopoulos,[7] K. Roles,[7] and B. Wunderlich,[4] "A Possible Glass Transition for Poly(L-methionine) and Poly(-serine)," American Physical Society Meeting, Seattle, WA, March 22-26, 1993.

---

1. ORNL Solid State Division.
2. University of Pennsylvania, Philadelphia, PA.
3. University of Massachusetts, Amherst, MA.
4. ORNL/UT Distinguished Scientist.
5. Massachusetts Institute of Technology, Cambridge, MA.
6. ORNL Metals and Ceramics Division.
7. The University of Tennessee, Knoxville, TN.
8. Mettler Instrument Co., Greifensee, Switzerland.
9. University of Akron, Akron, OH.
10. Case Western Reserve University, Cleveland, OH.
11. Sandia National Laboratory, Albuquerque, NM.

12. University of Illinois, Urbana, IL.
13. Phillips Petroleum Co., Bartlesville, OK.
14. University of Arkansas, Little Rock, AR.
15. ORAU/ORNL Postdoctoral program.
16. Dow Chemical Co., Plaquemine, LA.
17. ORNL, retired.
18. ORNL Chemical Technology Division.
19. University of Minnesota, Minneapolis, MN.
20. Riso National Laboratory, Denmark.
21. Shell Development Co., Houston, TX.
22. Brookhaven National Laboratory, Upton, NY.
23. Princeton University, Princeton, NJ.
24. Y-12 Quality Service Division.
25. ORNL, deceased.
26. Anderson College, Anderson, IN.
27. N. I. Lobachevsky State University, Nishny Novgorod, Russia.
28. Lawrence Berkeley Laboratory, Berkeley, CA.
29. Polytechnic Institute, Lodz, Poland.
30. College of William and Mary, Williamsburg, VA.
31. Biosym Corp., San Diego, CA.
32. The Colorado College, Colorado Springs, CO.
33. ORNL Computing and Telecommunications Division.
34. National Institute of Standards and Technology, Gaithersburg, MD.
35. University of Nebraska, Omaha, NE.
36. Stanford University, Stanford, CA.
37. Northern Illinois State University, DeKalb, IL.
38. Lyndon B. Johnson Space Center, Houston, TX.
39. Proctor and Gamble Co., Cincinnati, OH.
40. University of Palermo, Palermo, Italy.
41. Fudan University, Shanghair, China.
42. Universitat Politechnica de Catalunya, Barcelona, Spain.
43. ORNL Health and Safety Research Division.
44. Collaborator on research funded by ORNL.

CHEMISTRY OF TRANSURANIUM ELEMENTS AND COMPOUNDS

PUBLICATIONS

U. Benedict,[1] S. Dabos-Seignon,[1] J. P. Dancausse,[1] M. Gensini,[1] E. Gering,[1] S. Heathman,[1] H. Luo,[1] J. Stan Olsen,[2] L. Gerward,[3] and R. G. Haire, "Actinide Compounds Under Pressure," *J. Alloys and Compounds* **1992**, *181*, 1.

C. D. Caldwell,[4] S. B. Whitfield,[4] M. G. Flemming,[4] and M. O. Krause, "Electron Correlation Explored Through Electron Spectrometry Using Synchrotron Radiation," Atomic and Molecular Physics, eds. C. Cisneros, I. Alvarez, T.J. Morgan, *World Scientific* **1992**, 435.

C. D. Caldwell,[4] S. J. Schaphorst,[4] M. O. Krause and J. Jimenez-Mier,[4] "Photoexcited K-Auger Spectra of Atomic and Molecular Oxygen," *J. Electr. Spectrosc.* (in press).

C. D. Caldwell[4] and M. O. Krause, "K-Shell Auger Spectrum of Atomic Oxygen," *Phys. Rev. A* **1993**, *47*, R759.

G. Chen,[5] N. A. Stump,[5] R. G. Haire, and J. R. Peterson,[6] "Study of the Phase Behavior of Eu_2O_3 Under Pressure via Luminescence of Eu^{3+}," *J. Alloys and Compounds* **1992**, *181*, 503.

G. Chen,[5] R. G. Haire, and J. R. Peterson,[6] "Effect of Pressure on Cubic (C-Type) Eu_2O^{3+} Luminescence," *High Pressure Res.* **1992**, *6*, 371.

G. Chen,[5] R. G. Haire, and J. R. Peterson,[6] "Eu^{3+} Ion Luminescence Spectra from Lanthanide Sesquioxides Exhibiting Three Different Crystal Structures," *Appl. Spectrosc.* **1992**, *46*, 273.

G. Chen[5] and J. R. Peterson,[6] "Systematics of the Phase Behavior in Lanthanide Sesquioxides," *J. Alloys and Compounds* **1992**, *186*, 233.

G. Chen,[5] N. A. Stump,[5] R. G. Haire, and J. R. Peterson,[6] "Temperature Dependence of the Luminescence Lifetime of the Eu^{3+} Ion in $EuCl_3$," *Appl. Spectrosc.* **1992**, *46*, 1198.

G. Chen,[5] R. G. Haire, and J. R. Peterson,[6] "Compressibilities of $TbVO_4$ and $DyVO_4$ Calculated From Spectroscopic Data," *Appl. Spectrosc.* **1992**, *46*, 1495.

G. Chen,[5] N. A. Stump,[5] R. G. Haire, J. R. Peterson,[6] and M. M. Abraham,[7] "Pressure-Induced Phase Transition in YVO_4:Eu^{3+}: A Luminescence Study at High Pressure," *J. Phys. Chem. Solids* **1992**. *53*, 1253.

G. Chen,[5] N. A. Stump,[5] R. G. Haire, J. R. Peterson,[6] and M. M. Abraham,[7] "Pressure-Induced Phase Transition in YVO_4:Eu^{3+}: An Emission Lifetime Study at High Pressure," *Solid State Communic.* **1992**, *84*, 313.

G. Chen,[5] R. G. Haire, and J. R. Peterson,[6] "Effect of Temperature on the Luminescence from Eu_2O_3," *J. Solid State Chem.* ***1992***, *102*, 126.

L. V. Coulter,[8] A. Mitchell,[8] S. Lee-Bechtold,[8] and J. K. Gibson, "The Heat Capacity and Thermodynamic Properties of the Thermal Transitions of Strontium Hexamine, *J. de Physique* **1991**, *C5*, 333.

L. E. Cox,[9] J. W. Ward,[9] and R. G. Haire, "X-ray Photoemission Spectroscopy Study of the Electronic Structure of Am Metal and AmH_x (for x=2)," *Physical Review B* **1992**, *45*, 13239.

G. D. Del Cul,[10] G. M. Murray,[11] S. E. Nave,[12] C.-T.P. Chang,[5] G. M. Begun,[13] and J. R. Peterson,[6] "Luminescence, Absorbance and Raman Studies of Europium Oxychloride at Various Pressures," *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 155.

G. D. Del Cul,[10] R. G. Haire, and J. R. Peterson,[6] "Effects of Pressure on the Luminescence, Raman and Absorption Spectra of $^{248}CmCl_3$," *Alloys and Compounds* **1992**, *181*, 63.

G. D. Del Cul,[10] S. E. Nave,[12] G. M. Begun,[13] and J. R. Peterson,[6] "Raman Spectra of Tetragonal Lanthanide Oxychlorides Obtained from Polycrystalline and Single Crystal Samples," *J. Raman Spectrosc.* **1992**, *23*, 267.

G. D. Del Cul,[10] S. E. Nave,[12] and J. R. Peterson,[6] "Polarized Raman Spectra of Single-Crystal Lanthanide Oxychlorides," *J. Alloys and Compounds* (in press).

B. Fricke,[14] E. Johnson, and G. Martinez Rivera,[14] "Ionization Potentials and Radii of Atoms and Ions of Element 105 (unnilpentium) and Ions of Tantalum Derived from Multiconfiguration Dirac-Fock Calculations," *Radiochimica Acta* (in press).

J. Fuger,[15] R. G. Haire, and J. R. Peterson,[6] "Molar Enthalpies of Formation of $BaCmO_3$ and $BaCfO_3$," *J. Alloys and Compounds* (in press).

M. Gensini,[16] R. G. Haire, U. Benedict,[1] F. Hulliger,[1] and J. Rebizant,[1] "High Pressure Behavior of CmBi, UBi and NpSe," *Physica B* (in press).

J. K. Gibson and R. G. Haire, "High-Temperature DTA of Transuranium Materials: Application to the Np-Zr Phase Diagram," *Thermochimica Acta* **1992**, *207*, 65.

J. K. Gibson and R. G. Haire, "Phase Relations in Neptunium, Americium and the Binary Alloy Systems Np-Am and Np-Ln (Ln = La, Nd, Lu)," *J. Nuclear Materials* **1992**, *195*, 156.

J. K. Gibson and R. G. Haire, "High Temperature Fluorination Studies of U, Np, Pu and Am," *J. Alloys and Compounds* **1992**, *181*, 23.

J. K. Gibson, "Mass Spectrometry of Halide and Oxide Halide (F & Cl) Vapor Species of Technetium, Tantalum and Tungsten," *J. Fluorine Chem* ***1991***, 55, 299.

J. K. Gibson, "High Temperature Oxide and Hydroxide Vapor Species of Technetium," *Radiochimica Acta* **1993**, *60*, 121.

J. K. Gibson and N. A. Stump,[5] "Spectroscopic Investigation of the Thermal Decomposition of Europium Oxalate, *Thermochimica Acta* (in press).

J. K. Gibson and R. G. Haire, "Investigation of the Neptunium-Zirconium Phase Diagram by Differential Thermal Analysis," *J. Nuclear Materials* (in press).

J. K. Gibson, "Mass Spectrometric Identification of Gaseous Potassium and Cesium Pertechnetates and Bimetallic Technetium-Rhenium Oxide Dimers," *Radiochimica Acta* (in press).

R. G. Haire, "High-Pressure Behavior of f-Element Materials," *Rare Earths*, (TMS Pub. Warrendale, Penn.) **1992**, 449.

R. G. Haire and J. K. Gibson, "The Pivotal Position of Plutonium in the Systematics of Actinide Metals and Compounds," Transuranium Elements, A Half Century, eds. L.R. Morss and J. Fuger, ACS Symposium in Books, (American Chemical Society, Washington, D.C.) **1992**, 426.

R. G. Haire, "Dependence of Actinide Solid State Chemistry/Physics and Material Science on the Changing Role of the 5f-Electrons," Advanced Nuclear Energy Research, Japan Atomic Energy Research Society, JAERI-M **1992**, 92.

R. G. Haire and L. Eyring,[17] "Comparative Chemistry of the Lanthanide and Actinide Oxides," Handbook of the Lanthanides and Actinides, North Holland, Amsterdam.

G. V. Ionova,[18] V. Pershina,[14] E. Johnson, B. Fricke,[14] and M. Schaedel,[19] "Redox Reactions for Group 5 Elements, Including Element 105, in Aqueous Solutions," *J. Phys. Chem.* **1992**, *96*, 11096.

G. V. Ionova,[18] V. Pershina,[14] B. Fricke,[14] and E. Johnson, "Influence of Electronic Configuration on Atomic Volatility: Group 5b Elements Nb, Ta and Element 105, Ha," *J. Phys. Chem* (in press).

M. O. Krause, S. B. Whitfield,[4] C. D. Caldwell,[4] J.-Z. Wu,[4] P. van der Meulen, C. A. de Lange,[20] and R.W.C. Hansen,[20] "Outer ns,np Correlation Satellites in the Rare Gases - A Photoelectron Spectrometry Study with an Undulator Photon Source," *J. Electr. Spectrosc.* **1992**, *58*, 79.

M. O. Krause, C. D. Caldwell,[4] S. B. Whitfield,[4] S. J. Schaphorst,[4] and Y. Azuma,[4] "State-of-the-Art Resolution in Photoelectron Spectrometry," *Synchrotron Radiation News* **1992**, *5*, 25.

M. O. Krause, C. D. Caldwell,[4] S. B. Whitfield,[4] C. A. de Lange,[20] and P. van der Meulen, "Population of the $^3P_{2,1,0}$ Fine-Structure States in the 3s and 3p Photoionization of Atomic Chlorine," *Phys. Rev. A* (in press).

G. M. Murray,[11] G. D. Del Cul,[10] S. E. Nave,[12] C.-T.P. Chang,[5] R. G. Haire, and J. R. Peterson,[6] "Anti-Stokes Luminescence of Selected Actinide(III) Compounds," *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 105.

M. Pahler,[4] C. D. Caldwell,[4] S. J. Schaphorst,[4] and M. O. Krause, "Intrinsic Line Widths of Neon $2s2p^5(^{1,3}P)nl(^2L)$ Correlation Satellites," *J. Phys. B* (in press).

V. Pershina,[14] B. Fricke,[14] G. V. Ionova,[17] and E. Johnson, "Thermodynamic Functions of Element 105 in Neutral and Ionized States," *J. Phys. Chem.* (in press).

L. L. Pesterfield,[21] N. A. Stump,[5] G. K. Schweitzer,[5] and J. R. Peterson,[6] "Perturbations of the Luminescence Spectra of Europium-EDTA Salts Caused by Selected Monovalent Counterions," *J. Alloys and Compounds* **1992**, *180*, 201.

J. R. Peterson,[6] S. Heathman,[1] and U. Benedict,[1] "Energy Dispersive X-ray Diffraction Analysis of $NdBr_3$ at Pressures up to 52 GPa," *J. Alloys and Compounds* (in press).

J. R. Peterson,[6] "Some Experiences with Absorption, Phonon Raman, and Luminescence Spectroscopic Probes of Crystal Structure of f-Element Compounds," *J. Alloys and Compounds* (in press).

N. A. Stump,[5] L. L. Pesterfield,[21] G. K. Schweitzer,[5] and J. R. Peterson,[6] "A High Resolution Spectral Study of $Li_3Eu(2,6\text{-pyridinedicarboxylato})_3$," *J. Alloys and Compounds* **1992**, *180*, 141.

G. R. Stewart,[22] R. G. Haire, J. C. Spirlet,[1] and J. Rebizant,[1] "Specific Heats of NpTe and PuTe, *J. Alloys and Compounds* **1992**, *177*, 167.

N. A. Stump,[5] G. Chen,[5] J. R. Peterson,[6] and R. G. Haire, "Emission Spectrum from Eu^{3+} Ions in Anhydrous $EuCl_3$," *Inorg. Chim. Acta* **1992**. *196*, 209.

N. A. Stump,[5] S. Dai,[5] G. D. Del Cul,[10] and J. R. Peterson,[6] "Absorption Spectrum from Eu^{3+} Ions in EuOCl," *Spectrosc. Letters* **1992**, *25*, 1003.

N. A. Stump,[5] G. K. Schweitzer,[5] L. L. Pesterfield,[21] J. R. Peterson,[6] and G. M. Murray,[11] "Synthesis and Spectral Study of Several Solid $M_3[Eu(2,6\text{-pyridinedicarboxylate})_3]$ Salts ($M = Li^+$, Na^+, K^+, Rb^+, Cs^+, NH_4^+, and pyridinium$^+$)," *Spectrosc. Letters* **1992**, *25*, 1421.

N. A. Stump,[5] G. M. Murray,[11] G. D. Del Cul,[10] R. G. Haire, and J. R. Peterson,[6] "Stokes and Anti-Stokes Luminescence from the Trihalides of Cm-248," *Radiochim. Acta* (in press).

P. van der Meulen, M. O. Krause, and C. A. de Lange,[20] "Angle-Resolved Photoelectron Spectrometry of Atomic Bromine Using Synchrotron Radiation," *J. Phys. B* **1992**, *25*.

P. van der Meulen, E. de Beer,[20] A. A. de Lange,[20] N.P.C. Westwood,[20] and M. O. Krause, "Atomic Spectroscopy with Laser and Synchrotron Radiation," AIP Conference Proceedings No. 258, American Institute of Physics, New York, NY, ed. A. Beswick **1992**, 18.

P. van der Meulen, M. O. Krause, C. D. Caldwell,[4] S. B. Whitfield,[4] and C. A. de Lange,[20] "Angle-Resolved Photoelectron Spectrometry of Atomic Chlorine Using Synchrotron Radiation," *Phys. Rev. A* **1992**, *46*, 2468.

J. W. Ward,[9] B. Cort,[9] J. Goldstone,[9] A. Lawson,[9] L. Cox,[9] and R.G. Haire, "Electronic, Structural, and Transport Properties of (Almost) Rare-Earth-Like Actinide Hydrides," in Transuranium Elements, A Half Century, eds. L.R. Morss and J. Fuger, ACS Symposium in Books (American Chemical Society, Washington, D.C.) **1992**, 404.

S. B. Whitfield,[4] C. D. Caldwell,[4] C. X. Huang,[4] and M. O. Krause, "Near Threshold 4d Photoexcitation and Photoionization of Xe," *J. Phys. B* **1992**, *25*, 4755.

W. R. Wilmarth[12] and J. R. Peterson,[6] "Characterization of Selected Solid-State Actinide (and Related) Compounds via Raman and Absorption Spectrophotometry," Handbook on the Physics and Chemistry of the Actinides, eds. A.J. Freeman and C. Keller (North-Holland, Amsterdam) **1991**, *6*, 1.

PRESENTATIONS

U. Benedict,[1] S. Daboos-Seignon,[1] J. P. DanCausse,[1] M. Gensini,[1] E. Gering,[1] S. Heathman,[1] H. Luo,[1] J. Staun Olsen,[3] L. Gerward,[1] and R.G. Haire, "Actinide Compounds Under Pressure," 19th Rare Earth Research Conference, Lexington, KY, July 14-19, 1991.

J. B. Burns,[5] N. E. Bores,[5] G. R. Hayes,[5] and J. R. Peterson,[6] "Enthalpies of Formation of Selected Lanthanide Oxychlorides," 19th Rare Earth Research Conference, Lexington, KY, July 14-19, 1991.

G. Chen,[5] N. A. Stump,[5] R. G. Haire. and J. R. Peterson,[6] "An Emission Lifetime Study of $YVO_4:Eu^{3+}$ at High Pressure," 182nd Meeting of the Electrochemical Society, Toronto, Canada, Oct. 11-16, 1992.

G. Chen,[4] N. A. Stump,[5] R. G. Haire, and J. R. Peterson,[6] "Study of the Phase Behavior of Eu_2O_3 Under Pressure Via Luminescence of Eu^{3+}," 19th Rare Earth Research Conference, Lexington, KY, July 14-19, 1991.

G. D. Del Cul,[10] R. G. Haire, and J. R. Peterson,[6] "Effects of Pressure on the Luminescence, Raman and Absorption Spectra of $^{248}CmCl_3$," 19th Rare Earth Research Conference, Lexington, KY, July 14-19, 1991.

G. D. Del Cul,[10] S. E. Nave,[12] and J. R. Peterson,[6] "Polarized Raman Spectra of Single-Crystal Lanthanide Oxychlorides," The International Conference Rare Earths '92 in Kyoto, Kyoto, Japan, June 1-5, 1992.

J. K. Gibson, "Mass Spectrometric Study of Alkali Pertechnetate Vapor Species," 205th National Meeting of the American Chemical Society, Denver, CO, March 28 - April 2, 1993.

J. K. Gibson and N. A. Stump,[5] "Spectroscopic Investigation of the Thermal Decomposition of Lanthanide Oxalates," 21st Annual Conference of the North American Thermal Analysis Society, Atlanta, GA, Sept. 13-16, 1992.

J. K. Gibson and R. G. Haire, "Investigation of the Neptunium-Zirconium Phase Diagram by Differential Thermal Analysis," 12th IUPAC Conference on Chemical Thermodynamics, Snowbird, UT, Aug. 16-21, 1992.

J. K. Gibson and R. G. Haire, "Phase Relations in Transuranium Elements and Alloys," 203rd National Meeting of the American Chemical Society, San Francisco, CA, April 5-10, 1992.

J. K. Gibson and R. G. Haire, "High-Temperature Thermodynamic Studies of Actinides," 19th Rare Earth Research Conference, Lexington, KY, July 14-19, 1991.

J. K. Gibson, "Transition Metal Fluoride and Oxyfluoride Vapor Species," 201st National Meeting of the American Chemical Society, Atlanta, GA, April 14-19, 1991.

R. G. Haire, S. Heathman,[1] and U. Benedict,[1] "The Structural Behavior of f-Element Metals and Alloys Under Pressure: Significance to the Systematics of f-Electron Delocalization," National American Chemical Society Meeting, Atlanta, GA, April 14-19, 1991.

R. G. Haire, "The Vaporization/Decomposition Behavior of Californium Sesquioxide," 19th Rare Earth Research Conference, Lexington, KY, July 14-19, 1991.

R. G. Haire, M. Gensini,[16] and U. Benedict,[1] "The Structural Behavior of Curium Bismuthide Under Pressure," 19th Rare Earth Research Conference, Lexington, KY, July 14-19, 1991.

R. G. Haire, "Dependence of the Solid State Chemistry and Physics on the Changing Role of the 5f Electrons," 4th International Symposium on Nuclear Energy Research, Mito, Japan, Feb. 5-9, 1992.

R. G. Haire, "High-Pressure Behavior of f-Elements," International Symposium on Rare Earths, San Diego, CA, March 1-8, 1992.

R. G. Haire, "The Changing Role of the 5f-Electrons: How It Affects the High-Temperature and High-Pressure Chemistry of the Actinides," Transactinium Science Symposium, ACS National Meeting, San Francisco, CA, April, 1992.

R. G. Haire, "High-Temperature Vaporization of Actinide Sesquioxides," 12th IUPAC Conference on Chemical Thermodynamics, Snowbird, UT, Aug. 16-21, 1992.

E. Johnson, B. Fricke,[14] and G. Martinez Rivera,[14] "A Quantum and Statistical Mechanical Study of Group 4b and 5b Elements," 21st Southeastern Theoretical Chemistry Association Conference, University of Alabama in Huntsville, AL, May 28-30, 1992.

M. O. Krause, "Photoelectron Angular Distributions: From the Past to the Future," International Workshop on Photoionization, Berlin, FRG, Aug. 24-28, 1992.

M. O. Krause, "Gas-Phase Actinide Studies with Synchrotron Radiation," Workshop on Synchrotron Radiation in Transactinium Research, LBL, Berkeley, CA, Oct. 1-2, 1992.

M. O. Krause, "Photoelectron Spectrometry of the Chlorine Atom with the Use of Synchrotron Radiation," Seminar, Physics Division, Argonne National Lab, Argonne, IL, Oct. 8, 1992.

M. O. Krause, "Photoelectron Spectrometry of Halogen and Chalcogen Atoms," National Synchrotron Day, University of Groningen, Groningen, The Netherlands, Nov. 4, 1992.

M. O. Krause, "Photoelectron Spectrometry of Halogen and Chalcogen Atoms," Seminar, Physics Department, University of Amsterdam, Amsterdam, The Netherlands, Nov. 6, 1992.

M. O. Krause, "Synchrotron Radiation in Atomic and Molecular Physics," American Physical Society Meeting, Washington, D.C., April 12-15, 1993.

L. L. Pesterfield,[21] N. A. Stump,[5] G. K. Schweitzer,[5] and J. R. Peterson,[6] "Perturbations of the Fluorescence Spectra of Europium-EDTA Salts Caused by Selected Monovalent Counterions," 19th Rare Earth Research Conference, Lexington, KY, July 14-19, 1991.

L. L. Pesterfield,[21] W. P. Pan,[21] C. M. Dieckmann,[21] J. R. Peterson,[6] and N. A. Stump,[5] "A Thermogravimetric and Spectroscopic Investigation of Eu-EDTA Salts," 1992 Joint 44th Southeastern-26th Middle Atlantic Regional American Chemical Society Meeting, Arlington, VA, Dec. 6-9, 1992.

J. R. Peterson,[6] "Recollections of a Newcomer: 25 Years in Transplutonium Element Chemistry and Not Yet Age 50," 50th Anniversary of the Discovery and First Chemical Identification of Plutonium Symposium, University of California, Berkeley and Lawrence Berkeley Laboratory, Feb. 22-23, 1991.

J. R. Peterson,[6] "The Transcurium Elements: Lessons Learned About the Consequences of Radioactive Decay," San Jose State University, San Jose, CA, July 26, 1991.

J. R. Peterson,[6] "The Transcurium Elements: Lessons Learned About the Consequences of α and β^- Decay in the Bulk-Phase Solid State," University of Kentucky, Lexington, Kentucky, Oct. 25, 1991.

J. R. Peterson,[6] "Recollections of a Newcomer: 25 Years in Transplutonium Element Chemistry and Not Yet Age 50," University of Tennessee, Knoxville, TN, Feb. 20, 1992.

J. R. Peterson,[6] "Chemistry on the Edge of Matter: The Transplutonium Elements and Lessons Learned About the Consequences of Radioactive Decay," University of Saskatchewan, Saskatoon, Canada, Mar. 24, 1992.

J. R. Peterson,[6] "Some Advances and Prospects in Transplutonium Element Research from the UT-Knoxville/ORNL Group," 203rd American Chemical Society Meeting, San Francisco, CA, April 5-10, 1992.

J. R. Peterson,[6] "Chemistry on the Edge of Matter: The Transplutonium Elements and Lessons Learned About the Consequences of Alpha and Beta (β^-) Decay in the Bulk-Phase Solid State," Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken, Japan, May 25, 1992.

J. R. Peterson,[6] "Bulk Phase Chemical Studies on the Edge of Matter," The Atomic Energy Society of Japan, Tohoku Section, Sendai, Japan, May 25, 1992.

J. R. Peterson,[6] "Some Experiences with Absorption, Phonon Raman, and Luminescence Spectroscopic Probes of Crystal Structure of f-Element Compounds," The International Conference Rare Earths '92 in Kyoto, Kyoto, Japan, June 1-5, 1992.

J. R. Peterson,[6] S. Heathman,[1] and U. Benedict,[1] "Energy Dispersive X-Ray Diffraction Analysis of $NdBr_3$ at Pressures up to 52 GPa," The International Conference Rare Earths '92 in Kyoto, Kyoto, Japan, June 1-5, 1992.

J. R. Peterson,[6] "Chemistry on the Edge of Matter: The Transcurium Elements," San Jose State University, San Jose, CA, June 30, 1992.

J. R. Peterson,[6] "High Pressure Phase Behavior of Lanthanide and Actinide (Lanact) Trihalides," 4th Workshop on Actinides Under Pressure, Karlsruhe, Germany, Oct. 12-13, 1992.

J. R. Peterson,[6] "Bulk Phase Chemical Studies on the Edge of Matter," University of Southern Mississippi, Hattiesburg, MI, Nov. 12, 1992.

N. A. Stump,[5] L. L. Pesterfield,[21] G. K. Schweitzer,[5] and J. R. Peterson,[6] "A High Resolution Spectral Study of $Li_3Eu(2,6\text{-pyridinedicarboxylato})_3$," 19th Rare Earth Research Conference, Lexington, KY, July 14-19, 1991.

M. A. Williamson,[9] P. D. Kleinschmidt,[9] and R. G. Haire, "The Sublimation of Californium Trifluoride," 12th IUPAC Conference on Chemical Thermodynamics, Snowbird, UT, Aug. 16-21, 1992.

---

1. European Institute for Transuranium Elements, Karlsruhe, Germany.
2. University of Copenhagen, Copenhagen, Denmark.
3. Technical University of Denmark, Lyngby, Denmark.
4. University of Central Florida, Orlando, FL.
5. Department of Chemistry, University of Tennessee, Knoxville, TN.
6. Department of Chemistry, University of Tennessee, Knoxville, TN; Part-time employee of ORNL Chemistry Division.
7. ORNL Solid State Division.
8. Boston University, Boston, MA.
9. Los Alamos National Laboratory, Los Alamos, NM.
10. ORNL Chemical Technology Division.
11. University of Maryland, Baltimore, MD.
12. Savannah River Laboratory, Aiken, SC.
13. Consultant, ORNL (retired).
14. University of Kassel, Kassel Germany.
15. European Institute for Transuranium Elements, University of Liege, Liege, Belgium.
16. ORNL Physics Division.
17. University of Arizona, Tempe, AZ.
18. Institute of Physical Chemistry, Russian Academy of Science, Moscow, Russia.
19. Institute for Heavy Ion Research, Darmstadt, Germany.
20. University of Amsterdam, Amsterdam, The Netherlands.

21. Western Kentucky University, Bowling Green, KY.
22. Physics Department, University of Florida, Gainsville, FL.

CHEMICAL AND STRUCTURAL PRINCIPLES IN SOLVENT EXTRACTION

PUBLICATIONS

C. F. Baes, Jr.,[1,2] B. A. Moyer, and G. N. Case,[2] "SXLSQA, A Computer Program for Including both Complex Formation and Activity Effects in the Interpretation of Solvent Extraction Data," *Sep. Sci. Technol.* **1990**, *25(13-15)*, 1675-1688; Proc. Sixth Symp. on Separation Science and Technology for Energy Applications, Knoxville, TN, October 22-27, 1989.

J. H. Burns and G. J. Lumetta,[3] "Complexes of Manganese and Zinc Di-*t*-butylnaphthalenesulfonate with Cyclohexano-15-Crown-5 Ether (Toluene Solvates)," *Acta Cryst.* **1991**, *C47*, 2069.

J. H. Burns and R. A. Sachleben, "Synthesis and Structural Studies of Sodium Complexes of sym-Dibenzo-14-crown-4 Ionizable Lariat Ethers," *Inorg. Chem.* **1990**, *29*, 788.

J. H. Burns and R. A. Sachleben, "Complexes of Lithium and Sodium with *sym*-(Dibenzo-14-crown-4-)methylphenyl Phosphinic Acid," *Acta Cryst.* **1991**, *C47*, 2339.

G. J. Lumetta[3] and B. A. Moyer, "FTIR Spectroscopic Investigations of the Complexation of *t*-Butylcyclohexano-15-crown-5 with Divalent Transition Metal Ions," *J. Coord. Chem.* **1991**, *22*, 331.

W. J. McDowell,[1,2] G. N. Case,[2] J. A. McDonough,[4] and R. A. Bartsch,[4] "Selective Extraction of Cesium from Acidic Nitrate Solutions with Didodecylnaphthalenesulfonic Acid Synergized with Bis(*tert*-butylbenzo)-21-crown-7," *Anal. Chem.* **1992**, *64*, 3013.

B. A. Moyer, C. F. Baes, Jr.,[1,2] S. A. Bryan,[5] J. H. Burns, G. N. Case,[2] G. J. Lumetta,[3] W. J. McDowell,[1,2] and R. A. Sachleben, "Developing New Chemical Tools for Solvent Extraction," *Proc. First Hanford Separation Science Workshop* (in press).

B. A. Moyer, C. F. Baes, Jr.,[1,2] G. N. Case,[2] G. J. Lumetta,[3] and N. M. Wilson,[6] "Equilibrium Analysis of Aggregation Behavior in the Extraction of Cu(II) from Sulfuric Acid by Didodecylnaphthalene Sulfonic Acid," *Sep. Sci. Technol.* **1993**, *28*, 81. Proc. Seventh Symp. on Separation Science and Technology for Energy Applications, Knoxville, TN, October 20–24, 1991.

B. A. Moyer, F. J. Baltich,[7] and K. C. Andrews,[8] "Interfacial Precipitates Containing Dodecamolybdophosphate and Dodecamolybdoarsenate Anions in Tertiary Amine Solvent Extraction," *Hydrometallurgy* **1991**, *27*, 113.

B. A. Moyer and F. I. Case,[2] "On the Origin of Haze in Extraction Solvents: Dilution-Induced Supersaturation of Water," *Solvent Extr. Ion Exch.* **1991**, *9(2)*, 277.

B. A. Moyer, L. H. Delmau,[6] G. J. Lumetta,[3] and C. F. Baes, Jr.,[1,2] "Extraction of Mn(II) from Nitric Acid by Crown Ether-Synergized Cation Exchange: Extended Equilibrium and Infrared Analysis," *Solvent Extr. Ion Exch.* (in press).

B. A. Moyer, W. J. McDowell,[1,2] C. F. Baes, Jr.,[1,2] G. N. Case,[2] and F. I. Case,[2] "Liquid-Liquid Equilibrium Analysis in Perspective. Part 1. Slope Analysis of the Extraction of Uranyl Nitrate from Nitric Acid by Di-2-ethylhexylsulfoxide," *Solvent Extr. Ion Exch.* **1991**, *9*, 833.

B. A. Moyer, R. A. Sachleben, and G. N. Case,[2] "Synergism in the Extraction of Cu(II) by Polydentate Thia Ligands Combined with Didodecylnaphthalene Sulfonic Acid," *Proc. International Solvent Extraction Conference (ISEC '93)*, to be held in York, England, Sept. 9-15, 1993, Society for Chemical Industry, London (in press).

R. A. Sachleben and J. H. Burns, "Lithium Dibenzo-14-crown-4-acetate-ethanol (2/1)," *Acta Cryst.* **1991**, *C47*, 1968.

R. A. Sachleben and J. H. Burns, "Conformational Changes of Substituted 14-Crown-4 Ethers Upon Complexation," *J. Chem. Soc. Perkin*, **1992**, *2*, 1971.

R. A. Sachleben, B. A. Moyer, F. I. Case,[2] and J. L. Driver,[9] "Extraction of Alkali Metal Cations Using a Lipophilic Lariat Ether Having a C-pivot Carboxylic Acid Sidearm," *Proc. International Solvent Extraction Conference (ISEC '93)*, to be held in York, England, Sept. 9-15, 1993, Society for Chemical Industry, London (in press).

R. A. Sachleben, B. A. Moyer, F. I. Case,[2] and S. A Garmon,[6] "Alkylated Lariat Ethers As Solvent Extraction Reagents: Surveying the Extraction of Alkali Metals by Bis-(*t*-octylbenzo)-14-crown-4-acetic Acid by Potentiometric Two-Phase Titrimetry," *Sep. Sci. Technol.* **1993**, *28*, 1; Proc. Seventh Symp. on Separation Science and Technology for Energy Applications, Knoxville, TN, October 20-24, 1991.

PRESENTATIONS

J. H. Burns and R. A. Sachleben, "Conformations of Nonamethyl-14-crown-4 Before and After Complexation with LiSCN," Am. Cryst. Assoc. Ann. Mtg. Toledo, OH, July 23, 1991.

J. H. Burns and R. A. Sachleben, "Conformational Changes in Substituted 14-Crown-4 Ethers on Complexation with LiSCN," XVII Int. Symp. on Macrocyclic Chemistry, Provo, UT, Aug. 9, 1992.

J. H. Burns and R. A. Sachleben, "Crown Ethers as Complexing Agents for Solvent Extraction: Structural, Molecular Mechanics, and Solution Studies," Ohio State University Seminar, Columbus, OH, Apr. 22, 1993.

J. H. Burns, R. A. Sachleben, and M. C. Davis,[6] "Selectivity for the Li^+ Ion by Substituted 14-Crown-4 Ligands," Amer. Cryst. Assoc. Ann. Mtg., Albuquerque, NM, May 28, 1993.

M. T. Caudle,[10] A. L. Crumbliss,[10] P. L. Choo,[10] F. Chaubet,[10] and B. A. Moyer, "Thermodynamics and Kinetics of Ferric Hydroxamic Acid Complexes," 203rd ACS Nat. Mtg., San Francisco, CA, Apr. 5-10, 1992.

Y. Deng,[11] G. G. Wu,[12] B. A. Moyer, and R. M. Izatt,[13] "Calorimetric Study of the Interaction of Divalent Transition Metal Ions with a Crown Ether: Inverting the Irving-Williams Order," XVIII International Symp. on Macrocyclic Chemistry, Provo, UT, Aug. 9-14, 1992.

Y. Deng,[11] G. G. Wu,[12] B. A. Moyer, and R. M. Izatt,[13] "Complexation of Cyclohexano-15-Crown-5 with Transition Metal Ions: A Thermodynamic Approach," 204th ACS Nat. Mtg., Washington, DC, Aug. 23-28, 1992.

A. A. Kriger,[14] S. D. Alexandratos,[14] C. G. Ciaccio,[14] and B. A. Moyer, "Metal Ion Separations Using Bifunctional Interpenetrating Polymer Networks," 1992 Joint 44th ACS Southeastern - 26th Middle Atlantic ACS Regional Mtg., Arlington, VA, Dec. 6-9, 1992.

B. A. Moyer, "Detailed Equilibrium Analysis of the Solvent Extraction of Metal Cations," Chemistry Division Information Mtg., Oak Ridge Nat. Laboratory, Oak Ridge, TN, Oct. 9, 1991.

B. A. Moyer, "Selective Separations of Metal Ions," USDOE Science and Engineering Research Semester Seminar, Oak Ridge Associated Universities, Oak Ridge, TN, Feb. 12, 1992.

B. A. Moyer, "Oak Ridge National Laboratory: Past, Present, and Future Directions in Technology," Atomic Energy Corporation of South Africa, Pretoria, South Africa, Apr. 14, 1993 (Invited).

B. A. Moyer, "Investigating Crown Ethers As Selective Extractants for Metal Ions," JCI Minerals Processing Research Laboratories, Randburg, South Africa, Apr. 16, 1993 (Invited).

B. A. Moyer, "Investigating Crown Ethers As Selective Extractants for Metal Ions," Dept. of Chemistry, University of Port Elizabeth, Port Elizabeth, South Africa, Apr. 27, 1993 (Invited).

B. A. Moyer, "Investigating Crown Ethers As Selective Extractants for Metal Ions," Dept. of Chemistry, University of Natal, Durban, South Africa, Apr. 28, 1993 (Invited).

B. A. Moyer and C. F. Baes, Jr.,[1,2] "Understanding Solvent Extraction with the Aid of a Computer," Plenary Lecture at the International Symposium on Metal Ions in Solution, Malelane Lodge, Malelane, South Africa, Apr. 21-23, 1993 (Invited).

B. A. Moyer, C. F. Baes, Jr.,[1,2] S. A. Bryan,[5] J. H. Burns, G. N. Case,[2] G. J. Lumetta,[3] W. J. McDowell,[1,2] and R. A. Sachleben, "Developing New

Chemical Tools for Solvent Extraction," First Hanford Separation Science Workshop, Richland, WA, July 23-25, 1991 (Invited).

B. A. Moyer, G. N. Case,[2] G. J. Lumetta,[3] and N. M. Wilson,[6] "Equilibrium Analysis of Aggregation Behavior in the Extraction of Cu(II) by Didodecylnaphthalene Sulfonic Acid," Seventh Symp. on Separation Science and Technology for Energy Applications, Knoxville, TN, Oct. 20-24, 1991.

B. A. Moyer, Y. Deng,[11] G. Wu,[12] and R. M. Izatt,[13] "Pursuing the Origin of an Inverted Irving Williams Order in the Binding and Separation of Transition Metal Ions by Crown Ethers," Symp. on Synthetic Hosts for Recognition of Molecular and Ionic Guests, 48th Southwest ACS Regional Mtg., Oct. 21-23, 1992 (Invited).

B. A. Moyer, G. J. Lumetta,[3] C. F. Baes, Jr.,[1,2] and G. N. Case,[2] "Investigating the Selective Extraction of First Row Transition Metals by Use of Crown Ethers," AIChE Nat. Mtg., New Orleans, LA, Mar. 29-Apr. 2, 1992 (Invited).

B. A. Moyer, G. J. Lumetta,[3] and G. N. Case,[2] "Complexation Equilibria in the Selective Binding of Transition Metal Cations by Macrocyclic Extractants," 203rd ACS Nat. Mtg., San Francisco, CA, Apr. 5-10, 1992 (Invited).

B. A. Moyer, W. J. McDowell,[1,2] C. F. Baes, Jr.,[1,2] G. N. Case,[2] and F. I. Case,[2] "Analysis of the Liquid-Liquid Extraction System Di-2-ethylhexylsulfoxide, Dodecane, Uranyl Nitrate, Nitric Acid, Sodium Nitrate, Water: Comparing Graphical and Computer Methods," American Institute of Chemical Engineers Nat. Mtg., Pittsburgh, PA, Aug. 18-21, 1991 (Invited).

B. A. Moyer, R. A. Sachleben, and J. H. Burns, "Binding and Extraction of Alkali Metal Cations by Neutral and Ionizable Crown Ethers," Dept. of Chemistry, University of the Witwatersrand, Johannesburg, South Africa, Apr. 15, 1993 (Invited).

B. A. Moyer, R. A. Sachleben, J. R. Watson, III,[15] N. M. Wilson,[6] G. N. Case,[2] and S. D. Alexandratos,[14] "Macrocyclic and Acyclic Multidentate Thia Ethers as Synergists for Ion-Exchange Separations of Cu(II) in Solvent and Resin Extraction Systems," 201st ACS Nat. Mtg., Atlanta, GA, Apr. 14-19, 1991 (Invited).

R. A. Sachleben, J. H. Burns, M. C. Davis,[6] J. L. Driver,[9] Z. Chen,[11] Y. Deng,[11] and B. A. Moyer, "Recognition of Lithium Cation by Substituted 14-crown-4 Macrocycles," 205th ACS Nat. Mtg., Denver, CO, Mar. 28 - Apr. 2, 1993.

R. A. Sachleben, B. A. Moyer, J. H. Burns, W. J. McDowell,[1,2] G. N. Case,[2] F. I. Case,[2] S. A. Bryan,[5] and G. J. Lumetta,[3] "Macrocycle-Mediated Cation Separations in Solvent Extraction," 201st ACS Nat. Mtg., Atlanta, GA, Apr. 14-19, 1991 (Invited).

R. A. Sachleben, B. A. Moyer, F. I. Case,[2] and S. A. Garmon,[6] "Alkylated Lariat Ethers As Solvent Extraction Reagents: Surveying the Extraction of Alkali Metals by Bis-(*t*-octylbenzo)-14-crown-4-acetic Acid by Potentiometric Two-Phase Titrimetry," Seventh Symp. on Separation Science and Technology for Energy Applications, Knoxville, TN, Oct. 20-24, 1991.

R. A. Sachleben, B. A. Moyer, S. A. Kelleher,[6] F. I. Case,[2] S. A. Garmon,[6] and G. J. Noeth,[16] "Macrocycle Solubility and Organophilicity: Effect of Alkyl Substitution on the Extraction Properties of Benzo-Substituted Ionizable Lariat Ethers," 201st ACS Nat. Mtg., Atlanta, GA, Apr. 14-19, 1991 (Invited).

---

1. Consultant.
2. Retired, ORNL.
3. Postdoctoral Research Associate, Oak Ridge Associated Universities. Now at Battelle Pacific Northwest Laboratories.
4. Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX.
5. Visiting Scientist, Georgia Southern University. Now at Battelle Pacific Northwest Laboratories.
6. Undergraduate Research Participant.
7. Chevron Resources Company. Now at American Gilsonite Company.
8. Chevron Resources Company.
9. Oak Ridge Research Institute.
10. Department of Chemistry, Duke University.
11. Postdoctoral Research Associate, Oak Ridge Associated Universities.
12. Postdoctoral Research Associate, Brigham Young University. Now at Dow Chemical Company.
13. Department of Chemistry, Brigham Young University.
14. Department of Chemistry, University of Tennessee, Knoxville.
15. Oak Ridge High School, Oak Ridge, TN.
16. South Side High School, Memphis, TN.

SURFACE SCIENCE RELATED TO HETEROGENEOUS CATALYSIS

PUBLICATIONS

C. S. Feigerle,[1] S. H. Overbury and D. R. Huntley, "Effects of Preadsorbed Oxygen on the Bonding and Desorption Kinetics of CO on Ni(110)," *J. Chem. Phys.*, **1991**, *94*, 6264.

F.A. Grimm[1] and D. R. Huntley, "A Theoretical Study of the Binding Energy and Bonding of Benzene to the Ni(111), (100) and (110) Surfaces," *J. Phys. Chem.*, **1993**, *97*, 3800.

I. G. Hughes,[2] C. C. Havener,[2] S. H. Overbury, M. T. Robinson,[3] D. M. Zehner,[3] P. A. Zeijlmans van Emmichoven[2] and F. W. Meyer,[2] "Incident Ion Charge State Dependence of Electron Emission During Slow Multicharged Ion-Surface Interactions". *Proceedings of the 6th International*

Conference on the Physics of Highly-Charged Ions, Manhattan, KS, Sept. 28 - Oct. 2, 1992, published by AIP.

D. R. Huntley, S. L. Jordan,[4] and F. A. Grimm,[1] "Adsorption and Thermal Decomposition of Benzene on Ni(110) Studied by Chemical, Spectroscopic, and Computational Methods," *J. Phys. Chem.*, **1992**, *96*, 1410.

D. R. Huntley, "The Mechanism of the Desulfurization of Benzenethiol by Ni(110)," *J. Phys. Chem.*, **1992**, *96*, 4550.

Yi-Sha Ku[5] and S. H. Overbury, "Surface Structure Analysis of Sn on Ni(111) by Low Energy Alkali Ion Scattering," *Surf. Sci.*, **1992**, *273*, 341.

Yi-Sha Ku[5] and S. H. Overbury, "Structure Analysis of S Adsorbed on Ni(111) by Low Energy Li^+ Ion Scattering," *Surf. Sci.*, **1992**, *276*, 262.

F. W. Meyer,[2] S. H. Overbury, C. C. Havener,[2] P. A. Zeijlmans van Emmichoven,[2] and D. M. Zehner,[3] "Evidence for Above- and Sub-Surface Neutralization During Interactions of Highly Charged Ions with a Metal Target," *Phys. Rev. Lett.*, **1991**, *67*, 723.

F. W. Meyer,[2] S. H. Overbury, C. C. Havener,[2] P. A. Zeijlmans van Emmichoven,[2] J. Burgdorfer,[6] and D. M. Zehner,[3] "Electron Emission during Interactions of Multi-charged N and Ar Ions with Au(110) and Cu(001) Surfaces," *Phys. Rev. A*, **1991**, *44*, 7214.

F. W. Meyer,[2] J. Burgdorfer,[1] L. Folkerts,[2] I. G. Hughes,[2] S. H. Overbury, D. M. Zehner[3] and P. A. Zeijlmans van Emmichoven,[2] "Neutralization of Slow Multicharged Ions Above a Cesiated Au Surface". *Proceedings of the 6th International Conference on the Physics of Highly-Charged Ions*, Manhattan, KS, Sept. 28 - Oct. 2, 1992, published by AIP.

D. R. Mullins, P. F. Lyman,[7] and S. H. Overbury, "Interaction of S with W(001)," *Surf. Sci.*, **1992** *277*, 64.

D.R. Mullins and P.F. Lyman,[7] "Sulfur-Induced Changes in the W(001) Surface Core Level Shift," *Surf. Sci.* (in press).

S. H. Overbury, D. R. Mullins, M. T. Paffett,[8] and B. E. Koel,[9] "Surface Structural Determination of Sn Deposited on Pt(111) by Low Energy Alkali Ion Scattering," *Surf. Sci.*, **1991**, *254*, 45.

S. H. Overbury, D. R. Mullins, M. T. Pattett,[8] and B. Koel,[9] "Structure of Metal Overlayers by Low Energy Alkali Ion Scattering: Cu/Ru (0001) & Sn/Pt(III)," Structure of Surfaces III, eds. S. Y. Tong, M. A. Van Howe, K. Tutianayagi and X. Xie, *Springer-Verlag, Berlin*, **1991**, 323.

S. H. Overbury, F. W. Meyer[2] and M. T. Robinson,[3] "Computer Simulations of Relaxation Processes in Scattering of Multi-charged Ions From Metal Surfaces," *Nucl. Inst. and Meth. B*, **1992**, *B67*, 126.

S. H. Overbury and Yi-Sha Ku,[5] "Formation of Stable, Two-Dimensional Alloy Surface Phases: Sn in Cu(111), Ni(111) and Pt(111)," *Phys. Rev. B*, **1992**, *46*, 7868.

S. H. Overbury, R.J.A. ven den Oetelaar[10] and D. M. Zehner,[3] "Surface Segregation in Mo_{75} Re_{25} (001) Studied by Low Energy Alkali Ion Scattering", *Phys. Rev. B* (in press).

R. A. Pheneuf,[2] F. W. Meyer,[2] D. C. Gregory,[2] C. C. Havener,[2] P. A. Zeijlmans van Emmichoven,[2] S. H. Overbury, D. M. Zehner,[3] G. H. Dunn,[11] J. S. Thompson,[11] E. K. Wahlin,[11] A-C.H. Smith,[12] "Low-Energy Collisions of Multiple Charged Ions with Electrons, Atoms, and Surfaces", in "*Proceedings of 3rd U.S.-Mexico Atomic and Molecular Physics Symposium,*" Cocoyoc, Mexico, March 13-16, 1991, World Scientific.

P. A. Zeijlmans van Emmichoven,[4] C. C. Havener,[2] I. G. Hughes,[2] S. H. Overbury, M. T. Robinson,[3] D. M. Zehner,[3] F. W. Meyer,[2] "Electron Emission During Multicharged Ion-Metal Surface Interactions". *Proceedings of the 14th Werner Brandt Workshop on Charged Particle Penetration Phenomena*, Oak Ridge, TN, **1992**, ORNL-Conf-92-0414.

PRESENTATIONS

D. R. Huntley, "Model Hydrodesulfurization Systems: Reaction of Polyfunctional Organosulfur Molecules with Ni(110)," The Catalysis Society 12th North American Meeting, Lexington, KY, May 5-9, 1991.

D. R. Huntley, "Adsorption and Thermal Decomposition of Benzene on Ni(110)," Gordon Research Conference on Catalysis, New London, NH, June 1991.

D. R. Huntley, "Mechanisms of Thiol Desulfurization on Ni(110)," 8th DOE/BES Conference on Heterogeneous Catalysis and Surface Science, Santa Monica, CA, March 11-13, 1992.

D. R. Huntley, "Mechanisms of Thiol Desulfurization on Ni(110)," National ACS Meeting, San Francisco, CA, April 1992.

D. R. Huntley, "Controlling the Selectivity of Surface Reactions: Reaction Pathways for Polyfunctional Thiols on Ni(110)," Am. Vac. Soc. 39th Nat'l. Symp. & Topical Conf., Chicago, IL, November 9-13, 1992.

D. R. Huntley, "Selectivity of Ethane and Ethylene Formation from the Reaction of Ethanethiol on Clean and Modified Ni(110)," National ACS Meeting, Denver Colorado, March 1993.

D.R. Huntley, "Controlling Reaction Selectivity: Effects of Co-Adsorbed H and O on Ethanethiol Reactions on Ni(110)," 13th North American Meeting of the Catalysis Society, Pittsburg, Pennsylvania, May 2-7, 1993.

P. F. Lyman,[7] D. R. Mullins, and S. H. Overbury, "Photoemission Spectroscopy Study of the S/W(100) Surface," Am. Phys. Soc. Meeting, Indianapolis, IN, March 16-20, 1992.

P.F. Lyman[7] and D.R. Mullins, "Effect of C Adsorption on the W(100) Surface Environment as Studied by Core Level Spectroscopy," APS Meeting, Seattle, Washington, March 22-26, 1993.

P. F. Lyman,[7] D. R. Mullins, and S. H. Overbury, "Core Level Spectroscopy of S on W(001)," presented at the Annual NSLS User's Meeting, Brookhaven National Laboratory, May 1992.

P. F. Lyman[7] and D. R. Mullins, "Core Level Spectroscopy Study of S on W(001)," Am. Vac. Soc. 39th Nat'l. Symp. & Topical Conference, Chicago, IL, November 9-13, 1992.

D. R. Mullins, S. H. Overbury, D. R. Huntley, and M. Castro,[13] "Characterization of Sulfur Containing Species on Ru(001) and W(001) Using Synchrotron," Annual Conference of Physical Electronics, Rutgers University, New Jersey, June 17-19, 1991.

D. R. Mullins, S. H. Overbury, D. R. Huntley, and M. E. Castro,[13] "Photoemission from Sulfur Adsorbed on Ru(0001) and W(001)," 24th Annual Synchrotron Radiation Users' Meeting, Stoughton, WS, October 14-15, 1991 [Proceedings: Page 31].

D. R. Mullins, S. H. Overbury, D. R. Huntley and M. Castro,[13] "Characterization of Sulfur Containing Species on Ru(0001) and W(001) Using Synchrotron Radiation," presented at the Annual NSLS User's Meeting, Brookhaven National Laboratory, May 1991.

D. R. Mullins, "Characterization of Surface Reactions Using Synchrotron Radiation," presented at the Eighth DOE/BES Heterogeneous Catalysis and Surface Chemistry Meeting, Santa Monica, CA, March 1992.

D. R. Mullins, S.H. Overbury and P.F. Lyman,[7] "The Adsorption of Sulfur on W(001)," 25th SRC USERS Group Meeting, University of Wisconsin, Stoughton, Wisconsin, October 5-6, 1992.

D.R. Mullins and P.F. Lyman,[7] "Methanethiol on W(001) and Ru(0001)," 25th SRC USERS Group Meeting, University of Wisconsin, Stoughton, Wisconsin, October 5-6, 1992.

D. R. Mullins and P. F. Lyman,[7] "Reactions of Sulfur Containing Species on Metal Surfaces Characterized by Synchrotron Radiation," Am. Vac. Soc. 39th Nat'l. Symp. & Topical Conference, Chicago, IL, November 9-13, 1992.

S. H. Overbury, "Structure of Alloying Metal Overlayers by Low Energy Ion Scattering", Physical Chemistry Seminar Series, University of Tennessee, March 14, 1991.

S. H. Overbury, "Structure of Bi-metallic Surfaces by Low Energy Alkali Ion Scattering: Sn/Pt and Cu, Ni/W," The Catalysis Society 12th North American Meeting, Lexington, KY, May 5-9, 1991.

S. H. Overbury, F. W. Meyer,[2] M. T. Robinson,[3] C. C. Havener,[2] P. A. Zeijlmans van Emmichoven[2] and D. M. Zehner,[3] "Computer Simulation of Neutralization Processes in Scattering of Multi-Charged Ions from Metal Surfaces," 14th International Conference on Atomic Collisions in Solids, University of Salford, United Kingdom, July 28-August 2, 1991.

S. H. Overbury and Y. S. Ku,[5] "Analysis of Surface Strain in Alloying Metal Overlayers by Low Energy Alkali Ion Scattering," 14th International Conference on Atomic Collisions in Solids, University of Salford, United Kingdom, July 28 - August 2, 1991.

S. H. Overbury and Y. S. Ku,[5] "Surface Alloy Formation from Metal Overlayers Studied by Low Energy Alkali Ion Scattering," 38th Annual Symposium American Vacuum Society, Seattle, WA, November 11-15, 1991.

S. H. Overbury, "Structure of Model Catalytic Surfaces Studied by Alkali Ion Scattering," 8th DOE/BES Heterogeneous Catalysis and Surface Chemistry Research Conference, Santa Monica, CA, March 11-13, 1992.

S. H. Overbury, "Determination of Structure and Composition of Alloy and Metal Overlayer Surfaces by Alkali Ion Scattering," presented at Gordon Research Conference on Catalysis, Colby-Sawyer College, London, New Hampshire, June 29 - July 3, 1992.

S. H. Overbury, "Structure and Composition of Alloy and Metal Overlayer Surfaces by Low Energy Alkali Ion Scattering," presented at G. M. Research Center, Warren, MI, August 27, 1992.

S. H. Overbury and D. M. Zehner,[3] "Composition and Structure of Clean and Oxidized $Mo_{.75}Re_{.25}$(001) Alloy Surface," presented at the 39th National American Vacuum Society Meeting, Chicago, IL, November 9-13, 1992.

S. H. Overbury and Yi-Sha Ku,[5] "Structure Analysis of Sulfur Adsorbed on Ni(111) by Low Energy Alkali Ion Scattering," presented at the 39th National American Vacuum Society Meeting, Chicago, IL, November 9-13, 1992.

S. H. Overbury, "Low Energy Alkali Ion Scattering," presented at Workshop on "Recent Advances in Surface Science Techniques" at the 39th National American Vacuum Society Meeting, Chicago, IL, November 9-13, 1992.

---

1. Department of Chemistry, University of Tennessee, Knoxville.
2. Physics Division, ORNL.
3. Solid State Division, ORNL.
4. Great Lakes Colleges Association Science Semester, Student Guest.
5. Institute of Nuclear Science, Nationial Tsing Hua University, Taiwan.

6. Department of Physics, University of Tennessee, Knoxville.
7. NSLS, Brookhaven National Laboratory, Upton, NY.
8. Los Alamos National Laboratory, Los Alamos, NM.
9. University of Southern California, Los Angeles, CA.
10. Eindhoven University of Technology, Amsterdam, The Netherlands.
11. Institute for Laboratory Astrophysics, Boulder, CO.
12. University College, London, United Kingdom.
13. University of Texas, Austin, TX.

PHOTOLYTIC TRANSFORMATIONS OF HAZARDOUS ORGANICS

PUBLICATIONS

J. T. Barbas,[1] M. E. Sigman, A. C. Buchanan, III and E. A. Chevis,[2] "Photolysis of Substituted Naphthalenes on SiO_2 and Al_2O_3," *Photochem. Photobio.* (in press).

J. E. Coffield,[3] G. Mamantov,[3] S. P. Zingg, G. P. Smith and A. C. Buchanan, III, "Reduction of Aromatic Compounds in Organic Chloroaluminate Melts: II. Perylene," *J. Electrochem. Soc.* **1992**, *139*, 355.

J. E. Coffield,[3] S. P. Zingg, K. D. Sienerth,[3] S. Williams,[3] C. Lee,[3] G. Mamantov,[3] and G. P. Smith, "Electrochemistry of Aromatic Compounds in Ambient Temperature Chloroaluminate Melts," *Materials Science Forum* **1991**, *73-75*, 25.

J. M. MacInnis,[4] K. A. McDonald,[5] M. E. Sigman and E. Greenbaum,[6] "Simultaneous Measurement of Photosynthetic Oxygen Evolution and Carbon Dioxide Assimilation for Determination of Time-Dependent Photosynthetic Quotients under Anaerobiosis," *Photochem. Photobiol.* (in press).

M. E. Sigman and S. P. Zingg, "Photodecomposition of Anthracene in Aqueous and Heterogeneous Media," *Prepr. Pap. Am. Chem. Soc., Div. Environ. Chem.* **1992**, *32*, 188.

M. E. Sigman and S. P. Zingg, "Anthracene Photochemistry in Aqueous and Heterogeneous Media," in *Environmental Aspects of Surface and Aquatic Chemistry*, American Chemical Society Monograph Series, eds. G. Helz, R. Zepp, and D. Crosby, Lewis Publishers (in press).

M. E. Sigman, S. P. Zingg, R. M. Pagni,[3] and J. H. Burns, "Photochemistry of Anthracene in Water," *Tetrahedron Letters* **1991**, *32*, 5737.

S. P. Zingg and M. E. Sigman, "Influence of an SiO_2/Cyclohexane Interface on the Photochemistry of Anthracene," *Photochem. Photobio.* **1993**, *57*, 453.

PRESENTATIONS

J. T. Barbas[1] and M. E. Sigman, "Photolysis of Acenaphthylene on Silica Surfaces," Inter-American Photochemical Society 5th Winter Conference, Clearwater Beach, FL, January 2-6, 1993.

M. E. Sigman, "Mechanisms of Polynuclear Aromatic Hydrocarbon Photo-oxidation in Environmental Systems," Department of Chemistry, Hampton University, Hampton, VA, January 29, 1992, DOE Traveling Lecture Program, administered by Oak Ridge Associated Universities.

M. E. Sigman, "Mechanisms of Polynuclear Aromatic Hydrocarbon Photo-oxidation in Environmental Systems," Department of Chemistry, Southwest Missouri State University, Springfield, MO, March 11, 1992, DOE Traveling Lecture Program, administered by Oak Ridge Associated Universities.

M. E. Sigman, "Mechanisms of Polynuclear Aromatic Hydrocarbon Photo-oxidation in Environmental Systems," Department of Chemistry, University of Southern Mississippi, Hattiesburg, MS, September 3, 1992, DOE Traveling Lecture Program, administered by Oak Ridge Associated Universities.

M. E. Sigman, "Mechanisms of Polynuclear Aromatic Hydrocarbon Photo-oxidation in Environmental Systems," Department of Chemistry, Mississippi State University, Starkville, MS, September 4, 1992, DOE Traveling Lecture Program, administered by Oak Ridge Associated Universities.

M. E. Sigman and J. T. Barbas,[1] "Photochemistry of Substituted Naphthalenes at an SiO_2/air Interface," Inter-American Photochemical Society 5th Winter Conference, Clearwater Beach, FL, January 2-6, 1993.

M. E. Sigman and S. P. Zingg, "Photodecomposition of Anthracene in Aqueous and Heterogeneous Media," 203rd American Chemical Society National Meeting, San Francisco, CA, April 5-10, 1992.

M. E. Sigman, S. P. Zingg, and R. M. Pagni,[3] "Photooxidation of Anthracene in Water," 201st American Chemical Society National Meeting, Atlanta, GA, April 14-19, 1991.

---

1. Valdosta State University, Valdosta, GA.
2. Oak Ridge Research Institute, Oak Ridge, TN.
3. University of Tennessee, Knoxville, TN.
4. Health and Safety Research Division, ORNL.
5. Appalachian State University, Boone, NC.
6. Chemical Technology Division, ORNL.

DNA SEQUENCING AND MAPPING

PUBLICATIONS

D. P. Allison,[1] R. J. Warmack,[1] L. A. Bottomley,[2] T. Thundat,[1] G. M. Brown, J. J. Schrick,[3] K. B. Jacobson,[3] and T. L. Ferrell,[1] "Scanning Tunneling Microscopy of DNA: A Novel Technique Using Radiolabeled DNA to Evaluate Chemically Mediated Attachment of DNA to Surfaces," *Ultramicroscopy* **1992**, *42*, 1088.

D. P. Allison,[1] L. A. Bottomley,[2] T. Thundat,[1] G. M. Brown, R. P. Woychik,[3] J. J. Schrick,[3] K. B. Jacobson,[3] and R. J. Warmack,[1] "Immobilization of Deoxyribonucleic Acid for Scanning Probe Microscopy," *Proc. Natl. Acad. Sci. USA* **1992**, *89*, 10129.

H. F. Arlinghaus,[4] N. Thonnard,[4] M. T. Spaar,[4] R. A. Sachleben, G. M. Brown, R. S. Foote,[3] F. V. Sloop,[3] J. R. Peterson,[3] and K. B. Jacobson,[3] "Comparison of Sputter-Initiated Resonance Ionization Spectroscopy and Laser Atomization Resonance Ionization Spectroscopy to Localize Tin-Labeled Deoxyribose Nucleic Acid," *J. Vac. Sci. Technol.* **1991**, *A9*, 1312.

L. A. Bottomley,[2] J. N. Haseltine,[2] D. P. Allison,[1] R. J. Warmack,[1] T. Thundat,[1] R. A. Sachleben, G. M. Brown, R. P. Warmack,[1] K. B. Jacobson,[3] T. L. Ferrell,[1] and J. J. Schrick,[3] "Scanning Tunneling Microscopy of DNA: The Chemical Modification of Gold Surfaces for Immobilization of DNA," *J. Vac. Sci. Technol.* **1992**, *A 10*, 591.

G. M. Brown, D. P. Allison,[1] R. J. Warmack,[1] K. B. Jacobson,[3] F. W. Larimer,[3] R. P. Woychik,[3] and W. L. Carrier,[3] "Electrochemically Induced Adsorption of Radio-Labeled DNA on Gold and HOPG Substrates for STM Investigations," *Ultramicroscopy* **1991**, *38*, 253.

R. A. Sachleben, G. M. Brown, F. V. Sloop,[3] H. F. Arlinghaus,[4] M. W. England,[1] R. S. Foote,[3] F. W. Larimer,[3] R. P. Woychik,[3] N. Thonnard,[4] and K. B. Jacobson,[3] "Resonance Ionization Spectroscopy Multiplex Sequencing of Tin-Labeled DNA," *Genetic Analysis Techniques and Applications* **1991**, *8*, 167.

F. V. Sloop,[3] G. M. Brown, R. S. Foote,[3] K. B. Jacobson,[3] and R. A. Sachleben, "Synthesis of TESPA: An Organotin Mass Label for DNA," *Bioconjug. Chem.* (in press).

T. D. Thundat,[1] D. P. Allison,[1] R. J. Warmack,[3] G. M. Brown, K. B. Jacobson,[3] J. J. Schrick,[3] and T. L. Ferrell,[1] "Atomic Force Microscopy of DNA on Mica and Chemically Modified Mica," *Scanning Microscopy* **1992**, *6*, 911.

PRESENTATIONS

G. M. Brown, M. L. Garrity,[5] and R. A. Sachleben, "Lanthanide Complexes of Bifunctional Chelating Agents," Symposium on *Molecular Design and*

Bioinorganic Chemistry, American Chemical Society National Meeting, San Francisco, CA, April 5-10, 1992.

G. M. Brown, M. L. Garrity,[5] R. A. Sachleben, and T. J. Sworski,[6] "Reversible Energy Transfer between Naphthalene and Terbium(III) in Complexes of Multidentate Chelating Agents," American Chemical Society National Meeting, Washington, DC, August 23-28, 1992.

G. M. Brown, M. L. Garrity,[5] J. E. Elbert,[5] R. A. Sachleben, F. V. Sloop,[3] M. J. Doktycz,[3] and K. B. Jacobson,[3] "Luminescent Lanthanide Ion Complexes as Labels for DNA Sequencing and Mapping," DOE Genome Program Contractor-Grantee Meeting, Santa Fe, NM, Fev. 7-11, 1992.

G. M. Brown, T. Thundat,[1] D. P. Allison,[1] R. J. Warmack,[1] and T. L. Ferrell,[1] "Electrochemical and *in situ* AFM-STM Investigations of Titanium in Oxalic Acid Solution," 38th Meeting of the American Vacuum Society, Seattle, WA, November 11-15, 1991.

---

1. ORNL Health and Safety Research Division.
2. Georgia Institute of Technology, Atlanta, GA.
3. ORNL Biology Division.
4. Atom Sciences, Inc., Oak Ridge, TN.
5. ORAU/ORNL Postdoctoral program.
6. ORNL, retired.

SPECIAL TOPICS

PUBLICATIONS

G. M. Brown, T. Thundat,[1] D. P. Allison,[1] and R. J. Warmack,[1] "Electrochemical and *in situ* AFM-STM Investigations of Titanium in Oxalic Acid Solution," *J. Vac. Sci. Technol.* **1992**, *A 10*, 3001.

E. Caponetti,[2] A. Lizzio,[2] R. Triolo,[2] W. L. Griffith, and J. S. Johnson, Jr.,[3] "Alcohol Partition in a Water-in-Oil Microemulsion from Small-Angle Neutron Scattering," *Langmuir* **1992**, *8*, 1554.

A. L. Compere and W. L. Griffith, "The U.S. Calutron Program for Uranium Enrichment: History, Technology, Operations, and Production," *Oak Ridge National Laboratory Report*, ORNL-5928, **1991**.

W. L. Griffith, A. L. Compere, J. M. Googin,[4] and W. P. Huxtable,[5] "Aluminum Nitrate Recrystallization and Recovery from Liquid Extraction Raffinates," *Oak Ridge National Laboratory Report*, ORNL/TM-11471, **1991**.

W. L. Griffith, A. L. Compere, J. M. Googin,[4] and W. P. Huxtable,[5] "Reducing Emissions from Uranium Dissolving," *Oak Ridge National Laboratory Report*, ORNL/TM-12211, **1992**.

W. P. Huxtable,[5] A. L. Compere, W. L. Griffith, and J. M. Googin,[4] "Process Waste Minimization Opportunities at the Y-12 Plant," *Martin Marietta Energy Systems Report*, Y/EN-4841, 1993.

PRESENTATIONS

G. M. Brown, T. Thundat,[1] D. P. Allison,[1] R. J. Warmack,[1] and T. L. Ferrell,[1] "Electrochemical and *in situ* AFM-STM Investigations of Titanium in Oxalic Acid Solution," 38th Meeting of the American Vacuum Society, Seattle, WA, November 11-15, 1991.

---

1. ORNL Health and Safety Research Division.
2. University of Palermo, Italy.
3. ORNL, retired.
4. Y-12 Development Division.
5. ORNL Engineering Division.

FUNDING SUMMARY
April 1, 1993

Funding Source	Budget ($K)
DOE PROGRAMS	
Office of Basic Energy Sciences	
Chemical Sciences	5099
Materials Sciences	2786
Geosciences	930
	8815
Other DOE	
Conservation/Renewables	625
Defense Programs	790
Env Restor/Waste Mgmt	440
Other	350
	2205
WORK FOR OTHERS PROGRAMS	
Department of Defense	400
EPRI	150
	550
ORNL LDRD PROGRAM	145
TOTAL PROGRAMS	11715

CHEMISTRY DIVISION
April 1, 1993

M. L. POUTSMA, DIRECTOR
C. J. Steele

J. P. HALL*, ADMINISTRATIVE ASSISTANT
F. J. SMITH, ENVIRONMENTAL, SAFETY, AND HEALTH COORDINATOR

C. E. BAMBERGER*, TECHNOLOGY TRANSFER OFFICER
P. F. BRITT*, SEMINAR COMMITTEE CHAIRMAN
M. N. BURNETT*, COMPUTER SECURITY OFFICER
J. K. GIBSON*, LASER SAFETY OFFICER
J. P. HALL*, AFFIRMATIVE ACTION COORDINATOR AND UNITED WAY COORDINATOR
E. JOHNSON*, QUALITY ASSURANCE COORDINATOR AND ASSISTANT AFFIRMATIVE ACTION COORDINATOR
M. H. LIMBURG (b), MATERIALS REQUISITIONER
T. S. REAGAN (a), FINANCE OFFICER
J. A. SCIRCLE (c), RADIATION CONTROL OFFICER

AQUEOUS CHEMISTRY, GEOCHEMISTRY, SEPARATIONS CHEMISTRY, AND POLYMER SCIENCE

R. E. MESMER*, SECTION HEAD
L. R. Pyles

HIGH TEMPERATURE/PRESSURE AQUEOUS CHEMISTRY

R. E. MESMER*, GROUP LEADER
P. C. Ho
H. F. Holmes
D. A. Palmer
J. M. Simonson
R. W. Carter (f)
R. C. Moore (f)
M. R. Narkhede (f)
H. R. Corti (d)
K. E. Hyde (d)
C. Nguyen-Trung (d)
C. S. Oakes (e)

GEOCHEMISTRY

D. J. WESOLOWSKI, GROUP LEADER
J. G. Blencoe
D. R. Cole
J. L. Bell (f)
T. E. Burch (f)
J. Horita (f)
D. B. Joyce (f)
S. E. Drummond (d)
T. H. Giordano (d)
D. L. Hamilton (d)
I. J. Richards (e)
J. C. Seitz (e)

SPECIAL PROJECTS

C. K. JOHNSON
M. N. Burnett*
J. W. Terry

CONSERVATION PROGRAMS

A. L. Compere
W. L. Griffith
V. Krishnan (e)

STRUCTURE AND DYNAMICS OF POLYMERS

GROUP LEADER (VACANT)
B. K. Annis
A. Habenschuss
D. W. Noid
B. G. Sumpter
B. Wunderlich (g)
J. Cheng (f)
Y. Fu (f)
C. Getino (f)
Y. Jin (f)
J. D. Londono (f)
C. E. Wozny (f)
A. Xenopoulos (f)
A. Boller (e)
W. Chen (e)
S. V. Gerdes (e)
G. Liang (e)
M. T. Spiming (e)
Q. Wang (e)

SEPARATIONS CHEMISTRY

B. A. MOYER, GROUP LEADER
G. M. Brown
J. H. Burns
R. A. Sachleben
Z. Chen (f)
Y. Deng (f)
J. E. Elbert (f)
Y. Sun (f)
S. D. Alexandratos (d)
L. H. Delmau (e)
J. L. Driver (h)
K. M. Kelly (e)
A. A. Kriger (e)

ORGANIC, INORGANIC, TRANSURANIUM, AND CATALYTIC CHEMISTRY

L. M. FERRIS*, SECTION HEAD
K. E. Elliott
F. S. Keith (b)
R. G. Violet

ORGANIC CHEMISTRY AND CHEMISTRY OF FOSSIL FUELS

A. C. BUCHANAN, GROUP LEADER
P. F. Britt*
E. W. Hagaman
F. M. Schell (b)
K. B. Thomas
S-K. Lee (f)
G. W. Kabalka (d)
E. A. Malcolm (h)
M. C. Woody

PHOTOCHEMISTRY

R. T. Dabestani
M. E. Sigman
E. A. Chevis (h)

HETEROGENEOUS CATALYSIS

S. H. OVERBURY, GROUP LEADER
F. A. Grimm (b)
D. R. Huntley
D. R. Mullins

TRANSURANIUM ELEMENT CHEMISTRY

L. M. FERRIS*, ACTING GROUP LEADER
J. K. Gibson*
R. G. Haire (i)
E. Johnson*
M. O. Krause
J. R. Peterson (b)
G. Chen (f)
M. Gensini (f)
N. A. Stump (f)
J. E. Bloor (d)
J. J. Fuger (d)
A. Maeda (d)
S. E. Nave (d)
N. E. Bores (e)
J. B. Burns (e)
C. L. Kay (e)
L. L. Pesterfield (e)
S. S. Shoup (e)

INORGANIC CHEMISTRY OF ADVANCED MATERIALS

GROUP LEADER (VACANT)
C. E. Bamberger*
J. Brynestad
L. Maya
C. E. Vallet
T. J. Haverlock (h)
D. E. Heatherly

LEGEND: *DUAL CAPACITY
(a) ON LOAN FROM F&BM DIVISION
(b) PART-TIME EMPLOYEE
(c) ON LOAN FROM ORP
(d) VISITING SCIENTIST
(e) STUDENT GUEST
(f) POSTDOCTORAL GUEST
(g) UT/ORNL DISTINGUISHED SCIENTIST
(h) SUBCONTRACTOR EMPLOYEE
(i) HEAD, TRANSURANIUM ELEMENT RESEARCH

APPROVED: M. L. POUTSMA

ORNL-6756
Distribution Category UC-4

INTERNAL DISTRIBUTION

1. Biology Library
2-3. Central Research Library
4. ORNL Patent Office
5. ORNL Y-12 Technical Library Document Reference Section
6-8. Laboratory Records Department
9. Laboratory Records, ORNL R.C.
10-12. Technical Publications Department, ORNL
13. B. R. Appleton
14. J. B. Ball
15. C. E. Bamberger
16. B. A. Berven
17. A. C. Buchanan
18. R. S. Carlsmith
19. D. F. Craig
20. J. L. Dippo
21. R. E. Fenstermaker, Jr.
22-26. L. M. Ferris
27. R. K. Genung
28. H. A. Glovier
29. A. Habenschuss
30. R. G. Haire
31. F. C. Hartman
32. R. A. Hawsey
33. R. B. Honea
34. C. K. Johnson
35. J. K. Johnson
36-40. R. E. Mesmer
41. B. A. Moyer
42. S. H. Overbury
43-143. M. L. Poutsma
144. J. B. Roberto
145. M. J. Saltmarsh
146. J. Sheffield
147. W. D. Shults, II
148. V. J. Tennery
149. A. W. Trivelpiece
150. R. I. Van Hook, Jr.
151. R. C. Ward
152. D. A. Waters
153. D. J. Wesolowski
154. B. Wunderlich

EXTERNAL DISTRIBUTION

155. Office of the President, Electric Power Research Institute, P. O. Box 10412, 3412 Hillview Avenue, Palo Alto, CA 94303
156. J. R. Peterson, Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600
157. P. L. Johnson, Executive Director, Oak Ridge Associated Universities, P. O. Box 117, Oak Ridge, TN 37831
158. L. C. Ianniello, Director, Office of Basic Energy Sciences, DOE, Washington, DC 20545
159. C. B. Harris, Molecular and Materials Sciences Division, LBL, Berkeley, CA 94720
160. L. M. Stock, Chemistry Division, ANL, 9700 South Cass Avenue, Argonne, IL 60439
161. N. Sutin, Chairman, Chemistry Department, BNL, Upton, NY 11973
162. Gleb Mamantov, Head, Chemistry Department, University of Tennessee, Knoxville, TN 37916
163. W. S. Millman, Division of Chemical Sciences, Office of Basic Energy Sciences, DOE, GTN, Washington, DC 20545
164. W. Wiley, Director, PNL, Richland, WA 99352
165. Director, Chemical Technology Division, ANL, 9700 South Cass Avenue, Argonne, IL 60439
166. John L. Burnett, Division of Chemical Sciences, Office of Basic Energy Sciences, DOE, Washington, DC 20545

167. Office of Assistant Manager for Energy Research and Development, DOE-ORO
168. A. Schriesheim, Director, ANL, 9700 South Cass Avenue, Argonne, IL 60439
169. F. D. Stevenson, Division of Chemical Sciences, Office of Basic Energy Sciences, DOE, GTN, Washington, DC 20545
170. W. Luth, Division of Engineering and Geosciences, Office of Basic Energy Sciences, DOE, Washington, DC 20545
171. Oak Ridge Associated Universities, MERT Division Library, P. O. Box 117, Oak Ridge, TN 37831
172. R. S. Marianelli, Division of Chemical Sciences, Office of Basic Energy Sciences, DOE, GTN, Washington, DC 20545
173. A. Laufer, Division of Chemical Sciences, Office of Basic Energy Sciences, DOE, Washington, DC 20545
174. R. T. Chung, DOE-ORO, Oak Ridge, TN 37831
175. I. L. Thomas, Division of Materials Sciences, Office of Basic Energy Sciences, DOE, GTN, Washington, DC 20545
176. Beth Jinkerson, Oak Ridge Associated Universities, University Programs Division, P. O. Box 117, Oak Ridge, TN 37831
177. J. S. Coleman, Division of Engineering, Mathematical and Geosciences, Office of Basic Energy Sciences, DOE, Washington, DC 20545
178. M. J. Reed, Division of Geothermal Technology, Office of Energy Efficiency and Renewable Energy, DOE, Washington, DC 20545
179. S. Butter, Division of Chemical Sciences, Office of Basic Energy Sciences, DOE, Washington, DC 20545
180. R. Kelley, Division of Materials Sciences, Office of Basic Energy Sciences, DOE, Washington, DC 20545

181-282. Given distribution as shown in TID-4500 under Chemistry Category (25 copies - NTIS).

283. Professor Jerome L. Duggan, University of North Texas, P.O. Box 5368, Denton, TX 76203
284. Dr. Martin Bakker, Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487
285. P. S. Braterman, Chair, Department of Chemistry, University of North Texas, P.O. Box 5068, Denton, TX 76203
286. D. H. Lester, Hoechst Celanese Commercial Development, Fibers and Film Group, Hoechst Celanese Corporation, P.O. Box 32414, Charlotte, NC 28232
287. C. R. Yonker, Division of Chemical Sciences, Office of Basic Energy Sciences, DOE, Washington, DC 20545
288. Dr. José-Luis Boldú, Secretary for the Coordination of Science, Instituto de Física, Universidad Nacional Autonoma de Mexico, Apartado Postal 20-364, 01000 Mexico, D.F.
289. Dr. Marcos Rosenbaum, Director, Instituto de Ciencias Nucleares, Universidad Nacional Autonoma de Mexico, Circuito Exterior, Ciudad Universitaria, Delgación Coyoacán, Apartado Postal 70-360, 04510 Mexico D.F.
290. Office of Assistant Manager for Energy Research and Development, U.S. Department of Energy, Oak Ridge Operations, P.O. Box 2001, Oak Ridge, TN 37831-8600

DATE
FILMED
11/15/93

END