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RESEARCH ACTIVITIES IN THE FIELD OF MATERIALS  
SCIENCE

North Carolina University  
Chapel Hill, North Carolina

June 1967

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**Annual Technical Report**  
**on**  
**Materials Research**  
**at**  
**The University of North Carolina**

**July 1, 1966 to June 30, 1967**

**Materials Research Center**  
**University of North Carolina**  
**Chapel Hill**



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THE UNIVERSITY OF NORTH CAROLINA

Chapel Hill, North Carolina

TECHNICAL PROGRESS REPORT

for the period

1 July 1966 - 30 June 1967

on

Research Activities in the Field of Materials Science

supported by the

Advanced Research Projects Agency  
Department of Defense  
under Contract SD-100

as well as the

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Alfred P. Sloan Foundation  
American Cancer Society  
Army Research Office (Durham)  
Atomic Energy Commission  
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North Carolina Board of Science & Technology  
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## I. Introduction.

This report comprises brief summaries of materials research projects at the University of North Carolina at Chapel Hill for the year ending 30 June 1967. It is submitted to the Advanced Research Projects Agency, in accordance with the terms of Contract SD-100, but includes descriptions of materials work supported by other agencies, including the following agencies of the United States Government.

Air Force Office of Scientific Research  
Army Research Office (Durham)  
Atomic Energy Commission  
National Institutes of Health  
National Science Foundation  
United States Public Health Service

The following pages contain brief reports of progress in the various individual research programs active during the period July 1966 - June 1967. They are arranged by Academic Departments and Schools, and within departments alphabetically by the name of the principal investigator.

During 1966-67 the Materials Research Center, which was established in order to broaden the base of the materials program at the University of North Carolina, extended support for the first time to research in several departments other than Physics and Chemistry. A total of five investigators in the Departments of Biochemistry, Bioengineering and Biomathematics, Dental Materials, Geology, and Surgery were given support for materials-related research.

The Executive Committee of the Materials Research Center consists (June 1967) of the following members:

James H. Crawford, Jr., Physics Department  
R. C. Jarnagin, Chemistry Department  
W. F. Little, Chemistry Department  
L. M. Slifkin, Physics Department  
D. F. Taylor, School of Dentistry

Except for Dr. Crawford, who replaced Dr. E. Merzbacher in February 1967 on assuming the Chairmanship of the Physics Department, the Executive Committee remained unchanged from the previous year.

Faculty Member: James P. Collman  
Professor of Chemistry

Research Associates: P. W. Schneider  
J. W. Hosking

Graduate Students: F. Vastine  
J. Y. Sun  
M. F. Sullivan  
E. Kimura  
P. Slagen

ARPA-Supported Students: F. Vastine  
J. Y. Sun  
M. F. Sullivan

Degrees Granted: Ph.D.: F. Vastine  
J. Y. Sun  
E. Kimura  
P. Slagen

Other Supporting Agencies: National Science Foundation  
National Institutes of Health  
Alfred P. Sloan Foundation

Summary of Research Activity:

(1) Chemistry of  $d^8$  Complexes

The scope, mechanisms and stereochemistry of oxidative-addition reactions of  $d^8$  complexes have been explored and a review of the subject has been written. The relevance of these reactions to the mechanisms of homogeneously catalyzed organic reactions is now evident. The relationship between oxidative-addition reactions of  $d^8$  and  $d^{10}$  complexes has become clear. The latter have not yet been fully explored. The mechanism by which an iridium complex of molecular nitrogen is formed has been thoroughly elucidated - by identifying the intermediate steps of the reaction and by studying the reaction kinetics. The synthesis and chemistry of molecular nitrogen complexes are a part of the important subject of nitrogen fixation.

A new class of transition metal promoted reactions has been discovered. This subject has been designated "metal promoted atom transfer redox reaction." This represents a very large field of



chemistry, most of which remains to be explored. The most significant aspect of this work involves reactions of metal complexes containing molecular oxygen. Coordinated oxygen has been found to be a potent kinetic oxidizing agent. Organic substrates and inorganic gases are rapidly and selectively oxidized by such complexes. Catalytic oxidations have been achieved, and the potential of this to chemical synthesis is very great indeed.

A new class of complexes termed metalocycles has been uncovered. The chemistry of these compounds, which contain five-membered rings with two olefinic groups and a transition metal, has yet to be fully explored. These complexes have been shown to be the intermediates in the cyclic trimerization of acetylenes to form aromatic rings.

A new reaction whereby peptide bonds are formed through the interaction of coordinated amino acid esters and the N-terminal amino groups of other amino acids of peptides has been discovered and the qualitative features of the mechanism have been elucidated. A series of complexes of cobalt(III) containing coordinated peptide groups have been isolated and thoroughly characterized. The mechanism of the reaction previously discovered in this laboratory whereby N-terminal acid residues are hydrolyzed from peptide bonds through the intermediacy of cobalt(III) complexes has now been elucidated. New tetradentates containing four amino groups and three amino and one carboxyl group have been prepared and a series of their cobalt(III) complexes examined.

Crystals containing inorganic complexes which interact so as to form solid state intermetallic polymers have been shown to behave as highly anisotropic intrinsic semiconductors, the principal axis of conduction being coincident with the axis of the metal-metal bonds. Photoconductivity studies on these complexes have been used to estimate the mobility of the principal charge carriers - electrons. The fine structure associated with these photoconductivity spectra have been ascribed to vibronic coupling with harmonics of the principal stretching modes of carbon monoxide ligands attached to the

metal chain.

Publications:

"Acetylene Complexes of Iridium and Rhodium," J. Am. Chem. Soc. 88, 844 (1967), with J. W. Kang.

"The Mechanism of the Formation of an Iridium Complex of Molecular Nitrogen," J. Am. Chem. Soc. 89, 169 (1967), with M. Kubota, J. Y. Sun, and F. Vastine.

"Metal Ion Facilitation of Atom Transfer Redox Reactions," J. Am. Chem. Soc. 89, 4809 (1967), with M. Kubota and John Hosking.

"Sequential Synthesis of Iridium and Rhodium Metalloacycles of Acetylene," Third International Symposium on Organometallic Chemistry, Munich, August 28, 1967; Abstracts p. 334, with J. W. Kang, W. F. Little, and M. F. Sullivan.

"Stereochemistry of Oxidative Addition Reactions of Iridium(I) Complexes," Inorg. Chem. 7, in press (1968), with C. T. Sears, Jr.

"Penta-Coordinate Iridium(I) Complexes Derived from Metal Carbonyl Anions," J. Am. Chem. Soc. 90, in press (1968), with F. D. Vastine and W. R. Roper.

"Oxidative-Addition Reactions of  $d^8$  Complexes," in Advances in Organometallic Chemistry, Ed. F. G. A. Stone and R. West, Vol. 7, Academic Press, in press, (1968) with W. R. Roper.

"Hydrolysis of N-Terminal Peptide Bonds by Hydroxy(aquo)triethylenetetraminecobalt(III) Ions," J. Am. Chem. Soc. 89, 1082 (1967), with D. A. Buckingham, A. Happer, and L. Marzelli.

"The Formation of Peptide Bonds in Coordination Sphere of Cobalt(III)," J. Am. Chem. Soc. 89, in press (1967), with E. Kimura.

Faculty Member: Henry H. Dearman  
Associate Professor of Chemistry

Research Associates: K. Akasaka  
K. Ishizu  
Frank T. Lang

Graduate Students: David Baker  
Henry Drott  
John Flowers  
Alice C. Ho  
William Huggins  
David Kellogg  
Jean Pearson  
Jerry C. Smith

ARPA-Supported Students: Henry Drott  
Alice Ho

Degrees Granted:

Other Supporting Agencies: National Science Foundation  
National Institutes of Health

Summary of Research Activity:

(1) Spectroscopy and Photochemistry of Organic Molecules

We are attempting to relate the photochemical activity of conjugated organic molecules with electronic structure. The anthraquinone system has received the majority of our attention. The electronic structure of anthraquinone has been investigated experimentally by the determination of the polarization of transitions from the ground to excited electronic states. Results have permitted assignment of the lowest triplet and three low energy singlet states of this molecule. A model which accounts for the order of the singlet  $\pi-\pi^*$  states in terms of intramolecular exciton interactions predicts the existence of several "hidden" states. Evidence for existence of these states is being sought by chemical substitution and by the use of magnetic circular dichroism spectroscopy.

Publications:

"Polarization of the T  $\leftrightarrow$  S Transition in 9,10-Anthraquinone,"  
J. Chem. Phys. 45, 4363 (1966), with N. Sundarachari and D. Ulkü.

"The Binding of N-Methyl Pehnazinium Cations to DNA," Science 154,  
421 (1966), with K. Ishizu, M. T. Huang and J. R. White.

Faculty Member: William E. Hatfield  
Associate Professor of Chemistry

Research Associates: Robin Whyman  
Derek B. Copley

Graduate Students: Fred L. Bunger  
William E. Parker  
Judith Crissman  
Peter Nassiff  
Arthur F. Eidson  
Marshall Millman  
Guy Inman  
James Barnes

ARPA-Supported Students: William E. Parker  
Peter Nassiff (summer only)

Degrees Granted:

Other Supporting Agencies: National Science Foundation  
American Cancer Society

Summary of Research Activity:

(1) Spin-Spin Coupling in Binuclear Complexes

The magnetic and spectral properties of 1:1 and 1:2 copper(II) halide complexes with substituted quinoline N-oxides have been investigated. The condensed complexes may be divided into three types based on these properties and dependent upon the donor characteristics of the ligands, as measured by their  $pK_a$  values. Members of the first class, containing ligands of relatively high  $pK_a$ 's display the subnormal magnetic moments typical of the pyridine N-oxide-copper(II) halide systems. Complexes derived from ligands of low  $pK_a$  values constitute the second class, and the third is formed by species of empirical formula  $(CuCl_2)_m L_n$ , where  $1 \leq m/n \leq 2$ , containing ligands of intermediate  $pK_a$ 's. Both of these types exhibit normal magnetic moments. The differences in magnetic behavior are correlated with a change in structure from oxygen-bridged to halogen-bridged entities, a conclusion which is supported by infrared evidence for the chlorides. The

1:2 complexes all display normal magnetic moments which are temperature independent.

A complete one-electron energy level diagram has been constructed for  $\text{CuCl}_2 \cdot 2\text{C}_6\text{H}_5\text{NO}$  and  $((\text{C}_6\text{H}_5\text{NO})\text{CuCl}_2)_2$ , using the Wolfsberg-Helmholz approximation. Reasonable values for the parameters involved in these calculations were determined by fitting the bands in the spectrum of the monomer to an energy level diagram. The same set of parameters were then used in the treatment of the binuclear complex in an attempt to explain the interaction that takes place between the unpaired electrons on the two adjacent copper atoms.

The one-electron calculation gave rise to a degenerate ground state which included three singlet spin-states and one triplet spin-state. Coulomb and exchange interactions still predicted a triplet ground state in accord with Hund's rule, but the inclusion of first order configuration interaction caused the doubly degenerate excited singlet state to split. These interactions predicted a singlet-triplet splitting in agreement with the value determined by magnetic studies. No attempt was made to account for the band system at  $11,350 \text{ cm}^{-1}$ , but it is suggested that this band arises from molecular transitions to states which result from configuration interaction in degenerate excited singlet states, and from electronic transitions which may be thought of as being located on individual metal ions.

## (2) Structural Variations and Bonding Trends in Transition Metal Complexes

A model has been developed for the estimation of ionicities in molecules and complex ions which utilize the minimization of total energy by the method of differential ionization energies. The effect of Madelung corrections to the energies were investigated, and the results refined by an evaluation of a covalent bond energy.

In the mechanics of the Wolfsberg-Helmholz calculations, it is found that the Madelung corrections make the metal ionization energy curves less steep and the ligand ionization energies nearly invariant with charge. This creates a situation which has previously been artificially imposed by selecting the ligand ionization energies to give desirable terms in the secular determinants. The effect of Madelung energy was shown to be the primary influence in determining the ionicity while covalent bonding effects are secondary when the ligands and the central atom have fairly different electronegativities.

Publications:

"Spin-Spin Coupling in Binuclear Complexes. III. The Magnetic Properties of Copper Salts of Substituted Benzoic Acids," *Inorg. Chem.* 5, 1855 (1966), with Carol S. Fountain and Robin Whyman.

"Influence of Madelung (Interatomic Coulomb) Energy on Wolfsberg-Helmholz Calculations," *International J. Quantum Chem.* 1, 191 (1967), with Chr. Klíxbull Jørgensen, Sally M. Horner, and S. Y. Tyree.

"Spin-Spin Coupling in Binuclear Complexes. IV. Heterocyclic N-Oxide Complexes of Copper(II) Halides. III. Magnetic and Spectral Properties of Complexes with Substituted Quinoline N-Oxides," *J. Am. Chem. Soc.* 89, 3135 (1967), with Robin Whyman and Derek B. Copley.

Faculty Member: Richard G. Hiskey  
Professor of Chemistry

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Sandra Boatman

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W. C. Jones, Jr.  
V. G. Matl  
Ronald Meck  
J. D. Morrisett  
W. G. Rhodes  
M. E. Safdy  
J. N. Smith  
J. T. Sparrow  
A. M. Thomas  
R. A. Upham  
A. S. Vanek  
B. F. Ward  
E. B. Williams

ARPA-Supported Students: J. T. Sparrow (October 1, 1966 to December 31, 1966)

Degrees Granted: M.S.: A. S. Vanek  
Ph.D.: M. A. Harpold

Other Supporting Agencies: National Institutes of Health

Summary of Research Activity:

(1) Conformational Stability of Synthetic Polypeptides.

The objective was to obtain polymers containing specific sequences of amino acids and to study the helicity of these molecules as a function of the side-chain substituent.

The projected synthetic scheme involves the stepwise formation of several tripeptides containing a L-glutamyl-L-glutamyl sequence. The side-chain of the third unit would be varied



from alanine (R=CH<sub>3</sub>-) to valine [R=(CH<sub>3</sub>)<sub>2</sub>CH-] to phenylalanine (R=C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-). Homopolymerization of the tripeptides would provide the desired sequence polymers. Helicity studies would be carried out by tetration of the glutamic acid side-chains.

The tripeptide L-glutamyl-L-glutamylglycine has been synthesized and polymerized. The synthesis of a versatile intermediate N-carbobenzoxy-L-glutamyl-L-glutamic 8-t-butyl ester has been realized in good yield. Conditions for the polymerization of the tripeptide esters have also been examined.

Publications:

"Sulfur Containing Polypeptides. II. Selective Removal of S-Protective Groups from Some L-Cysteinyl-L-Cysteine Derivatives," J. Org. Chem. 31, 1188 (1966), with Tomishigr Mizoguchi and Hiroshi Igeta.

"Sulfur Containing Polypeptides. III. S<sub>N</sub> Benzoyl Group Migration in Cysteine Derivatives," J. Org. Chem. 31, 1192 (1966), with Tomishigr Mizoguchi and Toshishigr Iniu.

"Sulfur Containing Polypeptides. IV. Synthetic Routes to Cysteine Peptides," J. Org. Chem. 31, 2178 (1966), with John B. Adams, Jr.

"Sulfur Containing Polypeptides. V. Studies on N-(2-Hydroxyarylidene) and Enamine Protective Groups," J. Org. Chem. 31, 3501 (1966), with George L. Southard.

"Chemistry of Aliphatic Disulfides. XII. Synthesis of Unsymmetrical Open-Chain Cystine Derivatives," J. Org. Chem. 32, 97 (1967), with Tomishigr Mizoguchi and Edward L. Smithwick, Jr.

"Sulfur Containing Polypeptides. VI. Stability Studies on Unsymmetrical Open-Chain Cystine Derivatives," J. Am. Chem. Soc. 89, 437(1967), with Edward L. Smithwick, Jr.

"A Novel Synthesis of 1,1-Dimethyl-3,3-diphenylindan," J. Org. Chem. 32, 1986(1967), with M. A. Harpold.

"S-Benzhydryl L-cysteine," Biochemical Prep. 12, 38(1967), with J. B. Adams, Jr.

"Chemistry of Aliphatic Disulfides. XIII. Formation of Unsymmetrical Disulfides from S-Benzhydryl Thioethers," Tetrahedron 23, 3923 (1967), with M. A. Harpold.

"Sulfur-Containing Polypeptides. VII. Synthesis of S-Trityl-L-Cysteine Peptides Using Acid-Labile Amino and Carboxy Protective Groups," J. Org. Chem. 32, 2772 (1967), with J. T. Staples and R. L. Smith.

"Chemistry of Aliphatic Disulfides. XIV. The Preparation of Disulfide Sulfoxides by Selective Oxidation," J. Org. Chem. 32, 3191 (1967), with M. A. Harpold.

"Chemistry of Aliphatic Disulfides. XV. Bis-Disulfide Peptide Derivatives," J. Org. Chem. 33, 0000 (1968), in press, with M. A. Harpold.

"Chemistry of Aliphatic Disulfides. XVI. Studies on the Alkoxide Cleavage of 1,6-Diphenyl-3,4-dithia-1,6-hexanedione," J. Org. Chem. 33, 0000 (1968), in press, with A. J. Dennis.

Faculty Member: Richard C. Jarnagin  
Professor of Chemistry

Research Associates: Peter Fielding  
Klass de Groot

Graduate Students: Robb Cobb  
Lee P. Gary, Jr.  
Nathan Houser  
Louis Powell  
Peter Holzman

ARPA-Supported Students: Louis Powell  
Peter Holzman  
Lee P. Gary, Jr.

Degrees Granted: Ph.D.: Louis Powell

Other Supporting Agencies: Army Research Office (Durham)  
National Science Foundation

Summary of Research Activity:

- (1) Nature of Charge Transport in Organic Substances (with M. Silver)
- Triplet-triplet interactions have been shown to lead directly to production of current carriers in solutions of aromatic hydrocarbons. A complete kinetic analysis has been made which is consistent with all of our results to date. The yield of carriers is proportional to  $\exp[-e^2/\epsilon kTR_0]$  where  $R_0$  is the intermolecular distance between two nearest neighbors. Confirming measurements have been made as a function of dielectric constant of the medium and triplet concentration.

Calculations have been made correlating ion mobilities to the apparent size of the ion and the viscosity of the medium. Using a simple criterion relating the apparent radius of the ion to the electrostatic energy contained in the field, very good agreement for large dielectric constant solvents is obtained.

Publications:

Faculty Member: Donald C. Jicha  
Associate Professor of Chemistry

Research Associates:

Graduate Students: Mary S. Fowier  
Robert Lovell  
Louis J. Rivela

ARPA-Supported Students: Robert Lovell

Degrees Granted: M.S.: Louis J. Rivela

Other Supporting Agencies: Petroleum Research Fund

Summary of Research Activities:

(1) Platinum Metal Complexes of  $\text{GeCl}_3^-$  and  $\text{GeCl}_2$

A number of novel compounds containing platinum metal-germanium bonds have been prepared by the interaction of trichlorogermane with appropriate platinum metal salts in methanol saturated with hydrogen chloride. Salts of stable four and five coordinate complexes of platinum(II), palladium(II), and rhodium(I) have been isolated with 2, 3, 4, and 5  $\text{GeCl}_3^-$  groups in the coordination sphere. Except for the ion  $\text{Pt}(\text{SnCl}_3)_5$ , the species  $\text{Rh}(\text{GeCl}_3)_5^{-4}$ ,  $\text{Pt}(\text{GeCl}_3)_5^{-3}$ , and  $\text{Pd}(\text{GeCl}_3)_5^{-3}$  represent the only known examples of five coordinate complexes of these metal ions with inorganic ligand systems. By the application of synthetic techniques conducive to the formation of complex acids, additional complex anions, not isolatable as complex salts, have been identified. The most notable of these,  $\text{H}_2[(\text{GeCl}_3)_2\text{Rh}(\text{GeCl}_2)_2\text{Rh}(\text{GeCl}_3)_2]$ , has been formulated as a  $\text{GeCl}_2$ -bridged dimer. Support for the existence of  $\text{GeCl}_2$ -bridging groups in this species has been provided by the isolation of the compound  $[(\text{CO})(\text{GeCl}_3)\text{Rh}(\text{GeCl}_2)_2\text{Rh}(\text{GeCl}_3)(\text{CO})]$  and the bridge-cleavage products formed by the addition of hydrogen chloride to methanol solutions of these compounds. The coordinated  $\text{GeCl}_3^-$  ion undergoes solvolysis reactions with a number of hydroxylated compounds with full retention of the metal-germanium bonds. This behavior is of

particular interest in view of the complete reversibility of these reactions in methanol saturated with hydrogen chloride gas. A comparison of the ligand behavior of the  $\text{GeCl}_3^-$  ion with that reported for  $\text{SnCl}_3^-$ , with the metal ions considered, reveals some marked differences which may be applicable to other transition metal ions. In this connection, the ligand behavior of  $\text{GeCl}_3^-$  and  $\text{GeCl}_2$  toward other heavy transition metals and the reactions of these compounds with hydroxylated substances is presently under investigation.

(2) Reactions of Halophosphine Complexes of Nickel(0) with Selected Hydroxylated Compounds

The hitherto unknown reactions of  $\text{NiL}_4$  (where  $\text{L} = \text{C}_6\text{H}_5)_2\text{PCl}$ ,  $(\text{C}_6\text{H}_5)\text{PCl}_2$ , or  $\text{PCl}_3$ ) with hydroxylated compounds has been investigated for phenylboric acid and boric acid. Although the proper experimental conditions for the formation of reaction products, in which the integrity of the complex moiety is preserved, is hampered by the great instability of the  $\text{NiL}_4$  species in solvent systems, low-temperature melts of the two reactants has resulted in the isolation of stable complexes. The characterization of the major product formed from  $[\text{Ni}(\text{C}_6\text{H}_5)_2\text{PCl}]_4$  and either hydroxylated compound confirms the existence of a 2:1 boric acid adduct in which the nickel atom has been oxidized to the divalent state. Although structural assignments have not been completed, this novel compound can be formulated as involving two  $(\text{C}_6\text{H}_5)\text{POB}(\text{OH})_2\text{OP}(\text{C}_6\text{H}_5)_2^-$  ligands bonded to nickel(II). A systematic study of the magnetic and spectral properties of this compound and the nature of the reactions sustained by this species with  $\text{BF}_3$  etherate are presently under investigation. Similar reactions involving  $[\text{Ni}(\text{PCl}_3)_4]$  and  $[\text{Ni}(\text{C}_6\text{H}_5)_2\text{PCl}]_4$  have also been carried out; however, further confirmation of the reaction products is required before even tentative structural assignments can be made.

Publications:

Faculty Member: John Charles Morrow, III  
Professor of Chemistry

Research Associates: Dinçer Ülkü

Graduate Students: B. Huddle  
G. Oldham

ARPA-Supported Students:

Degrees Granted:

Other Supporting Agencies: National Science Foundation

Summary of Research Activities:

(1) X-Ray Diffraction and Molecular Structure of Crystalline Materials

The crystal structure of dicarbonylpentan-2,4-dionatorhodium and of dicarbonylpentan-2,4-dionatoiridium have been determined from x-ray diffraction by single crystals. These compounds are remarkable because of their electrical conductivities. The iridium compound has the higher conductivity, by a factor of a million, and is a semiconductor and photoconductor. Conductivity of both materials is highly anisotropic. The crystal structures have been determined to aid in interpretation of the conductivity data obtained by Professor L. Slifkin and his coworkers. From the three-dimensional integrated Weissenberg intensity data, structures were obtained by the heavy atom method and were refined in three-dimensions by full matrix least squares methods which included anisotropic thermal parameters as variables. Conventional R values are 0.09 and 0.12 for rhodium and iridium structures respectively. The molecules are planar, and the metal atoms have square planar coordination. Intramolecular bond distances and angles are unremarkable. The metal atoms are very nearly at  $(1/4, 1/2, 1/2)$  and thus are almost exactly  $a/2$  distant from one another in long chains parallel to the a-axis. The needle axis of the crystals is parallel to the a-axis of the unit cells:  $a = 6.546$ ,  $b = 7.752$ ,  $c = 9.196$ ,  $\alpha = 105^\circ 49'$ ,  $\beta = 91^\circ 1'$ ,

$\gamma = 100^{\circ}12'$  for the rhodium compound and  $a = 6.465$ ,  $b = 7.734$ ,  $c = 9.180$ ,  $\alpha = 105^{\circ}35'$ ,  $\beta = 90^{\circ}41'$ ,  $\gamma = 100^{\circ}25'$  for the iridium compound. Both crystallize in space group PT with two molecules per unit cell.

Publications:

"Anisotropic Electron Transport in Compounds Containing Polymeric Metal-Metal Bonds," J. Amer. Chem. Soc. 88, 4286 (1966), with C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, W. R. Roper, and D. Ülkü.

Faculty Member: Royce W. Murray  
Associate Professor of Chemistry

Research Associates: J. N. Burnett  
G. W. O'Dom

Graduate Students: W. R. Heineman  
J. R. Cockrell  
S. E. O'Dell  
R. L. McNeely  
T. Neal

ARPA-Supported Students: W. R. Heineman  
R. L. McNeely

Degrees Granted:

Other Supporting Agencies: Air Force Office of Scientific Research

Summary of Research Activity:

(1) Studies of Metal  $\beta$ -diketonates in Acetonitrile Solvents

Electrochemical studies have shown that the fate of the reduction products of these complexes in acetonitrile depends strongly on the supporting electrolyte employed. Detailed studies on a variety of the complexes, notably  $\text{Fe}(\text{acac})_3$ ,  $\text{Fe}(\text{acac})_2^+$ ,  $\text{Fe}(\text{acac})^{++}$ , and  $\text{Cu}(\text{acac})_2$  have been conducted in tetraethylammonium and lithium perchlorate electrolytes, and it has been found in each case that the presence of lithium ion induces coordinative relaxation reactions in which the reduced complex is stripped of one or more ligands by the electrolyte environment. Such post-electron transfer reactions markedly modify the observed electrochemical behavior. In the coordinatively-unsatisfied Fe complexes, artifacts in the electrochemical patterns which indicate reduction of complexes known not to be present in the bulk solution have been found to arise from the novel instance of the product complex undergoing coordinative exchange reactions with incoming reactants. A variety of transient electrochemical techniques have been employed to study the above electrochemical prostheses; these techniques have been



substantially aided by the development of an optically transparent thin-layer electrochemical cell (see below).

(2) Thin-electrochemistry with Optically Transparent Electrodes

A frequent question in electrochemical studies centers on the nature of the electrode product. Useful information in answering this question is conventionally derived from a coulometric exhaustive electrolysis experiment (for calculating  $n$ ) coupled with spectral observations on this product solution. To minimize possible ambiguities arising from further chemical and electrochemical reactions of the initial electrolysis product, the coulometric electrolysis should be completed as rapidly as possible. Use of a thin-layer electrochemical cell allows optimally fast electrolysis, and if, in addition, the thin-layer cell is optically transparent, and in situ observation of the developing transmission spectrum of product is simultaneously possible.

A thin-layer cell with the useful optical transparency property has recently been developed in these laboratories. Its construction is extremely simple, being based upon a microgrid of gold sandwiched between two glass or quartz microscope slides. Not only does this cell render electrochemical thin-layer coulometric studies more convenient and simple to perform, it opens as well new routes to unique ways to observe in situ product spectra. Further studies are continuing to improve the design of the cell, as well as exploration of its numerous applications to chemical problems. A preliminary report of the cell design has been published.

(3) Adsorption of Metal Complexes at Electrode Surfaces

Work continues directed toward evaluation of monolayer and sub-monolayer adsorptions of metal complexes on mercury surfaces, elucidation of the nature of the adsorbed complexes, and the forces governing the adsorption process. In addition to the series of mercury and lead complexes studied previously,

experiments have been conducted on indium-thiocyanate and cadmium iodide systems. The adsorption of the latter has been characterized with respect to the electrode potential and ligand concentration dependencies. An instrument designed for more efficient read-out of adsorption data was constructed during these studies. A description of the instrument and of the adsorption results have been published. The information available on metal complex adsorption is currently too sparse to allow exacting generalizations on the nature of the adsorption forces. An attempt has been made recently to formulate a model for the adsorption electrode-potential dependency, and experiments are currently being planned to test the assumptions made in this model.

It has been previously found in these laboratories that adsorbed lead complexes inhibit the reduction of mercury complexes in iodide and bromide electrolytes. Further studies have been conducted of the inhibitory action of adsorbed lead iodide and bromide on systems which are reduced at more negative potentials than the lead. Amalgam oxidation studies, using a novel variant of chronopotentiometry, have failed to reveal any inhibition of amalgam oxidation by adsorbed lead halide layers. Further studies on the inhibitory action are planned to further characterize its supposed two-dimensional crystalline character.

Publications:

"Voltammetric Membrane Electrode Study of the Ion-Exchange Properties of Cellophane Membranes," Anal. Chem. 38, 461 (1966), with R. C. Bowers.

"Spherical, Shielding, and Streaming Effects in Current-Reversal Chrono-potentiometry at the Hanging Mercury Drop Electrode," J. Electroanal. Chem. 13, 132 (1967), with D. J. Gross.

"Instrument for Functional Readout of Chronocoulometric Data. Application to Cd Adsorption from Iodide Medium," Anal. Chem. 39, 51 (1967), with G. W. O'Dom.

"Reversed-Phase Thin Layer and Column Chromatography with Alkyl Amine

and Quarternary Ammonium Salt Stationary Phases," Anal. Chem. 39, 282 (1967), with R. J. Passarelli.

"Supporting Electrolyte Effects in Non-Aqueous Electrochemistry: Coordinative Relaxation Reactions of Reduced Metal Acetylacetonates in Acetonitrile," Anal. Chem. 39, 1221 (1967), with L. K. Miller.

"Chronocoulometric Measurement of Indium(III) Adsorption from Thiocyanate Medium," J. Electroanal. Chem. (in press), with G. W. O'Dom.

"An Optically Transparent Thin Layer Electrochemical Cell," Anal. Chem. 39, 1666 (1967), with W. R. Heineman and G. W. O'Dom.

"Electrochemical Masking with an Adsorbed Metal Complex: Determination of Silver-Mercury Mixtures," Anal. Chem. 39, 1661 (1967), with R. L. McNeely.

Faculty Member: Charles Norwood Reilley  
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R. W. Creekmore  
Attila Yildiz  
P. T. Kissinger  
T. H. Ridgway  
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D. C. Young

ARPA-Supported Students: J. W. Ashley, Jr.  
R. W. Creekmore  
J. B. Terrill  
Attila Yildiz

Degrees Granted: Ph.D.: J. W. Ashley, Jr.  
R. J. Day  
J. B. Terrill

Other Supporting Agencies: National Institutes of Health  
Air Force Office of Scientific Research

Summary of Research Activities:

(1) NMR Studies of Ion Exchange Materials

The objective of this research activity was to study water structuring in ion exchange resins and to compare the water structuring found in homogeneous electrolyte solutions---also, to study hydration numbers of ion exchange resins. Both cation and anion resins are being studied in order to understand factors influencing ion selectivity in resin systems. NMR has been proved to be very useful in viewing water structuring in electrolyte solutions and is readily adapted to the study of ion exchange resins. Chemical

shifts of electrolyte solutions were compared with the chemical shifts of resonance systems at various temperatures in order to discern water structuring in resin systems. The chemical shifts of a particular counter-ion were found to correspond closely with the chemical shifts found for the counter-ion in homogeneous solution. Hydration numbers of resin systems were determined using single-phase theory and found to correspond closely to hydration numbers found in electrolyte solutions of corresponding systems. The hydration numbers have been studied thus far only for resins of 8% cross linking. Future studies will be made on resins of different cross linkings.

(2) Conformational Effects in Mono-Protonated CyDTA

This research was undertaken to study the conformation of the mono-protonated amino polycarboxylic species in solution with special reference to CyDTA. Use of nuclear magnetic resonance in studying these systems has proved to be most suitable in that different conformations of CyDTA exhibit different types of AB patterns. Also, NMR lends itself to the study of exchange rates and intrinsic motions related to these compounds. CyDTA solutions were viewed by NMR at various pH's, over different concentration regions, and at different temperatures, and found to exhibit asymmetric broadening of the AB quartet. From this data, the conformations of the side chain of CyDTA were elucidated.

(3) Electrochemistry Using Thin-Layer Cells

Development of new thin-layer cells based on glass-deposited metal thin films and the application of these new designs to the following problems were undertaken: electrochemical processes, adsorption at thin-film surfaces, analysis for dissolved oxygen in various media and the mechanism of oxygen reduction at different thin-film surfaces, and hydrocarbon electrochemistry. Thin-layer electrode assemblies consisting of two glass plates (either one or both of which hold a deposited metal film) can be constructed. Various films (Pt, Au, Ag, etc.) can be

deposited on the glass by thermal evaporation under high vacuum. Such cells have the advantages of minimum edge effect, ease of construction, minimal cost, and spectroscopic utility. The reflectance and transmission properties of thin-films (100 Å-500 Å) suggest their potential for simultaneous spectroscopic and electrochemical experiments. Such experiments will provide information useful in elucidating electrochemical processes and will be a major part of this investigation. Since 09 66 the twin-electrode steady-state thin-layer principle has been utilized to extend the potential range (between the background dissolution limits) available for voltammetric experiments by elimination of background and charging currents at the current-measuring electrode. The utility of thin-layer electrochemistry for diagnostic analysis of various electrochemical reaction schemes has been investigated and found viable. The thin-layer principle was extended to an organic-phase carbon-paste thin-film electrode, which possesses increased sensitivity as an extraction electrode. Preliminary experiments on metal-thin film electrodes on glass indicate that many advantages may accrue from further development.

(4) Base-Catalyzed Hydrogen-Deuterium Exchange of the Acetate Methylene Hydrogen in Amino Acids and Aminopolycarboxylic Acids

This research has several objectives: (i) studying the role of nitrogen and oxygen intramolecular hydrogen bonding in obtaining mechanistic pathways for base-catalyzed hydrogen-deuterium exchange in such compounds as EDTA, (ii) investigating the role of hydrogen-deuterium exchange of amino acids having acetate, glycinate, and propionate substituents, and (iii) studying the effects of various alkali metals of the deuterium exchange. The rate of deuteration can be followed by observing the decrease in the signal intensity of the site, which is being deuterated (acetate methylene). Deuterioxide is added to catalyze the exchange rate in order to have rates which are conveniently measured by the aforementioned method. Two mechanistic pathways have been proposed for the deuterium exchange process, one being deuterioxide independent and the other deuterioxide dependent. The deuterioxide-independent process

showed that the role of the carboxylate group was important. The deuterioxide-dependent pathway is dependent on the acidity of the acetate methylene group which is influenced by inductive effects. Both rate constants were determined for a large number of amino acids. The rate of deuterium exchange for metal-amino acid systems was found to be too slow for measurement in the case of Li, and one-half the rate for unassociated EDTA was observed for Na-EDTA<sup>-3</sup>, suggesting that sodium associates only with a nitrogen and two carboxylate groups.

(5) Electrochemiluminescent Reactions

The threefold objective of this research activity was: (i) to study the mechanism of chemiluminescent reactions of aromatic hydrocarbo- anion and cation radicals generated electrochemically in non-aqueous solvents, (ii) to investigate the heterogeneous electron transfer processes which lead to generation of these radical ions, and (iii) to generate light emission more efficiently and in a more controllable manner in thin layers of solutions entrapped between two working electrodes. Use of suitable electrochemical techniques, especially thin-layer electrochemistry coupled with optical detection devices, to study the stability of radical ions, to determine the nature and the lifetimes of possible excited states involved in electrochemiluminescence, chemical and physical processes following electron transfer, rates of annihilation reactions which lead to light emission, light intensity vs. time and frequency characteristic of the emission. Electrooxidation of aromatic hydrocarbons have been studied using electrochemical techniques such as cyclic voltammetry and thin-layer electrolysis. Chemical reactions accompanying the electron transfer are found to be extant for the compounds studied. The optical absorption spectra of fairly stable radical cations of 9,10-diphenylanthracene and perylene were recorded following a macroscale oxidative electrolysis. By using twin-electrode thin-layer voltammetry and

recording the current at a fixed potential electrode the anodic window available for the detection of oxidation processes on Pt electrodes has been extended and the oxidation half-wave potentials obtained for a series of aromatic hydrocarbons; these may be correlated with the molecular orbital parameters.

Publications:

"Cobalt(III)-Catalyzed Deuterium Exchanges on Ligands with Glycinate Rings," *Inorg. Chem.* 5, 1988 (1966), with J. B. Terrill.

"Base-Catalyzed Hydrogen-Deuterium Exchange in Bivalent Metal-EDTA Chelates," *Anal. Chem.* 38, 1876 (1966), with J. B. Terrill.

"Twin-Electrode Thin-Layer Electrochemistry: Kinetics of Second-Order Disproportionation of Uranium(V) by Decay of Steady-State Current," *Anal. Chem.* 38, 1881 (1966), with B. McDuffie.

"Diagnostic Criteria for the Study of Chemical and Physical Processes by Twin-Electrode Thin-Layer Electrochemistry," *J. Electroanal. Chem.* 12, 477 (1966), with L. B. Anderson and B. McDuffie.

"Teaching Electroanalytical Chemistry: Diffusion-Controlled Processes," *J. Chem. Ed.* 44, 9 (1967), with L. B. Anderson.

"Rate Constants for Deuterium Exchange of Trimethylammonium Ion in Heavy Water," *J. Phys. Chem.* 71, 1588 (1967), with R. J. Day.

"The Kinetics of Ligand Exchange Reactions of Lead and Copper Complexes of Ethylenedinitrilotetraacetate and Propylenedinitrilotetraacetate," *Anal. Chem.* 39, 1358 (1967), with J. D. Carr and K. Torrance.



Faculty Member: Oscar K. Rice  
Kenan Professor of Chemistry

Research Associates: Neal Boehnke  
A. B. Bardawil

Graduate Students: N. F. Irani  
Do-Ren Chang  
E-Chung Wu

ARPA-Supported Students:

Degrees Granted: M.A.: E-Chung Wu  
Ph.D.: N. F. Irani

Other Supporting Agencies: National Science Foundation  
Army Research Office (Durham)

Summary of Research Activities:

(1) Statistical Thermodynamics of  $\lambda$ -Transitions

Some of the earlier considerations have been applied to phenomena occurring in  $^3\text{He}$ - $^4\text{He}$  mixtures. Along the  $\lambda$  line in  $^3\text{He}$ - $^4\text{He}$  mixtures, the specific heat at constant chemical potential presumably becomes infinite. It was suggested that the  $\lambda$  transition changes over to a first-order transition at a point at which the specific heat at constant composition becomes infinite. Possible reasons for such a change were discussed. The thermodynamic relationships were introduced through analogy with a system in which the variables are pressure and volume rather than chemical potential and composition.

(2) Critical Phenomena

Further work on the cyclohexane-aniline system, and the effect of water on its coexistence curve in the critical region, is now under way. An attempt is being made to measure the specific heat of a critical perfluoromethylcyclohexanecarbon tetrachloride mixture by observation of the rate of cooling. Some work is projected on critical phenomena in micelles.

Publications:

"Possible Relation Between Phase Separation and the  $\lambda$  Transition in  $^3\text{He}$ - $^4\text{He}$  Mixtures," Phys. Rev. Letters 19, 295 (1967).

"Coexistence Curve of the Cyclohexane + Methylene Iodide System in the Critical Region," Trans. Faraday Soc. 63, 2158 (1967), with N. F. Irani.

"Statistical Thermodynamics of  $\lambda$  Transitions, Especially of Liquid Helium," Phys. Rev. 153, 275 (1967).

"Deactivation by Collision in the Photolysis of Azoethane," J. Chem. Phys. 46, 2021 (1967), with Walter C. Worsham.

Faculty Member: Bernard F. Spielvogel  
Assistant Professor of Chemistry

Research Associates:

Graduate Students: J. K. Knight  
J. M. Purser  
L. Hall  
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ARPA-Supported Students: J. M. Purser

Degrees Granted: M.S. : E. Rothgery

Other Supporting Agencies: Petroleum Research Fund

Summary of Research Activity:

(1) Synthesis and Mechanistic Studies of Boron Compounds

The reaction of metal borohydrides and boron hydrides with hydrogen sulfide, metal hydrogen-sulfides, and trithiocarbonic acid has been investigated using high vacuum line techniques.  $B^{11}$  n.m.r. has been used to elucidate the mechanisms of the reactions and to help characterize the products.

Reaction stoichiometry and  $B^{11}$  n.m.r. evidence for species such as  $HSBH_3^-$ ,  $(HS)_2BH_2^-$ ,  $CS_3 \cdot BH_3^+$  and  $CS_3 \cdot 2BH_3^+$  has been obtained. To further understand  $B^{11}$  n.m.r. data, correlations with  $C^{13}$  n.m.r. are being investigated.

Publications:

"Correlations between Carbon-13 and Boron-11 Chemical Shifts. I. The Alkanes and Analogous Boron-Nitrogen Compounds," J. Am. Chem. Soc. 89, 5294 (1967).

Faculty Member: Paul C. Ragland  
Associate Professor of Geology

Research Associates:

Graduate Students: David A. Dobbins  
Gary C. Allen  
Vaneaton Price  
Kenneth F. Steele  
Robert Lemmon  
Charles C. Daniel  
Peter Weigand  
Joseph Cabaup  
Paul Beyer

ARPA-Supported Students: Kenneth F. Steele (July 1966 - June 1967)  
Paul Beyer (July - August, 1966)

Degrees Granted:

Other Supporting Agencies: North Carolina Board of Science and  
Technology

Summary of Research Activity:

- (1) Partition of Elements between Coexisting Silicate Minerals in Plutonic Rocks.

The objective was to obtain data on the partition of elements between coexisting silicate minerals in plutonic rocks of known origin. These data can be used as an indication of conditions of crystallization in plutonic rocks of unknown origin, as well as to obtain valuable information concerning the chemical nature of the continental crust.

Chemical analyses were made of rocks and their constituent minerals from a wide variety of plutonic rock environments--rocks that have crystallized at various levels in the continental crust. Analyses for K, Na, Ca, Rb, and Sr were performed by atomic absorption spectrometry on K-feldspars. Li, V, Cr, Co, Ni, Ti, Al, Si, Mn, Mg, Fe, Ca, Rb, and Na have been analyzed by atomic absorption and X-ray spectrography on biotites. These minerals were chosen because they are ubiquitous in felsic plutonic rocks. The data

were plotted to determine the degree of correlation with magmatic fractionation and depth of crystallization.

The above elements have been analyzed in approximately 50 K-feldspars, 50 biotites, and several hundred plutonic rocks. The main conclusion to date is that these elements can be considered on the basis of two groups: (1) "mobile," exemplified by the alkali metals; (2) "immobile," the remainder. Relative mobility is a function of the ionic nature of the metal-oxygen bond in the silicate structure in the presence of a polar solvent such as water vapor. Mobile elements do not reflect the initial partition coefficient but rather some subsequent event, whereas the partition of immobile elements seems to be controlled by conditions of initial crystallization.

Publications:

"Possible Rb-Fe covariance in K-Feldspars," *Nature* 210, 829-830 (1966), with O. K. Billings and J. A. S. Adams.

"Trace Metals in Quartz by Atomic Absorption Spectrophotometry," *Southeastern Geology* 7, 93-100 (1966), with Vaneaton Price.

"The Pre-metamorphic Origin of the Packsaddle Schist Amphibolites; Geochemical Evidence," *Tex. J. Sci.* 18, 277-290 (1966), with G. K. Billings and R. C. Harriss.

"Chemical Fractionation and its Relationship to the Distribution of Thorium and Uranium in a Zoned Granitic Batholith," *Geochim. et Cosmochim. Acta* 31, 17-34 (1967), with G. K. Billings and J. A. S. Adams.

"Quantitative Chemical Analysis of Minerals in Thin-Section with the X-ray Macroprobe," *Amer. Min.* 52, 493-508 (1967), with O. D. Hermes.

"Use of the X-Ray Macroprobe as a New Analytical Tool in Geochemistry," *Trans. Amer. Geophys. Union* 47, 217 (1966), with O. D. Hermes.

Faculty Member: Charles V. Briscoe  
Associate Professor of Physics  
(On leave during the 1966-67 academic year)

Research Associates:

Graduate Students: A. Lehoczky  
J. S. Legg, Jr.  
L. M. Stacey  
C. E. Tarr  
R. E. Hodder  
J. T. Lewis

ARPA-Supported Students: A. Lehoczky  
J. S. Legg, Jr.  
L. M. Stacey  
R. E. Hodder

Degrees Granted:

Other Supporting Agencies: Air Force Office of Scientific Research

Summary of Research Activity:

(1) Nuclear Magnetic Resonance in Alkali Halide Single Crystals

The spin-lattice relaxation time  $T_1$  was measured for the  $I^{127}$  resonance of LiI, NaI, KI, and CsI, for the  $Br^{79,81}$  resonances of KBr and RbBr, and for the  $Rb^{87}$  resonance of RbBr in the temperature range from  $15^\circ K$  to  $77^\circ K$ . Except for  $LiI^{127}$ ,  $T_1$  was also measured at room temperature. Good overall agreement was found between the observed temperature dependence of  $T_1$  and the Van Kranendonk theory of quadrupolar relaxation. Departures from the theoretical temperature dependence observed below  $\sim 60^\circ K$  in  $LiI^{127}$ ,  $NaI^{127}$ , and  $KI^{127}$  can be attributed to structure in the phonon spectra. In these cases, the agreement is improved by adding to the Debye spectrum an Einstein peak at approximately the infrared dispersion frequency to account explicitly for the optic modes. The results of this experiment indicate that the optic modes are important to the relaxation process even at temperatures as low as  $30^\circ K$ .

(2) Superconducting Tunneling

A cryostat suitable for the condensation of metallic films

onto substrates held at 4.2°K has been assembled. Attempts to fabricate tunnel junctions at 4.2°K by condensing gallium onto previously oxidized aluminum strips have so far been unsuccessful.

(3) Microwave Transmission- and Reflection-Coefficient Ratios of Thin Superconducting Films

Microwave transmission- and reflection-coefficient ratios have been measured for pure lead and lead plus manganese overlay films at wavelengths of 12, 8, and 4 mm. The results for pure lead agree very well with the BCS theory of superconductivity if one uses a  $2\Delta/kT_c$  ratio of 4.5 instead of the usual BCS predicted 3.52. This  $2\Delta/kT_c = 4.5 \pm 0.1$  is to be compared with  $4.3 \pm 0.1$  derived from tunneling studies. The thickness of the films ( $\sim 100 \text{ \AA}$ ) used in making microwave measurements may be responsible for the increase in  $2\Delta/kT_c$ . A manganese overlay of approximately 2  $\text{\AA}$  onto a 150  $\text{\AA}$  pure lead film caused a 40% reduction in the microwave measured gap. No decrease was observed in  $T_c$ . This large decrease in the gap to  $T_c$  ratio has not been predicted theoretically. It is probably due to a spin pair breaking interaction rather than the more usual proximity type effects.

Publications:

"Microwave Transmission- and Reflection-Coefficient Ratios of Thin Superconducting Films," Phys. Rev. 154, 414 (1967) with N. M. Rugheimer and A. Lehoczky.

"Nuclear Spin-Lattice Relaxation in Alkali Halides at Low Temperatures," Phys. Rev. 155, 272 (1967) with C. E. Tarr and L. M. Stacey.

"Strain Effects in the Tunneling Characteristics of Superconducting Lead," Second International Conference on Tunneling in Solids, June 29, 30, July 1, 1967, Risø, Denmark, with R. E. Hodder.

Faculty Member: Sang-il Choi  
Associate Professor of Physics

Research Associates: J. Hernandez  
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D. Pugh

Graduate Students: W. Rhim  
P. Flauss

ARPA-Supported Students: W. Rhim

Degrees Granted:

Other Supporting Agencies: Research Corporation

Summary of Research Activity:

(1) Theoretical Investigation of Molecular Crystals

The objective is to understand the properties of molecular crystals. The approach is (a) to find better methods of calculating electronic wave functions in molecular crystals by modified OPW methods; (b) to study electron-phonon and exciton-phonon interactions by Green's function method; (c) to study the energy transfer processes by excitonic mechanisms and the break down of the adiabatic separation of electronic and nuclear coordinates.

(1) Photoionization cross sections of an anthracene molecule in vacuum and in solid phase have been calculated based on an approximate continuum wave function which is an orthogonalized coulomb wave function. (2) Properties of small polaron propagator have been studied and the mobility expression is found to be different from that given by Holstein. (3) Exciton-exciton collision annihilation rate is formulated including the autoionizing states of molecules. (4) Energy transfer processes between lanthanide ions in lanthanide chelates mixed crystals have been interpreted in terms of ligand triplet exciton migration processes. (5) Exciton impurity states in one-dimensional molecular crystals have been studied by varying the angle that the impurity molecular axis makes with the chain.



Publications:

"Collision Annihilation of Singlet Excitons in Molecular Crystals"  
Phys. Rev. Letters 19, 358 (1967).

"Photoionization of Molecules near Threshold," Phys. Rev., in press,  
(1967), with J. Hernandez.

Faculty Member: James H. Crawford, Jr.  
Professor of Physics

Research Associates: W. C. Mallard  
Visiting Associate Professor

Graduate Students:

ARPA-Supported Students:

Degrees Granted:

Other Supporting Agencies: Atomic Energy Commission

Summary of Research Activity:

(1) Defect Behavior in Refractory Oxides

It is the objective of these experiments to gain information about the characteristics of composite defects in oxide systems. These include: symmetry, dipolar character, ease of polarization by electric and stress fields, and the activation energy for thermal reorientation.

We will use measurements of optical absorption, dielectric relaxation, ionic thermo-conductivity, application of uniaxial stress and if necessary electron paramagnetic resonance to determine the dipolar character, symmetry, and identity of composite imperfections in pure and doped specimens of oxides (MgO, CaO, ZnO, etc.).

To date we are mainly in the equipment procurement phase. Have studied the build up and decay of polarization of MgO in electric field in exploratory fashion.

Publications:

"Annealing of <sup>60</sup>Co Gamma Irradiated Germanium," Phys. Rev. 144, 725 (1966), with H. Saito and J. C. Pigg.

Review of Book Entitled "Effects of Radiation on Semiconductors" by V. S. Vavilov, Nuclear Science and Engineering 24, 421 (1966).

"Radiation Effects in Semiconductors," Interaction of Radiation with Solids, Edited by A. Bishay (Plenum Press, New York, 1967) 107-132.

"Annealing of Irradiated Silicon containing Phosphorous Atoms,"  
J. Phys. Soc. Japan 22, 1301 (1967), with Hirata and Saito.

"Effect of Impurities on the Annealing Behavior of Irradiated Silicon,"  
J. Appl. Phys. 38, 2433 (1967), with Hirata, Hirata and Saito.

Faculty Member: Paul S. Hubbard  
Associate Professor of Physics

Research Associates: M. Baud  
J. Kenworthy

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F. W. Harrell  
W. Hinshaw

ARPA-Supported Students:

Degrees Granted: Ph.D.: J. Chaffin

Other Supporting Agencies: National Science Foundation  
Alfred P. Sloan Foundation

Summary of Research Activity:

(1) Nuclear Magnetic Relaxation in Liquids

The longitudinal nuclear magnetic relaxation, transient and steady-state Overhauser effects, and diffusion coefficient of the protons and fluorine nuclei in liquid  $\text{CHF}_3$  have previously been measured by pulsed magnetic resonance techniques. Interpretation of the data gave values of the contributions to the relaxation of intra- and inter-molecular dipole-dipole, and spin rotational interactions. Similar measurements have been made on liquid  $\text{CH}_3\text{F}$  over the temperature range 133°K to 183°K. Attempts to interpret the data have indicated that data over a greater range of temperature is needed. Additional samples will be prepared in which the liquid can be studied at higher temperatures.

(2) Non-Exponential Relaxation

The non-exponential longitudinal nuclear magnetic relaxation of protons in methyl groups undergoing hindered rotations, which has previously been predicted by a calculation including the cross-correlations of the different dipole-dipole interactions, has been observed in solid  $\text{CH}_3\text{CN}$ . Measurements on solid mixtures of  $\text{CH}_3\text{CN}$  and  $\text{CD}_3\text{CN}$  are underway.

(3) Effects of Field Inhomogeneities

Calculations have previously been made of the effects of inhomogeneities in the rf and time independent magnetic fields

on the results of transient NMR experiments. Measurements have been made of longitudinal relaxation by means of a  $180^\circ$ - $90^\circ$  pulse sequence, using several different coil arrangements. Comparison of the measurements with the results of the calculations indicate that errors in the determination of the relaxation time of a few percent may occur in a typical experiment if corrections are not made for the effects of the inhomogeneities.

Publications:

"Nuclear Magnetic Relaxation and Overhauser Effects in Liquid  $\text{CHF}_3$ ,"  
J. Chem. Phys. 46, 1511-1520 (1967), with John H. Chaffin III.

Faculty Member: Horst Kessemeier  
Assistant Professor of Physics

Research Associates: Douglas Cutler

Graduate Students: Won Kyn Rhim

ARPA-Supported Students: Won Kyn Rhim

Degrees Granted:

Other Supporting Agencies:

Summary of Research Activities:

(1) Nuclear Magnetic Relaxation in Rotating Solids

The rate of rotation of the rotor-samples could be increased to about 12 kHz. By using an auxiliary coil tuned to audio frequencies it was possible to monitor the spinning frequency in the higher frequency range. At the present time facilities for filament winding are being set up for the purpose of reinforcing the rotor shells with composites.

(2) Off-Resonance Experiment in the Rotating Frame

The observation of the free induction decay in the rotating frame in which the effective field includes the magic angle with the dc magnetic field constitutes a complementary method to sample rotation in bringing about a narrowing of the resonance line in solids. A series of measurements on  $\text{CaF}_2$  and Teflon have been conducted at various rf field levels, large compared to the local field. The  $\text{F}^{19}$  resonance could be narrowed by about a factor of 10. By employing different transmitter coil geometries it was shown that the remaining line width is caused by inhomogeneities of the rf fields. Preparations are in progress for a search of rotary echoes.

(3) Slow Diffusion Measurements in Solids

An apparatus has been constructed for a study of low field relaxation in the rotating frame by the spin-lock technique. The system is capable of generating short rf pulses with  $\text{H}_1$  up

to 20 gauss and sustained  $H_1$  of 12 gauss for periods up to 10 sec duration. A crossed-coil system is used which produces a uniform  $H_1$  over a sample approximately 1/2 inch diameter and 3/4 inch long. Measurements of  $T_1$ ,  $T_2$  and  $T_{1 \text{ rot}}$  will be made on metals, metal phosphides and ionic crystals from room temperature to about 700°C to measure and study the effects of slow diffusion.

Publications:

"Pulsed Nuclear Magnetic Resonance in Rotating Solids," Phys. Rev. 155, 321 (1967), with R. E. Norberg.

Faculty Member: E. N. Mitchell  
Associate Professor of Physics

Research Associates:

Graduate Students: J. Fowler  
D. Landry  
R. T. Richard  
R. M. Sutton  
G. L. Wells

ARPA-Supported Students: D. Landry  
R. T. Richard  
R. M. Sutton  
G. L. Wells

Degrees Granted: M.S.: J. Fowler  
R. M. Sutton

Other Supporting Agencies: ARPA (Crystal Growth Facility Contract)  
Air Force Office of Scientific Research

Summary of Research Activity:

(1) Electric and Magnetic Properties of Thin Ferromagnetic Films.

It is the objective of these experiments to understand and explain the causes of residual magnetic biasing effects observed in permalloy films at low temperatures (near 4.2°K).

Ferromagnetic films are prepared by vapor deposition in vacuum onto glass substrates. The magnetic behavior of these films is observed at low temperatures as a function of the temperature at which biasing fields are applied.

It has been established that the anomalous anisotropies at low temperatures reported earlier are due to reducible surface layers (presumably oxides) which under proper conditions can also bias the easy axis loop of permalloy films. An apparatus has been built to be used to try to determine if this biasing layer is antiferromagnetic FeO. Preliminary data indicates that the observed temperature dependence is not consistent with that of bulk FeO.



(2) Tunneling in Single Crystal Superconductors

It is the objective of these experiments to study the superconducting energy gap as a function of crystallographic orientation.

It is planned to make a single crystal of a superconducting metal of known orientation, oxidize this surface, overcoat it with a second metal (hopefully but not necessarily a superconductor) and study the tunneling characteristics as a function of temperature and crystallographic orientation.

In addition to the successful growth of aluminum with a (100) direction normal to the [100] face of an alkali halide substrate reported last period, 90° twinned aluminum has been grown on the [100] face of KBr and NaCl with a (110) orientation perpendicular to the face by deposition on cleaved in vacuum substrates at temperatures near 225°C using evaporation rates of about 100 AU per minutes in a pressure of  $10^{-6}$  mm-Hg. The individual crystallites are about 10 microns in extent. A He<sub>3</sub> cryostat is currently being tested to use in investigating these films. Efforts to make single crystal tin films have thus far not been successful using high vacuum systems and liquid nitrogen cooled substrates. An ultra high vacuum system is being completed to carry on more work with tin.

(3) Antiferromagnetic Properties of Single Crystal Chromium Films

It is the object of these experiments to examine the antiferromagnetic properties of single crystal chromium films by means of electron microscopy.

It is planned to make a single crystal film of chromium, examine its properties by means of electron microscopy above and below the Neel temperature and see if any change is observable in this transition.

No antiferromagnetic transitions have been observed in the single crystal films grown here and reported in the last period. It has been tentatively established that the new orientations

observed are attributable not to impurities but to a different structure in chromium (either extensive faulting or a new crystallographic structure) from that observed in bulk. All of the observed crystallographic data can be explained in terms of a relatively simple new structure but one which energetically is not expected.

Publications:

"Spin-Wave Resonance of Permalloy Thin Films as Measured in Ultrahigh Vacuum and in Air," J. Appl. Phys. 37, 3253 (1966), with G. I. Lykken and W. L. Harmon.

Faculty Member: Dietrich Schroerer  
Assistant Professor of Physics

Research Associates:

Graduate Students: Robert C. Nininger, Jr.

ARPA-Supported Students: Robert C. Nininger, Jr.

Degrees Granted:

Other Supporting Agencies:

Summary of Research Activities:

(1) Nuclear Quadrupole Interaction and Radiation Damage in Crystals

The Morin transition temperature in hematite microcrystals has been investigated by the Mössbauer effect. Due to surface effects the lattice spacing in these microcrystals is larger than in bulk crystals. The Morin transition temperature is found to be depressed under this negative "equivalent pressure" at a rate comparable to the increase observed in bulk under hydrostatic pressures.

Publications:

Faculty Member: Paul E. Shearin  
Professor of Physics

Research Associates:

Graduate Students: C. G. Roberts  
W. P. Rickey  
P. B. Peters

ARPA-Supported Students: C. G. Roberts  
W. P. Rickey  
P. B. Peters

Degrees Granted:

Other Supporting Agencies:

Summary of Research Activity:

(1) Radiation Damage in Metals

Studies have been made in the recovery of resistivity in pure and alloyed aluminum in the range  $60^{\circ}$  -  $300^{\circ}$ K following 2 MeV electron irradiation. The alloys included 0.3 atomic percent Zn, Cu and Ge, respectively, in aluminum. Several different electron fluxes were used. The results show that Stage II exhibits prominent impurity trap release peaks, and that impurity effects may be important in Stage III.

Recovery of electron irradiated tungsten near liquid helium temperature after 2 MeV electron irradiation was studied using both isochronal and isothermal anneals. A very broad annealing peak extending from  $26^{\circ}$ K to  $50^{\circ}$ K with maximum at  $30^{\circ}$ K was the most important feature of the recovery. There is also a large narrow peak at  $22^{\circ}$ K.

Stage II recovery ( $60^{\circ}$ - $240^{\circ}$ K) of electron radiation damage in nickel was studied. Four distinct substages at  $80^{\circ}$ K,  $100^{\circ}$ K,  $160^{\circ}$ K and  $220^{\circ}$ K were observed. The recovery showed no dependence on initial defect concentrations and Stage II is thought to be due primarily to impurity effects.

Publications:

Faculty Member: Marvin Silver  
Associate Professor of Physics

Research Associates: K. Masuda  
D. Onn  
R. Sharma  
P. Smejtek

Graduate Students: R. Morris

ARPA-Supported Students:

Degrees Granted:

Other Supporting Agencies: National Science Foundation  
Army Research Office

Summary of Research Activity:

- (1) Electrical and Optical Properties of Molecular Solids and Liquids

Tunnel junctions have been used as electrodes to inject hot electrons into benzene and cyclohexane. The injected current can be made so large that it is space charge limited. Below the space charge limited region, the current is limited by the relative work function between the electrode and the liquid. From these measurements, we have determined the binding energy for an electron in benzene and cyclohexane. The difference in the binding energies is attributed to their relative electron affinities. Attempts have been made to inject electrons into liquid crystals and parafins. So far these attempts have been unsuccessful. The major problem to date has been purity.

Tandem excitation techniques have been used to photoionize excited states of anthracene crystals. Preliminary data indicates that the excited states are triplets.

- (2) Hot Electron Injection into Liquid Helium

Using the tunnel cathodes we have injected currents as large as  $2 \times 10^{-9}$  amps/cm<sup>2</sup> into helium. Besides the energetic

requirements, the current is limited by the penetration depth of the electrons and the image potential. Preliminary data indicates that only those electrons with a range greater than  $(e/4E_a)^{1/2}$  can escape. Since the range should be a function of the injected electron energy, barriers determined from photo or hot electron injection should be larger than the true value unless a free surface is penetrated.

Publications:

Faculty Member: Lawrence M. Slifkin  
Professor of Physics

Lawrence G. Rowan  
Instructor

Research Associates: A. Batra  
C. Childs  
A. Laskar  
R. Marzke

Graduate Students: J. S. Kim  
R. Lambe  
L. Whintont  
J. Gilreath  
M. Greene  
W. Alexander  
R. Sanders  
B. Klein

ARPA-Supported Students: B. J. Klein

Degrees Granted: M.S. : Richard Lee Whintont  
Ph.D.: Jin-Soon Kim

Other Supporting Agencies: Air Force Office of Scientific Research  
Atomic Energy Commission

Summary of Research Activity:

(1) Atomic Mobility in Crystals

(a) Further experiments on diffusion of tracers of Ag and Au in Ag/Au Kirkendall couples are being made. These studies give information on the effects of activity coefficient gradient and vacancy flux on the drift of radiotracers. (b) Experiments on self diffusion in alpha phase AgCd alloys have been completed. Although the activation energies for both constituents decrease with increasing Cd concentration from 0% Cd to about 30 atomic percent, for all compositions above 30% the activation energies are constant. It is suggested that this unexpected result is due to effects of short range order. (c) Diffusion along dislocations was studied in the alloy  $\text{Cu}_3\text{Au}$ , at temperatures above the ordering temperature. For both constituents, the activation energies for

dislocation diffusion were very close to one-half the values for diffusion in the bulk. (d) Tracers of bromide and iodide were diffused into AgCl, and it was found - surprisingly - that their activation energies equal that for self-diffusion of chloride to within the experimental accuracy. (e) Diffusion of Au tracer in AgCl is now being studied, and results to date indicate an interstitial mechanism. (f) Preliminary experiments on diffusion of Ag tracer into Al are being made; it has been found that the presence of a trace of chloride or chlorine can overcome the problem of surface oxide on aluminum.

## (2) Lattice Defects in Ionic Crystals

(a) In AgCl, the separate formation energy for the silver ion vacancy has been measured to be 0.6 ev. This result is consistent with the observation that at room temperature the dislocations (and presumably also the surfaces) are negatively charged, with a reversal of sign at higher temperatures. It is suggested that this surface charge can explain several photographic effects, such as the mechanism of the concentration of photoelectrons into one or a few latent image specks. (b) Internal friction of doped AgCl has been used to study dislocation-point defect interaction in AgCl. Oscillation of the dislocation loops at high amplitude pulls them free of their pinning points; subsequent oscillation at low amplitudes can be used to follow the re-aging. The observed kinetics can be quantitatively explained in terms of a simple drift-diffusion model. (c) Dislocations and nuclear tracks in AgCl can be decorated with photolytic silver by sweeping photoelectrons through the crystal, but trace impurity effects were found to interfere greatly with the reproducibility of the process. It has now been demonstrated that Cu aids in the decoration of old dislocations, Pb aids in the decoration of tracks (and, presumably, fresh dislocations), and Ni interferes with decoration of both dislocations and tracks. (d) Ionic conductivity in AgCl:Fe has been studied as a function of the state of oxidation of the Fe.



Starting with most of the iron in the ferric state, as the ferric is converted to ferrous the ionic conductivity goes through a minimum. This is as predicted from the model of the ferric-tetravacancy model. (e) Ionic thermocurrents (depolarization currents from thermally freed dipolar defects) have been observed in AgCl:Cd, presumably due to Cd-vacancy complexes. (f) Transient microwave spin echo experiments have been performed on  $V^{4+}$  paramagnetic impurities in  $TiO_2$  (rutile). Multiple spin echoes were observed in this system when the magnetization is near a dielectric microwave mode resonance of the sample. A temperature independent spin lattice relaxation time in the liquid helium temperature range has also been measured and appears to be the relaxation time of the phonon modes on resonance with the spin system.

Publications:

"Activity Coefficient and Vacancy-Flow Effects on Diffusion in Ag-Au Alloys," Phys. Rev. 149, 556 (1966), with R. Meyer.

"Electrically Charged Surfaces and the Photographic Process," Phot. Sci. & Engr. 11, 79 (1967), with W. McGowan, A. Fukai, and J. Kim.

"Diffusion of Mn in AgCl," Bull. Am. Phys. Soc. 11, 838 (1966), with A. Laskar.

"Self-Diffusion in the Volume and Dislocations of  $Cu_3Au$ ," Bull. Am. Phys. Soc. 12, 325 (1967) with W. Alexander.

"Internal Friction Study of Aging in AgCl," Bull. Am. Phys. Soc. 12, 338 (1967), with J. Kim.

Faculty Member: A. T. Stewart  
Professor of Physics

Research Associates: P. Varlashkin  
G. Randone

Graduate Students: S. M. Kim  
G. M. Beardsley  
J. Legg  
K. Werner

ARPA-Supported Students: S. M. Kim  
J. Legg

Degrees Granted:

Other Supporting Agencies: National Science Foundation

Summary of Research Activity:

(1) Fermi Surface Studies

(a) Li The data reported on last year has been prepared for publication and is in press. (b) Alloys A LiMg single crystal has finally been procured and Fermi surface studies are starting.

(2) Bubbles in Helium and Other Liquids

Analysis of the previous data on zero-point bubbles has been done and a paper submitted for publication. Experimental work is continuing.

(3) Positron Motion in Metals

Extensive measurements have been made determining positron motion in Li, Na, K, Rb, and Ca over a wide temperature range. The results show: (a) The effective mass of positrons in Li, Na, K, Rb, and Ca is  $1.8 \pm .3$ ,  $1.8 \pm .2$ ,  $2.1 \pm .3$ ,  $2.3 \pm .3$ ,  $1.8 \pm .4$ , respectively. (b) The minimum energy attained by a positron in metals at helium temperature is for: Li, Na, K, Rb, Ca about  $110 \pm 50$ ,  $90 \pm 40$ ,  $48 \pm 30$ ,  $26 \pm 30^\circ\text{K}$ . (c) The momentum dependence of electrons in the polarization cloud around the positron is observed to be in good agreement with calculations.

(4) Positronium in Zeolites

An attempt to measure the size of cavities in zeolite by positronium motion has been started.

## (5) Positron Annihilation in Hot and Liquid Metals

Much better data have been obtained for Sn, In, and Al at many temperatures. It is now clear that defects and imperfections are important. However, full understanding of the observations has not yet been obtained.

Publications:

"Motion of Positrons and Many-Body Effects in Metals," Bull. Am. Phys. Soc. 12, 532, (1967) with S. M. Kim.

"Zero Point Positronium Bubbles in Liquids," Bull. Am. Phys. Soc. 12, 688, (1967) with C. V. Briscoe, S. I. Choi.

"Positron Annihilation in a Dilute Metal: Li-NH<sub>3</sub> Solution," Phys. Rev. 148, 459, (1966) with P. G. Varlashkin.

"Minimum Energy of Positrons in Metals," Phys. Rev. Lett. 18, 385, (1967) with S. M. Kim and J. P. Carbotte.

"Positron Annihilation in Solid and Liquid Metals," Advances in Physics 16, 471, (1967) with J. H. Kusmiss.

"Positron Annihilation in Metals: A Review," "Positron Annihilation," p. 17, 1967 with L. O. Roellig, Ed., Academic Press, N. Y.

"Calculated Core Annihilation Momentum Distributions for Several Metals," with D. M. Rockmore. "Positron Annihilation," p. 259, 1967 with L. O. Roellig, Ed., Academic Press, N. Y.

"Band Gap in Beryllium," with J. B. Shand. "Positron Annihilation," p. 291, 1967 with L. O. Roellig, Ed., Academic Press, N. Y.

"Momentum Distribution of Photons from Positrons Annihilating in Lithium-Ammonia Solutions," with P. B. Varlashkin. "Positron Annihilation," p. 313, 1967 with L. O. Roellig, Ed., Academic Press, N. Y.

"Positronium Formation in Certain Metal Oxides," with J. H. Kusmiss. "Positron Annihilation," p. 341, 1967 with L. O. Roellig, Ed., Academic Press, N. Y.

"Search for Electric Field Effect in Teflon by Angular Correlation of Positron Annihilation Photons," with T. M. Patterson. "Positron Annihilation," p. 349, 1967 with L. O. Roellig, Ed., Academic Press, N. Y.

"Positron Annihilation in Liquid Gases," with C. V. Briscoe. "Positron Annihilation," p. 377, 1967 with L. O. Roellig, Ed., Academic Press, N. Y.

"Positron Annihilation in Liquid Helium," with C. V. Briscoe. "Positron Annihilation," p. 383, 1967 with L. O. Roellig, Ed., Academic Press, N. Y.

Books:

"Positron Annihilation." A. T. Stewart and L. O. Roellig Eds., Academic Press, New York, 1967.

Faculty Member: Duane F. Taylor  
Professor of Dental Materials

Research Associates: Howard C. Clark  
John W. Sowter

Graduate Students:

ARPA-Supported Students:

Degrees Granted:

Other Supporting Agencies: USPHS - Division of Dental Health

Summary of Research Activity:

(1) Polymerization of Acrylic Monosols, Slurries and Gels

The objective of this study is to identify and evaluate the factors which influence the polymerization of "self-curing" acrylic monosols, slurries, and gels of the types utilized in dental and medical applications. In particular it is to determine the relative influence of composition and concentration variables on reaction rate, temperature rise, and color formation. Availability of such information would permit rational formulation of the products to provide the clinically desired controlled curing times, completeness of cure and minimum color formation.

The initial work has been performed utilizing monosols of known composition and polymer concentration. Individual specimens are prepared with systematic variations of initiator and activator concentration. The course of the reaction is followed thermometrically. Evaluation of individual variables is achieved by statistical analysis of extended series of multi-variate observations.

Work with the most common peroxide initiator and tertiary amine activator systems in monosols has been completed, and a report is in preparation. Equipment and techniques are now being modified to begin the work with the corresponding monomer-polymer suspensions.

(2) Tissue Response to Mechanical Properties of Polymers

The objective of the study is to determine what influence variations in the properties of prosthetic materials have upon the response of oral tissues with which they are in contact. Specific interest is directed to determining if soft surfaces on dentures and other oral prostheses minimize inflammation and bone resorption.

A series of experimental polymers of similar composition and structure but differing mechanical properties will be used clinically to evaluate tissue response. Simultaneous laboratory determinations of properties will provide the needed information for conclusion.

Clinical control cases are being started using commercial products of this general type. This will provide controls and permit refinement of evaluation techniques. A series of experimental elastomeric polymers has been prepared. Techniques are being developed for adapting them to normal dental fabrication techniques.

Publications:

Faculty Member: Jan Hermans  
Associate Professor of Biochemistry

Research Associates: Dino Ferro

Graduate Students:

ARPA-Supported Students:

Degrees Granted:

Other Supporting Agencies: National Institutes of Health  
National Science Foundation

Summary of Research Activity:

(1) Interatomic Potential Functions and Protein Structure

To obtain Lennard-Jones type interatomic potential functions and to use these in predicting the crystal structure of organic molecules and the molecular structure (conformation) of protein molecules.

a. The packing of organic molecules of known structure into crystals is determined by up to twelve independent crystallographic parameters. We are assuming that the derivative of the energy with respect to each parameter is equal to zero. The energy is calculated as a sum over all atom pairs of repulsive and attractive terms of the form  $-A/r^6 + B/r^{12}$ . The Lennard-Jones coefficients A and B can be determined from this condition. b. The best values can then be used to determine the crystal structure of minimum energy. c. These techniques are to be extended to the calculation of the conformation of protein molecules in solution.

We have prepared the computer programs for a and b. Lennard-Jones coefficients for C-C, C-H and H-H interactions as well as a usable methyl(ene) - methyl(ene) average potential function have been obtained. These parameters give a crystal structure of minimum energy for octane which is close to that found experimentally. We are in the process of searching for other packings of octane of (locally) minimum energy in order to further test the approach.

The program for use with protein molecules has been partly completed.

(2) Thermodynamics of Folding of Protein and Polypeptide Molecules in Solution

Using potentiometric titration, UV spectrophotometry and spectropolarimetry, unfolding equilibria and kinetics for biological macromolecules are determined under a variety of conditions. Special attention is paid to obtaining molar thermodynamic functions for these processes ( $\Delta G^\circ; \Delta H^\circ; \Delta c_p^\circ$ ) and for detecting the presence of stable intermediates.

Publications:

"Calorimetric Heat of the Helix-Coil Transition of Poly-L-Glutamic Acid," J. Chem. Soc. 88, 5719 (1966), with G. Rialdi.

"Reversible Denaturation of Sperm-whale Myoglobin. I. Dependence on Temperature, pH and Composition," J. Am. Chem. Soc. 89, 1543 (1967), with G. Acampora.

"Reversible Denaturation of Sperm-whale Myoglobin. II. Thermodynamic Analysis," J. Am. Chem. Soc. 89, 1547 (1967), with G. Acampora.



Faculty Member: Ralph W. Stacy  
Professor of Bioengineering and Biomathematics

Richard M. Peters  
Professor of Surgery

Research Associates:

Graduate Students: C. Frank Starmer  
F. Milam Johnson

ARPA-Supported Students:

Degrees Granted:

Other Supporting Agencies: National Institutes of Health

Summary of Research Activity:

(1) Effect of Tissue Fluids on Mechanical Properties of Surgical Prosthetic Materials

10 cm. lengths of suture materials (surgical silk, nylon filament, Teflon wrapped filament) were sewn into the abdominal cavities of rats. At monthly intervals, strands of these materials were withdrawn and the following determinations made:

1. Stress relaxation curves,
2. Hysteresis curves,
3. Elastic diagrams,
4. Breaking strengths.

In general, the findings are that after six months of exposure to tissue fluids, the artificial fibers show little or no change in mechanical properties. Silk, on the other hand, shows marked changes after only 1 month of exposure. The "time constant" of stress relaxation is reduced from minutes to seconds; the hysteresis curve is broadened markedly; the elastic modulus is reduced at all lengths; and the breaking strength is 10% of original.

The data obtained from these studies are being subjected to computer analysis, to determine kinetic rate constants which produce the behavior noted.

These studies should provide insight into the molecular changes which occur by enzyme action on artificial materials. Our studies show that silk exhibits such changes rapidly, and is therefore a good study material. The kinetic theory of time-dependent mechanical behavior of materials represents a substantial contribution to materials science; this will be published soon.

Publications: