TID-4068

UNITED STATES ATOMIC ENERGY COMMISSION

DIVISION OF PHYSICAL RESEARCH

RESEARCH AND DEVELOPMENT IN PROGRESS

SUMMARIES OF THE USAEC BASIC RESEARCH PROGRAM IN CHEMISTRY

JANUARY 1973

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22151.

Price:	Paper Copy	$7.60
	Microfiche	$0.95

Printed in the United States of America
USAEC Technical Information Center, Oak Ridge, Tennessee

TID-4068
Distribution category UC-4

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FOREWORD

The Atomic Energy Act directs the Atomic Energy Commission to support and foster research in fields related to atomic energy and to the development of other environmentally acceptable energy sources. The Division of Physical Research is responsible for supporting basic research in the physical sciences as an aid in accomplishing these objectives. Basic research is supported at the AEC national laboratories, at other government laboratories, at universities, and at research institutes and foundations.

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

It is the purpose of this document to provide the scientific community with a single, accessible source of information on the current projects being supported by the Office of Chemistry Programs of the Division of Physical Research. This document summarizes the objectives and current status of the individual research efforts in effect during 1972-3.

Previous documents similar to this one reported off-site and on-site work separately. The off-site volumes are numbered: TID-4005(Pt. 2a), TID-4005(Pt. 2a) (2nd Ed.), TID-4005(Pt. 2a) (3rd Ed.), and TID-4051 (1st Ed.). The on-site volumes are numbered: TID-4005(Pt. 2b) and TID-4050(1st Ed.). This is the first combined volume.

The summaries are arranged in sections by discipline. Within each section they are ordered alphabetically by institution and department and then by principal investigator. At the end of each section there appear cross references to summaries listed under other disciplines but related in scope.

The entry includes the name of the institution, the names of the principal investigators, a title, the summary, and a list of publications in the open literature (none earlier than 1970). The summaries are followed by three indexes: of institutions, of investigators, and of subjects. All summaries were prepared between May and August 1972.

All of the research described in this document is unclassified. Investigators are encouraged to report their results in the open literature at the earliest opportunity for wide dissemination of the information.

In most cases the addresses of the individual universities are given in the summaries. The addresses of the AEC national laboratories and other major installations are given below:

Ames Laboratory
Iowa State University of Science and Technology
Box 1129
Ames, Iowa 50012

Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Brookhaven National Laboratory
Upton, L. I., New York 11973

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Oak Ridge National Laboratory
P. O Box X
Oak Ridge, Tennessee 37830

Knolls Atomic Power Laboratory
General Electric Company
P. O. Box 1072
Schenectady, New York 12301

Mound Laboratory
Miamisburg, Ohio 45342

Notre Dame Radiation Laboratory
University of Notre Dame
South Bend, Indiana 46556

Inquiries or comments concerning the researches described in this document should be addressed to the principal investigator or to

Dr. A. R. Van Dyken
Assistant Director for Chemistry Programs
Division of Physical Research
U. S. Atomic Energy Commission
Washington, D. C. 20545

ABSTRACTS

NUCLEAR SPECTROSCOPY

Studies of nuclear structure and models by spectroscopic measurement and analysis of radiative transitions of nuclei.

03:1 NUCLEAR AND ELECTRON SPECTROSCOPY. Freedman, M. S. and Porter F. T. (Argonne National Laboratory. Chemistry Division).

We are studying nuclear energy levels and transitions via electron, gamma, beta, and alpha spectrometry; nucleus–atom–environment interactions and atomic properties and transitions.

The following nuclear decay scheme analyses are underway* (data complete, reduction in process) or will soon be started: ^{241}Cm*, ^{237}Am*, ^{254m}Es*, ^{250}Es*, ^{229}Th, ^{249}Bk, ^{250}Bk, ^{252}Es, ^{249}Cf, ^{251}Fm, and ^{227}Ac. These studies mesh with the gamma and transfer reaction spectroscopy of the heavy element group on the same or related isotopes.

The K and L Auger spectra data of Pu, Am, Cf, and Fm are being analyzed; Coster–Kronig transition yields in these elements are being determined by a new technique using our recent resolution of spectator-vacancy satellites. Orbital electron binding energies in all shells will be measured in Np, Bk, and Es to complete our measurements in all transuranics to Fm. We intend to remeasure some Kα x-ray energies in transplutonium elements to explore a small systematic discrepancy (~50 eV) as compared with K–L binding energy differences. The orbital electron shakeoff spectrum in beta decay (we discovered the orbital component, in ^{143}Pr) will be measured in ^{210}Bi, ^{151}Sm, ^{90}Sr–^{90}Y, and ^{63}Ni to complete our survey of this phenomenon (the study of the ^{147}Pm spectrum has been completed). We are studying fast (10^{-12}-sec) ion recharging times on insulating oxide films on metals to determine the recharging mechanism. We will remeasure K orbital shakeoff in internal conversion to reduce the experimental error, and will attempt a measurement of double conversion by electron–electron coincidences. We will continue our search for outer-shell shakeoff in internal conversion and will measure chemical effects in internal conversion in ^{119m}Sn, ^{169}Er, ^{73}As, and ^{93}Mo.

PUBLICATIONS

Porter, F. T., M. S. Freedman, and F. Wagner, Jr., Ionization (Shakeoff) Accompanying K-Shell Internal Conversion, Phys. Rev., A, 3: 2246-2259 (1971).

Porter, F. T. and M. S. Freedman, Outer Shell Internal Conversion of the 14.4 keV Transition in ^{57}Fe: Chemical Effects and Line-Shape Differences, Phys. Rev., A, 3: 2285-2292 (1971).

Porter, F. T., and M. S. Freedman, Experimental Atomic-Electron Binding Energies in Fermium, Phys. Rev. Lett., 27: 293-297 (1971).

Freedman, M. S., F. T. Porter, and J. B. Mann, Experimental Inner Electron Binding Energies in ^{100}Fm and Limits on Electrodynamic Non-Linearities, Phys. Rev. Lett., 28: 711-713 (1972).

03:2 NUCLEAR CHEMISTRY. Kuroda, P. K. (University of Arkansas. Department of Chemistry, Fayetteville).

The University of Arkansas' 400-kV Cockcroft–Walton Linear Accelerator is being extensively used for the production of new isotopes and isomers. Decay schemes of the newly identified radionuclides, as well as those that were not too well established previously, are being investigated using coincidence counting techniques. The cross sections for (n,p), (n,α), (n,2n) and other rare nuclear reactions induced by fast neutrons are being measured. The distributions of mass and charge in fission of heavy elements are also being determined. The possible occurrence of elements heavier than uranium in nature is investigated. The existence of ^{244}Pu in the early solar system was postulated in this laboratory in 1960 and the first clear-cut experimental evidence for the existence of element 94 in nature was secured also in this laboratory in 1965. A search for the natural occurrence of transuranium (or super-heavy) elements other than ^{244}Pu will be continued for the future. Experimental determination of the temperature of the sun's core is one of the most challenging problems in nuclear chemistry today. In the March 8, 1971, issue of Nature, we proposed a new approach to this difficult problem, and we intend to pursue this problem during the 1970's.

PUBLICATIONS

Kuroda, P. K., Temperature of the Sun in the Early History of the Solar System, Nature, 230: 40-42 (1971).

Ward, T. E., N. A. Morcos, and P. K. Kuroda, Decay of ^{152}Pm Isomers, J. Inorg. Nucl. Chem., 34, 13-23 (1972).

Swindle, D. L., D. T. Moore, J. N. Beck, and P. K. Kuroda, Mass Distribution of 3 MeV Neutron Induced Fission of ^{232}Th, J. Inorg. Nucl. Chem., 33: 3643-3647 (1971).

Swindle, D. L., T. E. Ward, and P. K. Kuroda, New Isotope ^{180}Lu, Phys. Rev., C, 3: 259-265 (1971).

Rao, S. A., Charge Distribution in the Fission of ^{232}Th, Phys. Rev., C, 5: 171-177 (1972).

03:3 NUCLEAR STRUCTURE AND REACTIONS. Hillman, M. (Brookhaven National Laboratory. Department of Applied Science).

A study of the level densities and nuclear deformation is nearing a close. Interesting effects have been observed, e.g., different gaps in the vicinity of different minima vs. deformation and at different spins. An improved method was developed for normalization of the shell model energies to the liquid drop model.

In the future we plan to apply these results to a study of fission phenomena and other nuclear reactions.

03:4 DETERMINATION OF LONG HALF-LIVES. Harbottle, G. (Brookhaven National Laboratory. Chemistry Department).

The half-lives of most radionuclides up to about 5 to 10 years are in general known with at least fair accuracy, but for many longer-lived radionuclides, e.g., ^{32}Si, ^{931}Pt, ^{108m}Ag, ^{192m_2}Ir, half-lives are poorly known, or unknown. Two of these, ^{32}Si and ^{108m}Ag, are of particular interest for dating and environmental studies.

High-precision methods for measuring half-lives can also be used to study the effect of various forms of chemical binding upon the half-life of a radioisotope: experiments measuring this effect can be correlated with the results of Mössbauer and ESCA work.

To measure long half-lives, and chemical effects on half-lives, a differential proportional counter has been constructed and tested and is now operating. It was tested with a source of ^{60}Co; in 14 days the half-life was measured as 5.24 ± 0.21 years (i.e., ±4%) compared to a reported 5.26 years. The apparatus has also performed well in chemical-effects measurements. The instrument will be employed in a long-term program of measurements of a number of radioisotopes prepared at BNL, and supplied by collaborating laboratories including Los Alamos. As time permits, several additional chemical-effects studies are planned.

03:5 NUCLEAR SPECTROSCOPY. Perlman, M. L.; Chu, Y. Y.; Rubinson, W. (Brookhaven National Laboratory. Chemistry Department).

Nuclear spectroscopic studies are an essential part of the nuclear chemistry program at BNL, and the most modern radiation detection instrumentation is employed in this work. Some of the investigations are of intrinsic interest for the understanding of nuclear structure, others arise from the need to determine the radiation characteristics of previously unknown or poorly characterized nuclides encountered in nuclear reaction studies. Special emphasis has been given to conversion of electron studies, particularly in connection with chemical effects on nuclear transitions, and with x-ray photoelectron and Mössbauer spectroscopy.

The BNL electromagnetic isotope separator plays an important role in the preparation of isotopically pure samples for investigation.

PUBLICATIONS

Chu, Y. Y., and M. L. Perlman, Comparison of Measured and Theoretical Internal-Conversion Coefficients for L Through P Shells of Cm, Phys. Rev., C, 3: 2021 (1971).

Chu, Y. Y., Decay of ^{162}Tm, Phys. Rev., C, 4: 642 (1971).

Brenner, D. S., and M. L. Perlman, Subshell Conversion-Line Intensity Ratios for Some Pure Transitions, Nucl. Phys., A, 181: 207 (1972).

03:6 ELECTRON EJECTION IN RADIOACTIVE DECAY. Rubinson, W. (Brookhaven National Laboratory. Chemistry Department).

The act of nuclear transformation by radioactive decay (or other processes) constitutes a perturbation of the atomic electrons, with consequent electron ejection from the atom. The probabilities of ejection of deep-shell electrons can be measured by way of the intensities of the corresponding x rays characteristic of the daughter atom. This phenomenon has been studied off and on at Brookhaven and elsewhere for more than two decades, during which time a considerable amount of reasonably accurate data has been accumulated. Interest in the problem continues because it is not well understood theoretically. In the case of alpha decay, where the deep atomic electrons are subjected to an adiabatic perturbation, the measured excitation probabilities exceed the theoretical ones by one or two orders of magnitude. In the case of beta decay, where the perturbation is expected to be sudden, theory reproduces the experimental results to within ~50%. However, the results of more refined experiments recently reported in the literature have raised doubts concerning the "suddenness" of the beta decay perturbation. A number of new ideas for testing various aspects of the theory are being developed.

PUBLICATIONS

Rubinson, W., The Correction for Atomic Excitation Energy in Measurements of Energies of e^- Capture Decay, Nucl. Phys., A, 169: 629 (1971).

03:7 RESEARCH IN NUCLEAR CHEMISTRY. Kaplan, Morton (Carnegie-Mellon University, Pittsburgh. Department of Chemistry).

The current objectives of the experimental program are to develop a better understanding of nuclear hyperfine interactions, and to use these interactions in the study of nuclear moments and decay properties, and in the exploration of magnetic and electric quadrupole effects in crystals, frozen solutions, and liquids. Mössbauer resonance and gamma–gamma angular correlation techniques are being applied to measure the interactions of nuclei with their surrounding electron distributions, and can frequently yield such information in unique detail. An in-depth study of polycrystalline and single crystal $FeCl_3 \cdot 6H_2O$ has led to the discovery of antiferromagnetic ordering at temperatures below 1.46°K. Careful analysis of Mössbauer spectra for several crystal orientations and in externally applied magnetic fields permitted the accurate determination of the crystal field splitting, the location of the electric-field-gradient axes in the crystal, and the quantitative estimation of the important exchange interactions between adjacent Fe spins. Experiments with rapidly frozen solutions have shown that metal ions can be trapped in the ice matrix with the liquid state configuration "frozen in," and thus the nuclear-electronic interactions in a very dilute lattice are accessible. The rare earth compound $Eu(NH_3)_6$ is under investigation, and exhibits striking paramagnetic hyperfine structure and a very low Debye temperature.

PUBLICATIONS

Subrahmanyam, V. and M. Kaplan, Neutron and Photon Emission from Ba Compound Nuclei, Phys. Rev., C, 1: 322 (1970).

Barrett, J. S., J. A. Cameron, P. R. Gardner, L. Keszthelyi, W. V. Prestwich, and M. Kaplan, Perturbed Angular Correlation Study of the Environment of ^{111}Cd Nuclei in Ice, J. Chem. Phys., 53: 759 (1970).

Ehrlich, B. S., and M. Kaplan, Iodine Mössbauer Studies of Chemical Bonding in Iodobenzene and Several Polyvalent Iodine Derivatives, J. Chem. Phys., 54: 612 (1971).

Kaplan, M., A. J. Nozik, J. V. Di Lorenzo, and T. X. Carroll, Mössbauer Studies of Ions in Ice, in Proceedings of the Conference on the Application of the Mössbauer Effect, Tihany, 1969, p. 597, Akademiai Kiado, Budapest, 1971.

Kaplan, M., and T. X. Carroll, Anomalous Mössbauer Spectra of Ferric Chloride Hexahydrate, in Proceedings of the Conference on the Application of the Mössbauer Effect, Tihany, 1969, p. 169, Akademiai Kiado, Budapest, 1971.

03:8 NUCLEAR SPECTROSCOPY. Brenner, Daeg S. (Clark University, Worcester, Mass. Department of Chemistry).

The central objective of our decay scheme studies at Clark University is to gather information about the energy levels of nuclei that have permanently deformed ground state configurations. In particular, we have focused attention on the class of nuclei that have an unpaired proton, comparing the experimental energy level structure with that predicted using the collective theory of Nilsson. Finer details of the theory are also examined in those instances in which the experimental level structure is well-defined. Examples of these finer details are the nuclear Coriolis coupling between rotational and particle angular momentum and the predictions of the microscopic structure for collective vibrational levels.

Decay scheme studies of ^{159}Er, ^{163}Er, and ^{169}Yb are currently being carried out. In most cases γ-ray singles and coincidence spectra and conversion electron spectra are measured. Lifetimes of isomeric states are also under investigation.

Future plans are to extend our studies of nuclear systematics to lighter Er isotopes. This region of deformed nuclei has generated considerable theoretical interest because of the close proximity of strongly interacting nuclear states.

PUBLICATIONS

Wood, J. L., and D. S. Brenner, The Decay of ^{161}Er to Levels in ^{161}Ho, Nucl. Phys., A, 185: 58–80 (1972).

Brenner, D. S., and M. L. Perlman, Subshell Conversion-Line Intensity Ratios, Nucl. Phys., A, 181: 207–216 (1972).

Wood, J. L., and D. S. Brenner, The Decay of ^{162m}Ho to Levels in ^{162}Dy, Nucl. Phys., A, 174: 353–364 (1971).

03:9 AN EXPERIMENTAL STUDY OF NUCLEAR MODELS. I. DECAY SCHEMES AND NUCLEAR REACTIONS. II. MUONIC X-RAY STUDIES. Sheline, Raymond K. (Florida State University, Tallahassee. Department of Chemistry).

The primary objective of the program is to perform experimental tests of current nuclear models. These experiments involve three different types of nuclei. The first type is that of shell model nuclei. Studies will be performed on ^{90}Y, ^{138}La, a series of Ce isotopes, ^{211}Bi, ^{210}Bi, and ^{209}Bi. The second type is that of nuclei that lie in a transition region between spherical and well-deformed regions. A series of Os nuclei, ^{152}Eu, ^{105}Ru, ^{111}Pd, and some light Ba isotopes will be studied. The third type is that of deformed nuclei. Those strongly deformed nuclei that will be investigated are a series of Ho isotopes and a series of Hf isotopes. Experimental methods involve nuclear reaction spectroscopy in which a magnetic spectrograph of the Browne–Buechner type is coupled to the FSU tandem Van de Graaff. Collaborative studies will involve Los Alamos, the Risø Laboratory of the Danish Atomic Energy Commission, and the Technische Hochschule in Munich. The contact with Los Alamos is especially close. Their triton beam will be used to study proton excited states by means of the (t,α) reaction. A new program using the facilities of LAMPF will be initiated in collaboration with LASL scientists. This program involves a study of nuclear structure using muonic x rays.

PUBLICATIONS

Motz, H. T., E. T. Jurney, E. B. Shera, and R. K. Sheline, Low-Lying Configurations in ^{210}Bi, Phys. Rev. Lett., 26: 854 (1971).

Bennett, Michael J., Raymond K. Sheline, and Y. Shida, Levels in ^{153}Sm, Nucl. Phys., A, 171: 113 (1971).

Jones, H. D., and R. K. Sheline, Energy Levels of ^{168}Tm, Ann. Phys. (N. Y.), 63: 28 (1971).

Onishi, N., and R. K. Sheline, The Tetrahedral Deformation in the Nucleus ^{16}O, Nucl. Phys., A, 165: 180 (1971).

Slater, J. L., R. K. Sheline, K. C. Lin, and W. Weltner, Jr., Synthesis of Uranium Carbonyls Using Matrix Isolation, J. Chem. Phys., 55: 5129 (1971).

03:10 COULOMB EXCITATION. Diamond, Richard M. and Stephens, Frank S. (Lawrence Berkeley Laboratory. Nuclear Chemistry Division).

The use of ions heavier than ^{4}He (up to ^{40}Ar) has revolutionized Coulomb excitation studies, and made new types of experiments possible. Still heavier ions such as Kr, Xe, and even Hg or Pb, will allow a still wider range of studies. We plan to use Kr and Xe beams to Coulomb excite the ground-state band in well-deformed nuclei such as ^{238}U and in vibrational nuclei such as ^{194}Pt. In the case of ^{238}U we calculate that we should excite levels up to spin 30; the resulting energy level spacings would be a very stringent test of the rotor model. The information on the transition energies and on the intensities of the transitions should yield a great deal of information about the nature of the higher levels, that is, whether they are a continuation of the ground-state rotational band or have changed over into another type of state, as some recent experiments suggest. Another way to obtain information about nuclear rotation is to determine the transition moment between rotational levels. The use of Kr and Xe beams will be very helpful in this regard, as the accuracy of the recoil-distance Doppler-shift method for lifetimes in the 10^{-10} to 10^{-12} second range will be improved over what we have already achieved using ^{40}Ar beams. We have pointed out some of the advantages to be gained in the Coulomb excitation of rotational bands with very heavy ions. Comparable improvements should occur in the study of other collective modes of excitation related to the ground state.

03:11 ON-LINE ALPHA SPECTROSCOPY OF ELEMENTS BELOW URANIUM AT SUPERHILAC. Hyde, Earl K. and Eppley, Richard E. (Lawrence Berkeley Laboratory. Nuclear Chemistry Division).

During the past 10 years heavy ion reactions induced by ^{11}B, ^{12}C, ^{14}N, ^{20}Ne, and other ions up to ^{22}Ne have been used to produce new isotopes of the elements from osmium ($Z = 76$) to protactinium ($Z = 91$). By use of the helium-jet transport technique for rapid removal of reaction products and of surface-barrier semiconductor detectors for alpha particle analysis the decay properties of about 100 new nuclides have been characterized including many with half-lives in the millisecond time ranges.

With new beams of projectiles having mass 40 and much greater available at the SuperHILAC, these studies are being continued. In the course of this work it should be possible to establish for several elements the lightest isotope retaining the ability to bind the last proton. This proton-binding limit is a severe test of nuclear mass formulas. The phenomenon of delayed proton emission is also under study.

The identification among the products of nuclear reactions induced by complex projectiles of known alpha-emitting nuclei, and, in particular, the measurement of yield patterns for these nuclides are serving as useful means of study of the mechanism of these nuclear reactions. It is of particular interest to study the yields of products in the lead to thorium region when the compound nucleus for the reaction has a nuclear charge well over 100.

PUBLICATIONS

Borggreen, J., and E. K. Hyde, Alpha Decay of Neutron Deficient Osmium Isotopes, Nucl. Phys., A, 162: 407 (1971).

Borggreen, J., K. Valli, and E. K. Hyde, Production and Decay Properties of Protactinium Isotopes of Mass 222 to 225 Formed in Heavy Ion Reactions, Phys. Rev., C, 2: 1841 (1970).

Valli, K., E. K. Hyde, and J. Borggreen, Production and Decay Properties of Thorium Isotopes of Mass 221–224 Formed in Heavy Ion Reactions, Phys. Rev., C, 1: 2115 (1970).

03:12 STATISTICAL NUCLEAR PROPERTIES. Moretto, L. G. and Thompson, S. G. (Lawrence Berkeley Laboratory. Nuclear Chemistry Division).

The aim of this project is to obtain a suitable theoretical description of excited nuclei on the basis of statistical mechanics. Such an approach allows one to illustrate the mean properties and the fluctuations of the nucleus as well as its different modes of decay.

We are attempting to derive the relevant statistical and thermodynamical functions on the basis of realistic shell models with the inclusion of different residual interactions. In the calculations the constants of motion, like energy, particle number, angular momentum and parity are explicitly accounted for.

The statistical functions that are obtained are also dependent upon the nuclear deformation; this has an immediate application to the fission process. The stability of nuclei with respect to fission can be compared with the stability towards other modes of decay. Such an approach can be useful in evaluating the possibility of the synthesis of super-heavy elements by means of heavy-ion reactions. It is in fact possible to calculate the survival ratio of superheavy nuclei with respect to fission.

Although the above line of research has a well-established theoretical foundation, the actual results, when compared to experimental data, may be unsatisfactory because of the deficiencies of the shell model. In order to avoid this difficulty we are attempting to generate the statistical functions in a semiempirical way using available nuclear data like the nuclear masses and the positions of the nuclear magic numbers. This method should provide a long-needed and reliable tool for the interpretation of nuclear reactions.

PUBLICATIONS

Moretto, L. G., Nucl. Phys., A, 182: 641 (1972).
———, Nucl. Phys., A, 180: 337 (1972).
———, Phys. Lett., B, 38: 393 (1972).

03:13 HIGH-SPIN STATES IN NUCLEI. Stephens, Frank S. and Diamond, Richard M. (Lawrence Berkeley Laboratory. Nuclear Chemistry Division).

One of the general properties of heavy-ion reactions is that they involve large amounts of angular momentum and therefore often lead to the population of high-spin states in nuclei. For a number of years we have used one such reaction, heavy-ion-induced compound nucleus formation, in a systematic study these high-spin states. It has been known for some time that near closed shells angular momentum is most efficiently carried by one or a few nucleons in high-j shell-model orbits; whereas, far from closed shells the nuclei are deformed and rotate to carry angular momentum efficiently. The new and interesting features concern intermediate situations, two of which are: a) in even-even deformed nuclei at angular momenta around $16\hbar$, there is evidence that the rotational motion begins to be replaced by individual nucleons in high-j orbitals; and b) there is increasing evidence that the region between the closed shells and the deformed nuclei can be described as a reasonably simple mixture of these two types of motion. The study of high-spin states is an exciting area that has developed rapidly in the last few years and shows promise of becoming much better understood in the next few.

03:14 SELECTED NUCLEAR MEASUREMENT POSSIBILITIES WITH VERY HEAVY IONS. Stephens, Frank S. and Diamond, Richard M. (Lawrence Berkeley Laboratory. Nuclear Chemistry Division).

The availability of very heavy ions ($20 \le Z \le 100$) from the SuperHILAC opens up a number of entirely new experimental areas. We are quite interested in exploring some of these, and will mention briefly two examples that we hope to be studying in the next year. The first is the nuclear Josephson effect, which is the predicted very large probability for transferring a pair of nucleons in the (quasi-elastic) scattering of two superconducting nuclei. The analogy is to the Josephson current (pairs of electrons) that flows across a thin insulator separating two superconductors. This represents the most severe test yet envisioned for the superfluid theory of heavy ($Z \gtrsim 50$) nuclei. Projectiles at least as heavy as tin ($Z = 50$) are required. The other new experiment has to do with quantum electrodynamical effects in atoms having $Z \approx 170$. For such a large Z, the K-binding energy has been calculated to exceed $2m_0c^2$ and the Dirac theory breaks down. In a close collision of U on U, a system with $Z \sim 184$ exists for a short time, and should be affected by the unusual electron binding. Possible ways to detect these effects would be to observe K x-ray emission and/or β^+ emission. It seems clear that a number of other new and interesting experiments will be made possible using very heavy ions.

03:15 RESEARCH IN NUCLEAR CHEMISTRY: RADIOACTIVE DECAY SCHEMES. Gordon, G. E.; Viola, V. E. Jr.; and Walters, W. B. (University of Maryland, College Park. Department of Chemistry).

Our current program involves the study of radioactive decay of elements for which $Z < 67$ in order to determine the energies, intensities, and coincidence relationships of the emitted β and γ rays. Studies are also in progress to determine the half-lives, masses, and alpha-decay branching for highly neutron-deficient, uncharacterized isotopes of U, Pu, and Cm.

Studies are currently underway on the decay of neutron-deficient Dy isotopes of $A = 147$ to 155 in order to obtain a systematic picture of the changing structure of Tb nuclides as the shape of the nucleus changes from spherical near the closed neutron shell ($A = 147$) to deformed ($A = 155$). Other studies are in progress on the decay of ^{131}Te to further characterize the 6-ns isomer located at 1797 keV in ^{131}I. Recent studies on the decay of ^{127}Sn suggest this isomer may have spin and parity $^{15}/_{2}{}^{-}$.

A long-standing project involving the study of nuclear energy and half-life systematics for the heavy elements is also continuing. These studies involve experimental attempts to characterize short-lived heavy nuclides ($A > 160$) that have been previously unobserved, as well as semi-theoretical calculations of the properties of unknown nuclides. The calculations have recently been extended to the nuclides hypothesized to exist in the region near $Z = 114$ and $N = 184$.

PUBLICATIONS

Coryell, C. D., H. N. Erten, P. K. Hopke, W. B. Walters, R. Dams, and H. C. Griffin, Identification and Characterization of 3.8 min ^{134m}I, Nucl. Phys., A, 179: 684 (1972).

Macias, E. S., and W. B. Walters, Gamma–Gamma Directional Correlations in ^{135}Xe Following the Decay of ^{135}I, Nucl. Phys., A, 169: 305 (1971).

Apt, K. E., and W. B. Walters, A Three-Quasiparticle $15/2^-$ Isomer in ^{127}Sb, Phys. Rev. Lett., 26: 1189 (1971).

Erten, H. N., C. D. Coryell, and W. B. Walters, Decay of 45 sec and 83 sec ^{136}I Isomers, J. Inorg. Nucl. Chem., 33: 4005 (1971).

03:16 A GENERAL NUCLEAR CHEMISTRY RESEARCH PROGRAM COMBINING CONVENTIONAL NUCLEAR SPECTROSCOPIC TECHNIQUES WITH ON-LINE SPECTROSCOPY AND NUCLEAR REACTIONS. McHarris, Wm. C. and Bernthal, Frederick M. (Michigan State University, East Lansing. Department of Chemistry).

The primary objective of nuclear chemistry research at Michigan State is to contribute to the understanding of the fundamental properties and structure of the nucleus. The experimental techniques employed are primarily γ-ray, electron, and charged-particle spectroscopy. Experiments are carried out both on-line to the MSU sector-focused cyclotron, and off-line as studies of radioactive decay. Current areas of investigation include in-beam γ-ray spectroscopic studies of nuclei near the $Z = 50$ and $N = 82$ closed shells; in-beam $(\alpha,xn\gamma)$ and $(HI,xn\gamma)$ spectroscopy of nuclei near the edges of the rare earth region of deformation; investigations of the structure of odd–odd nuclei by $(p,n\gamma)$ studies of nuclei near and within the 20- and 28-nucleon shells; study of the radioactive decays of even–even neutron-deficient Pb isotopes; (p,d), (p,t), (^{3}He,d), and (α,t) direct reaction charged particle spectroscopy; study of anomalous EC/β^+ branching ratios. Research will continue in all of these areas, and future projects planned include investigation of the properties of nuclei at very high angular momentum, fission research, and decay studies of nuclei far from the line of β^- stability. In addition to these areas of ongoing basic research, the nuclear chemistry group at MSU has begun interdisciplinary cooperative research programs with the departments of geology and chemical engineering where nuclear instrumentation and technology are applied to problems in elemental analysis, and motoring of environmental pollutants.

PUBLICATIONS

Eppley, R. E., Wm. C. McHarris, and W. H. Kelly, Experimental Studies of Neutron-Deficient Gadolinium Isotopes. III. The Strange Case of ^{145g}Gd, Phys. Rev., C, 3: 282 (1971).

Black, J. N., Wm. C. McHarris, and W. H. Kelly, E6 and M5 Transitions Observed in ^{53m}Fe Decay, Phys. Rev. Lett., 26: 451 (1971).

Johnston, W. C., W. H. Kelly, S. K. Haynes, K. L. Kosanke, and Wm. C. McHarris, N-Shell Conversion Electrons from the 2.33-keV Transition in ^{205}Pb, Phys. Rev. Lett., 26: 1043 (1971).

Eppley, R. E., R. R. Todd, R. A. Warner, Wm. C. McHarris, and W. H. Kelly, The Decay of ^{141m}Sm—A Three-Quasiparticle Multiplet in ^{141}Pm, Phys. Rev., C, 5: 1084 (1972).

Guile, Jean, R. E. Doebler, Wm. C. McHarris, and W. H. Kelly, Decays of the Even–Even Lead Isomers: ^{202m}Pb and ^{204m}Pb, Phys. Rev., C, 5: 2107 (1972).

03:17 LOW-Z NEUTRON-DEFICIENT RARE EARTH NUCLIDES. Brosi, A. R. and Ketelle, B. H. (Oak Ridge National Laboratory. Chemistry Division).

In any given element among the low-Z neutron-deficient rare earths there is a transition from spherical to deformed nuclei as the neutron number is reduced from that of the 82-neutron shell. Because of the marked differences between spherical and deformed nuclei, the nuclear spectroscopy of the transition nuclides is of considerable interest. Several new praseodymium and neodymium isotopes in the transition region have been identified and the level structures of the daughter nuclei are now being studied.

The lower levels in the even–even isotope ^{136}Ce, populated by the decay of ^{136}Pr, can be separated into bands that are qualitatively similar to the gamma- and ground-state bands found in the deformed nuclei. The spins of the low levels of an odd–odd spherical nucleus can usually be predicted from the spins of adjacent odd neutron and odd proton nuclei. We have found the low-level spin sequence of ^{136}Pr, populated by ^{136}Nd decay, to be that predicted for a spherical nucleus.

We have worked out the level structure populated by ^{137}Nd decay and are now working on spin assignments. Among other nuclides for which considerable new data are at hand, ^{134}Pr is of particular interest because it is expected to populate a level structure analogous to that of ^{136}Ce.

PUBLICATIONS

Ketelle, B. H., A. R. Brosi, and J. R. Van Hise, The Decay of ^{136}Pr and the Level Structure of ^{136}Ce, Phys. Rev., C, 4: 1431 (1971).

03:18 COULOMB EXCITATION AND IN-BEAM REACTION γ-RAY SPECTROSCOPY. Eichler, E.; Johnson, N. R.; and O'Kelley, G. D. (Oak Ridge National Laboratory, Tenn. Chemistry Division).

By observing γ rays emitted from targets bombarded with heavy ions below (Coulomb excitation) and above the barrier (reaction γ-ray spectroscopy) a host of new information on nuclear collective states can be obtained.

In the Coulomb excitation area we will complete elaborate studies of the longer-lived and more abundant actinides: ^{232}Th, ^{234}U, ^{236}U, ^{238}U, and ^{242}Pu as well as several complementary investigations of Dy and Hf targets. Rotational bands will be excited to look for deviations from the collective model due to such effects as the nuclear phase transitions. These results will bear heavily on the question of hexadecapole moments in deformed nuclei. Our results have already been useful in removing the ambiguity in sign which handicaps the α-particle measurements.

With the reaction gamma-ray technique we will also study rotational states in deformed nuclei in an effort to map the I vs. A dependence of the phase transitions.

By using the Doppler shift-plunger method, we will measure accurate E2 lifetimes for several salient targets such as ^{238}U, ^{242}Pu, and ^{248}Cm. Correlation of these results with the measured Coulomb excitation probabilities should yield accurate hexadecapole moments.

Although we will utilize ORIC as the prime source of heavy ion beams, we plan to make complementary experiments with heavier ions, e.g., ^{84}Kr and ^{136}Xe, from the Super HILAC at Berkeley.

03:19 COLLECTIVE PROPERTIES OF NUCLEI. Johnson, N. R.; Eichler, E.; and O'Kelley, G. D. (Oak Ridge National Laboratory, Tenn. Chemistry Division).

We continue studies of deformed nuclei by spectroscopic techniques to understand how mixing of rotational and vibrational bands affects such quantities as level energies and reduced E2 transition probabilities. This contributes also to the microscopic description of excited states, as in ^{184}W where some states can be clearly identified with specific Nilsson representations. These studies from radioactive decay, serving as an important complement to our in-beam spectroscopy program on rare earth nuclei, will be extended to actinide nuclei.

In the region of medium-weight, even–even, spherical nuclei we will continue to examine the applicability of a vibrational treatment. Experiments on ^{62}Ni indicate that we probably will be able either to determine or to set a limit on the nuclear monopole matrix element for the ground-state transition from the excited 0^+ level. Since it can occur only while an electron senses the nuclear charge distribution by penetrating the nucleus, it is a sensitive test of the vibrational interpretation of the state.

The exciting collaboration with UNISOR will begin with placing the system and auxiliary equipment on-line. Our experiments will emphasize the advantages of heavy ions, i.e., the large recoil energies of the products. We hope to find a new region of deformation in the neutron-deficient rare earth nuclei.

PUBLICATIONS

Rester, A. C., J. H. Hamilton, A. V. Ramayya, and N. R. Johnson, Decay of ^{72}As to the Levels of ^{72}Ge, Nucl. Phys., A, 162: 481 (1971).

Johnson, N. D., J. H. Hamilton, A. F. Kluk, and N. R. Johnson, Decay of ^{108}Ag, Z. Phys., 243: 395 (1971).

Hamilton, J. H., P. E. Little, A. V. Ramayya, E. Collins, N. R. Johnson, J. J. Pinajian, and A. F. Kluk, M1 Admixtures of Transitions in ^{156}Gd, Phys. Rev., C, 5: 899 (1972).

Singhal, N. C., N. R. Johnson, E. Eichler and J. H. Hamilton, Energy Levels of ^{104}Pd Populated in the Decay of 43-sec ^{104}Rh and 4.41-min ^{104m}Rh, Phys. Rev., C, 5: 948 (1972).

Little, P. E., J. H. Hamilton, A. V. Ramayya, and N. R. Johnson, Level Structure of ^{178}Hf, Phys. Rev., C, 5: 252 (1972).

03:20 NUCLEAR CHEMISTRY RESEARCH. Naumann, Robert A. (Princeton University, N. J. Departments of Chemistry and Physics).

This research program is concerned with experimentally determining the properties of light- and medium-mass nuclei using the Princeton University sector-focus cyclotron. Of special interest are the location and the properties of excited nuclear states with high angular momentum. Current nuclear models predict two limiting categories for these: single particle states, where a few nucleons participate, and collective states involving many nucleons. These high-spin states are reached by radioactive decay or nuclear reaction.

Our equipment includes high-resolution germanium gamma spectrometers operated in coincidence with fast timing circuitry. Multiparameter data are accumulated in a Sigma 2 computer. An electromagnetic isotope separator of radius 150 centimeters is used both to prepare isobarically pure samples of short-lived radioisotopes and to implant radioisotopes in ferromagnetic media for perturbed gamma–gamma angular correlation studies. Presently the electromagnetic isotope separator is being installed in the external beam of the Princeton Cyclotron to form an on-line facility where isotopes of very short half-life can be prepared, separated, and studied. The investigation of the beta decay of light mirror nuclei will be of particular interest as well as the search for delayed proton or alpha emission after beta decay.

With the completion of the Princeton high-transmission particle spectrograph in the next year, we intend to supplement our studies of nuclei far from stability with charged particle spectroscopy involving pick-up reactions such as (p,t) or (^{3}He,^{6}He).

During the spring and summer of 1973, we will collaborate with staff members at the Los Alamos meson facility on an experimental investigation of the processes accompanying the capture of negative mu mesons when stopped in various absorbers. Recent experiments in the Soviet Union have claimed evidence for a marked effect of the chemical nature of the stopping medium on this capture process.

PUBLICATIONS

Dietrich, F. S., B. Herskind, R. A. Naumann, and R. G. Stokstad, Hole Vibration Coupling in ^{115}In, Nucl. Phys., A, 155: 209 (1970).

Hübel, H., R. A. Naumann, and E. H. Spejewski, Levels in ^{184}Pt, ^{186}Pt, ^{188}Pt, Phys. Rev., C, 3: 756 (1971).

Hübel, H., R. A. Naumann, and E. H. Spejewski, Decay of a Three Quasiparticle State in ^{177}Ta, Phys. Rev., C, 4: 2272 (1971).

Hopke, P. K., H. Hübel, R. A. Naumann, and A. T. Strigachev, The Decay of ^{195m}Pb and ^{197m}Pb, Nucl. Phys., A, 184: 497 (1972).

Krien, K., E. H. Spejewski, R. A. Naumann, and H. Hübel, Properties of Levels in ^{198}Pb and ^{200}Pb, Phys. Rev., C, 5: 1751 (1972).

03:21 RADIOCHEMICAL INVESTIGATIONS OF NUCLEAR PROPERTIES. Daly, Patrick J. (Purdue University, Lafayette, Ind. Chemistry Department).

The research work of our nuclear chemistry group is mainly devoted to investigations of the structure of nuclei in the important transitional mass range A = 180 to 200. The experimental techniques of on-line reaction spectroscopy with the Purdue Tandem Accelerator and of radioactive decay spectroscopy are used in various nuclear structure studies, and in several instances both techniques are used together to yield complementary information about the same final nuclei. The radioactivity investigations frequently involve the identification and characterization of short-lived radioisotopes and this work exploits the special radiochemical skills of the nuclear chemist. Work in progress includes (a) studies of the nuclei ^{182}W and ^{184}W by neutron-transfer reactions and radioactive decay spectroscopy; (b) an investigation of the ^{190}Os level structure from the decays of ^{190}Re and ^{190}Ir; (c) investigations of the level spectra of neutron-deficient, even–even Os nuclei be in-beam (p,2nγ) and (α,2nγ) spectroscopy and by radioactive decay; (d) characterization of a newly discovered 12^- isomer of ^{198}Au; (e) a comprehensive and important examination of high-spin negative parity band structure in even–even isotopes of Pt and Hg, using both the in-beam and radioactive decay techniques.

PUBLICATIONS

Wong, P., P. J. Daly, and N. T. Porile, Test of the Independence Hypothesis in the Decay of the ^{210}Po Compound Nucleus, Nucl. Phys., A, 151: 549 (1970).

Daly, P. J., Karin Ahlgren, K. J. Hofstetter, and R. Hochel, Levels of ^{181}W from the Decay of ^{181}Re, Nucl. Phys., A, 161: 177 (1971).

Casten, R. F., P. Kleinheinz, P. J. Daly, and B. Elbek, Coriolis Coupling in the Odd Wolfram Nuclei, Phys. Rev., C, 3: 1271 (1971).

Daly, P. J., S. W. Yates, and J. Cunnane, Implications of the Allowed Unhindered β-Decay of 3-min ^{190}Re, Nucl. Phys., A, 187: 446 (1972).

Ahlgren, Karin, and P. J. Daly, The Level Structure of ^{187}Os from the Decay of ^{187}Ir, Nucl. Phys., A, 189: 368 (1972).

03:22 NUCLEAR SPECTROSCOPY AND NUCLEAR REACTION WORK WITH (a) THE HEAVY ION ACCELERATOR, YALE UNIVERSITY AND (b) THE 4-MeV DYNAMITRON AT SUNY, ALBANY, N.Y. Bakhru, Hassaram (State University of New York at Albany. Physics Department).

The availability of various heavy ions (10-MeV/nucleon) at the Heavy Ion Accelerator at Yale University makes it possible to study the heavy-ion compound nucleus process. For example, competition between neutron, proton, and alpha emission has not been well studied under diverse combinations of mass region and level structure. Also the level spectra in the A > 100 suggest that proton emission is equally favored as compared to neutron emission. These methods will be utilized to study the reaction mechanism. The second approach is to utilize the heavy ions to produce the neutron-deficient, short-lived isotopes and study the level structure of these isotopes. The γ-ray spectroscopy work on Br, Rb, and Kr isotopes is in progress. Level structure studies on these isotopes both from the radioactive decay studies and also from the prompt gamma-ray studies have been undertaken.

The neutron- and α-particle-induced work at SUNY, Albany (using 4-MeV Dynamitron) would provide useful information on the cross sections, excitation energies, spins, and particles of resonance levels. Also, calculation of partial widths, quadrupole to dipole mixing ratio would yield useful information in clear understanding of theories. The (α,γ) work on ^{26}Mg, ^{31}P, ^{35}Cl, and ^{37}Cl targets using high-resolution solid state detectors is in progress.

PUBLICATIONS

Bakhru, H., I. M. Ladenbauer-Bellis, and B. Jones, Decay Properties of ^{98}Pd and ^{98}Rh, Nucl. Phys., A, 186: 321 (1972).

Bakhru, H., S. Shastry, and J. Boutet, Angular Correlation of Gamma Cascades in ^{155}Gd and Levels of ^{155}Gd Populated by the Decay of ^{155}Tb, Phys. Rev., C, 3: 1603 (1971).

Bakhru, H., Nanosecond Isomeric Transitions in ^{155}Gd, Phys. Rev., C, 3: 1706 (1971).

Alonso, J., H. Bakhru, F. M. Bernthal, J. Boutet, B. Olsen, I. Rezanka, and J. O. Rasmussen, Nucl. Phys., A, 160: 193 (1971).

Bakhru, H., I. M. Ladenbauer-Bellis, and I. Rezanka, Level Structure of ^{109}Cd from the Decay of ^{109}In, Phys. Rev., C, 3: 937 (1971).

03:23 ON-LINE ALPHA AND PROTON DECAY SPECTROMETRY. Macfarlane, R. D. (Texas A&M University, College Station. Department of Chemistry).

The major objective of this project is to obtain information on nuclei away from the valley of maximum nuclear stability. The purpose is to learn more about the nature of nuclear forces through a measurement of nuclear binding energies. The results have relevance to stellar nucleosynthesis and to the mechanism of nuclear fission.

The efforts of this project have, over the past several years, led to the discovery of close to 100 new radioactive isotopes. Work is being devoted to β-decay problems in the light elements which have some connection to elementary particle physics. New information is being obtained on mirror symmetry, β–γ directional correlations, and isospin mixing near isobaric analog states. New experimental techniques are continually being developed to probe the nature of the nucleus. The helium-jet recoil transport method can be used to transport short-lived nuclei over large distances. Recent applications include the studies of accelerator-produced activities, short-lived fission products from ^{252}Cf, and rapid transport of radiopharmaceuticals. A new approach to on-line mass spectrometry is being developed that utilizes recoils from radioactive decay processes to identify the mass of decaying species.

PUBLICATIONS

Macfarlane, R. D., N. S. Oakey, and R. J. Nickles, Beta-Neutrino Correlations and Longitudinal Nuclear Alignment in the Decay of ^{20}Na, Phys. Lett., B, 34: 133 (1971).

Jungelas, H., R. D. Macfarlane, and Y. Fares, Evidence for Large Cluster Formation of Nuclear Reaction Recoils Thermalized in Helium, Phys. Rev. Lett., 27: 556 (1971).

Mueller, D. W., R. D. Macfarlane, K. Bet, and A. D. Suttle, Jr., Crystal Lattice Effects in the ^{149}Sm(n,α)^{146}Nd Reaction Induced by Thermal Neutrons, Phys. Lett., B, 36: 74 (1971).

Macfarlane, R. D., and N. S. Oakey, Beta Recoil Effects in the Delayed Alpha Decay of ^{20}Na, Izv. Akad. Nauk SSSR, Ser. Fiz., 34: 2109 (1970). English translation, Bull. Acad. Sci. USSR, Phys. Ser. (Engl. Transl.), 34: 1880 (1971).

Macfarlane, R. D., N. S. Oakey, and R. A. Gough, On-Line Nuclear Spectroscopy of Short-Lived Isotopes, in The Uses of Cyclotrons in Chemistry, Metallurgy, and Biology, p. 232, Butterworth & Co. (Publishers) Ltd., London, 1970.

03:24 SPECTROSCOPY OF TRANSITIONAL AND DEFORMED NUCLEI. Sugihara, T. T. (Texas A&M University, College Station. Cyclotron Institute).

Stimulated by recent theoretical work by Tamura, Vogel, and others in describing collective states of transitional nuclei, we have studied the low-lying structure of neutron-deficient nuclei with neutron numbers 84, 86, and 88. Both the in-beam xnγ method and radioactive decay have been used to determine energy, spin, and parity of levels in ^{148,150,152}Gd, ^{150,152}Dy, and ^{154,156}Er. In the decay studies the odd–odd parent nuclides of Tb and Ho were found to exist in isomeric states; the systematics of isomerism are being explored. A modified version of the helium-jet recoil-transport system of Macfarlane has been devised to provide sources of short-lived nuclear reaction products in a low-background area and in a form suitable for γ-ray spectroscopy. Coincidence spectra, level lifetimes, and angular correlations can be obtained even for nuclides with half-lives of the order of a second. With only minor modifications the helium-jet system has also been adapted for conversion-electron spectroscopy. The electron-steering device of Watson will be used to obtain in-beam conversion-electron spectra from (α,xne) reactions, particularly to search for excited 0^+ states. An experimental determination of the energies of these states will permit an important test of Tamura's model.

PUBLICATIONS

Hofstetter, K. J., and T. T. Sugihara, Decay of ^{97}Ru, ^{97}Zr, and ^{97}Nb, Nucl. Phys., A, 140: 658 (1970).
Bowman, W. W., T. T. Sugihara, and F. R. Hamiter, Quasirotation Levels in ^{152}Gd and Excited Levels of ^{152}Tb from the Decay of 4.2-min ^{152m}Tb, Phys. Rev., C, 3: 1275 (1971).
Bowman, W. W., and T. T. Sugihara, Levels in ^{174}Hf from ^{174}Ta Decay and β-Band Mixing, Nucl. Phys., A, 178: 263 (1971).
Haenni, D. R., T. T. Sugihara, and W. W. Bowman, Decay of a New 5.8-min ^{150}Tb Activity, Phys. Rev., C, 5: 1113 (1972).

03:25 NUCLEAR STRUCTURE STUDIES OF NUCLEI IN THE $Z > 28$, $N < 50$ and $Z < 50$, $N > 50$ Major Shells. Sarantites, Demetrios G. (Washington, University, St. Louis. Department of Chemistry).

The efforts of this project are directed toward the advancement of our knowledge of the detailed properties of the lowest quantum states of nuclei in order to obtain new information necessary for a better understanding of the behavior of nuclei. At present, emphasis is given in the $Z > 28$, $N < 50$ and $Z < 50$, $N > 50$ major shells and in particular to nuclei with Z or N of 43, 45, or 47 in which the $g_{9/2}$ orbit is being filled. The detailed structure of these nuclei is not adequately described by any of the current models for nuclei. The detailed predictions of the pairing-plus-quadrupole model, the extended quasiparticle-phonon coupling model, and the Nilsson model for the collective behavior of nuclei are tested by comparison with experiment for nuclei in this region. Investigations are in progress that give information about the γ-decay properties of nuclear levels by selective excitation via in-beam nuclear reactions such as (p,nγ),((p,p$'\gamma$), (α,pγ), and (α,nγ), or following radioactive decay. Measurements are performed for determination of (a) nuclear level lifetimes either via delayed coincidence or Doppler shift attenuation techniques, (b) nuclear level spins and multipole mixing ratios via singles γ-ray, $\gamma\gamma$, or pγ coincidence angular correlation techniques, and (c) measurements of internal conversion coefficients.

Extensive use of high-resolution Si(Li) particle or electron and Ge(Li) γ-ray detectors is made in singles or in multiparameter coincidence arrangements. The structures of $^{74}_{34}\mathrm{Se}_{41}$, $^{77}_{54}\mathrm{Se}_{43}$, $^{95}_{43}\mathrm{Tc}_{52}$, $^{97}_{43}\mathrm{Tc}_{54}$, $^{85}_{38}\mathrm{Sr}_{47}$, and $^{81}_{38}\mathrm{Kr}_{45}$ together with $^{61}_{29}\mathrm{Cu}_{32}$ and $^{61}_{28}\mathrm{Ni}_{33}$ are currently being investigated.

PUBLICATIONS

Phelps, M. E., and D. G. Sarantites, Level Structure of ^{101}Rh from the Decay of 8.5h ^{101}Pd, Nucl. Phys., A, 159: 113-142 (1970).
Sarantites, D. G., and W. G. Winn, Structure of ^{51}Cr via ^{48}Ti(^{4}He,nγ) and ^{51}V(p,nγ) Prompt Gamma-Ray Spectrometry, Nucl. Phys., A, 155: 257-296 (1970).
Xenoulis, A. C., and D. G. Sarantites, Level Structure of ^{58}Co via ^{55}Mn(^{4}He,nγ) Prompt Gamma-Ray Spectrometry, Nucl. Phys., A., 170: 369-394 (1971).
Phelps, M. E., and D. G. Sarantites, Level Structure of ^{97}Tc from the Decay of 2.9d ^{97}Ru, Nucl. Phys., A, 171: 44-58 (1971).

03:26 YALE HEAVY ION ACCELERATOR IN-HOUSE RESEARCH. Rasmussen, J. O. and Rezanka, I. (Yale University, New Haven, Conn.).

The Yale Heavy Ion Accelerator is operated under AEC auspices and aids the far-ranging research of a large number of laboratories as well as maintaining its own in-house research group. This summary is confined to the in-house research activities.

The experimental program is based mainly on high-resolution gamma-ray spectroscopy with Ge(Li) detectors and data collection systems based on PDP8/I computers. With these capabilities threefold studies are concentrated on the energy level systems of particular nuclei, often inaccessible except with heavy ions: (1) in-beam studies of gamma radiation emitted essentially instantaneously with formation reactions of (heavy ion,xn) type, (2) between-beam-pulse studies of millisecond-delayed gamma radiation, and (3) complementary radioactive decay scheme studies populating the same nuclei. For example, millisecond isomerism and complementary studies are underway in the region of radium, radon, lead, and lutetium. The region around 89 neutrons has been of interest for in-beam and radioactivity measurements, including three dimensional (gamma–gamma–time) gigachannel coincidence work and angular distribution measurements. A series of odd-mass hafnium isotopes have also been studied. The above experimental studies have revealed highly perturbed bands, stimulating us to push theoretical studies of Coriolis band mixing, with special emphasis on more careful treatment of number conservation in the pairing force effects.

We have also developed computer programs for heavy ion reaction and scattering cross sections on deformed as well as spherical targets. As outside users of the Berkeley Super HILAC we plan to carry out reaction experiments aimed at elucidating the nuclear shape effects, both static and dynamic, in collisions of heavy nuclei.

PUBLICATIONS

Ma, C. W., and J. O. Rasmussen, Nuclear Rotation: Cranking Model Calculations and Their Relation to Other Treatments, Phys. Rev., C, 2: 798 (1970).
Alonso, J., H. Bakhru, F. M. Bernthal, J. Boutet, B. Olsen, I. Rezanka, and J. O. Rasmussen, In-Beam Gamma Spectroscopy of ^{161}Ho, Nucl. Phys., A, 160: 193 (1971).
Rasmussen, J. O., and K. Sugawara-Tanabe, Theoretical Studies of Nuclear Collision Processes of Deformed Nuclei, Nucl. Phys., A, 171: 497 (1971).
Rezanka, I., S. Hultberg, H. Ryde, J. O. Rasmussen, F. M. Bernthal, and J. Alonso, Rotational Bands in ^{171,173,175}Hf from (Particle,xn) Reactions, in International Conference on the Properties of Nuclei Far from the Region of Beta Stability, Leysin, Switzerland, 1970, Report CERN-70-30(Vol. 2), p. 949, European Organization for Nuclear Research, 1970.
Rezanka, I., F. M. Bernthal, J. O. Rasmussen, R. Stokstad, I. Fraser, J. Greenberg, and D. A. Bromley, High-spin States in ^{153}Gd and ^{154}Gd from (α,xnγ) Studies, Nucl. Phys., A, 179: 51 (1972).

ALSO SEE Nuclear Reactions: 03:30, 03:39, 03:40, 03:41, 03:44, 03:46, 03:48, 03:56, 03:57, 03:60, 03:62; Heavy Element Chemistry: 03:66, 03:67, 03:73, 03:75, 03:83, 03:84, 03:89; and Kinetics and Mechanisms: 03:214.

NUCLEAR REACTIONS

Studies of nuclear structure by detection and analysis of collision processes between nuclei.

03:27 HIGH ENERGY NUCLEAR CHEMISTRY. Steinberg, E. P.; Kaufman, S. B.; and Wilkins, B. D. (Argonne National Laboratory, Chemistry Division).

The program is directed toward the elucidation of the mechanisms of nuclear reactions — in particular, those induced by high-energy protons in complex nuclei. The mechanisms are generally classified as fission, spallation, fragmentation, and simple (i.e., (p, 2 nucleon)) reactions. Radiochemical and online counting techniques are employed and allied studies at low energies and with other projectiles are also pursued to aid in the interpretation of the high-energy phenomena and to develop new techniques.

We are currently completing the analysis of the data from an on-line, semiconductor detector study of the mass, energy, and angular correlations of the products of the interaction of 11.5-GeV protons with uranium. Studies of the pulse-height versus energy response of the detectors were recently investigated and a theory of their behavior with heavy ions proposed. Further studies of these detectors are continuing as a PhD thesis problem for a student. The results of recently completed studies of (1) the angular distribution of long-range alpha particles accompanying the spontaneous fission of ^{252}Cf, (2) the ^{63}Cu(p,n)^{63}Zn and ^{63}Cu(p,2n)^{62}Zn reactions from 1.5 to 11.5 GeV, (3) the ^{25}Mg(p,2p) ^{24}Na reaction from 3.0 to 11.5 GeV, (4) the ^{209}Bi(p,2p5n)^{203}Pb reaction from 0.15 to 11.5 GeV, and (5) the absolute cross section for the ^{12}C(p,pn)^{11}C reaction at 7.6 GeV are being prepared for publication. One of the purposes of the latter study was to establish the technique to be used in the measurement of this fundamental monitor reaction at NAL and LAMPF in the near future.

A major, new interpretation of nuclear fission involving a semi-empirical treatment of deformed nuclear shell effects has been developed. It accounts remarkably well for the main features of the fragment mass and charge distributions and kinetic energy and excitation energy of the fragments over the entire range of fissile nuclei. Further development of this idea is being actively pursued.

The origin of the so-called fragmentation products (A ≃ 20 to 70) and the existence of a high-excitation energy fission mechanism are still open questions. We have designed an experiment to test an explanation that couples the two phenomena in terms of a cascade-fission mechanism, i.e., fission at high excitation energy followed by a secondary fission from one (or both) of the excited fragments leading to a fragmentation product. This experiment will be carried out at the ZGS as soon as the accelerator is back in operation. Other radiochemical studies of fission–spallation competition at high energy are being planned to establish whether a high excitation energy fission mechanism is prominent.

A major effort in the near future will be directed toward survey studies of the reactions occurring at 200 GeV at NAL to determine the appearance of any new phenomena and a study of pion-induced, simple nuclear reactions at LAMPF for comparison with proton-induced reactions and the known pion–nucleon, free-particle parameters to establish the reaction mechanism.

PUBLICATIONS

Esterlund, R. A., Stehney, A. F., Steinberg, E. P., Secondary Reactions of 11.5 GeV Protons in Uranium: A Search for the Production of Transcurium Actinide Elements, Nucl. Phys. A, 179: 645-656(1972).

Steinberg, E. P., Kaufman, S. B., Wilkins, B. D., Gross, C. E., Fluss, M. J., Pulse-Height Response Characteristics for Heavy Ions in Silicon Surface-Barrier Detectors, Nucl. Instrum. Methods, 99: 309-320 (1972).

Wilkins, B. D., Fluss, M. J., Kaufman, S. B., Gross, C. E., Steinberg, E. P., Pulse-Height Defects for Heavy Ions in a Silicon Surface-Barrier Detector, Nucl. Instrum. Methods, 92: 381-391 (1971).

03:28 RADIOCHEMICAL RECOIL STUDIES OF HIGH-ENERGY NUCLEAR REACTIONS.

Cumming, J. B.; Remsberg, L. P. (Brookhaven National Laboratory, Chemistry Department).

In this work, measurements are made of the momentum transferred to products of nuclear reactions induced in complex nuclei by high-energy particles, particularly protons. Characteristic radioactive decay properties are used for the identification of products of interest. The data are interpreted in terms of mechanisms for the reactions, such as binary fission, spallation, or fragmentation.

Angular distributions are obtained by measuring yields of products which recoil out of thin target foils and are trapped in thick catchers at various angles to the beam direction. Momentum spectra are derived from the depth of penetration into a stack of thin catchers positioned at a given angle. Radiochemical separations are usually employed to facilitate the assay of specific nuclides.

Emphasis has been placed recently on studies of uranium targets. It was concluded that binary fission is the dominant process at 2.2 GeV, although there is some contribution to yields of neutron-deficient products from a spallation-like process. At 28 GeV, neutron-deficient rare earth nuclei are formed mainly by this spallation-like process which probably involves emission of light fragments. Experiments in progress include more detailed comparisons of results from U and Ta targets at 28 GeV, and studies of the interactions of bismuth and 2.2-GeV protons.

PUBLICATIONS

Crespo, V. P., Cumming, J. B., and Alexander, J. M., Production of ^{149}Tb from Gold by 2.2-GeV Protons, Phys. Rev., C, 2: 1777 (1970).

Bächmann, K., and Cumming, J. B., Fission of ^{238}U by 2.2-GeV Protons. II., Phys. Rev., C, 5: 210 (1972).

03:29 THE BROOKHAVEN SOLAR NEUTRINO EXPERIMENT.

Davis, R. Jr. (Brookhaven National Laboratory, Chemistry Department).

An experiment has been in progress to observe the neutrino radiation from the sun to test the current theories of the solar energy-producing processes. Neutrino detection is based upon the neutrino-capture process ^{37}Cl(ν,e$^-$)^{37}Ar that produces the 35-day radioactive product ^{37}Ar. The detector uses 10^5 gallons of perchloroethylene (C_2CL_4) as a neutrino-capturing medium. The radioactive ^{37}Ar is removed from the liquid by purging with helium gas, isolated on charcoal, purified and counted in a small proportional counter. The detector system is located a mile underground in the Homestake Gold Mine in Lead, S. Dakota.

Recently the sensitivity for observing and characterizing ^{37}Ar decay events in the small proportional counter has been increased by measuring the pulse height and rise-time of the pulse. It has been concluded from measurements extending over the last two years that the neutrino-capture rate in the detector is less than 0.2 per day. Current theoretical models of the sun predict the solar neutrino-capture rate should be 1.8 per day, a factor of 9 above the observed rate. Further experiments are underway and planned (1) to improve the statistical accuracy of the measurement, (2) to further confirm the validity of the experimental result. The unexpectedly low solar neutrino-capture rate cannot be explained without drastic changes in our ideas of the internal structure of the sun or possibly without introducing new properties of the neutrino that have not been revealed in laboratory experiments.

Systems for radiochemical detection of low-energy solar neutrinos, particularly the ^{7}Li(ν,e$^-$)^{7}Be system, are under intensive investigation.

PUBLICATIONS

Davis, R. Jr., A Progress Report on the Brookhaven Solar Neutrino Experiment, Acta Physiol. Acad. Sci., Hung., 29: 371 (1970).

Davis, R. Jr., Progress Report on the Brookhaven Solar Neutrino Experiment, Atti Accad. Naz. Lincei, Rend., Cl. Sci. Fis., Mat. Natur., 157: 59 (1971).

Bahcall, J. N., and Davis, R. Jr., Upper Limit on Neutrino Energy Associated with Weber Pulses, Phys. Rev. Lett., 26: 662 (1971).

03:30 FORMATION CROSS SECTIONS OF HIGH-ENERGY FISSION AND SPALLATION PRODUCTS.

Friedlander, G., Chu, Y. Y., Cumming, J. B., Hudis, J., Katcoff, S. (Brookhaven National Laboratory, Chemistry Department).

When a beam of high-energy (≫100-MeV) particles interacts with a medium- or high-Z target, a multitude of nuclides is produced. Formation cross sections for individual product nuclides are thus among the basic data needed for an understanding of high-energy nuclear reactions, and a program of measurements of such cross sections has been in progress at BNL for twenty years. Current emphasis is on (1) development of techniques for determination of many cross sections in medium-Z targets by direct gamma spectroscopy with Ge(Li) detectors and (2) detailed studies of charge and mass distributions in the region of rare earth products from 28-GeV-proton irradiations of Th and Ta targets. In the latter studies, chemical and mass separations are performed as needed to isolate particular products, but direct measurements of short-lived rare earth α emitters are also in progress since the measured yield of a given mass chain may have to be corrected for feeding or depletion by α decay.

Measurements of spallation cross sections in a Cu target irradiated with 3.9-GeV ^{14}N ions in the PPA will be compared with corresponding cross sections for protons of the same total kinetic energy. The direct gamma spectroscopy technique will be applied to spallation studies with 200-GeV protons at NAL and with pions at LAMPF.

PUBLICATIONS

Franz, E. M., and Friedlander, G., Cross Sections for the Production of ^{84}Rb, ^{86}Rb, ^{132}Cs, and ^{136}Cs from Thorium and Uranium by 28.5-GeV Protons, Phys. Rev., C, 4: 1671 (1971).

Chu, Y. Y., Franz, E. M., Friedlander, G., and Karol, P. J., Interaction of 28-GeV Protons with Uranium: Charge and Mass Distribution of Rare Earth Products, Phys. Rev., C, 4: 2202 (1971).

Thompson, S. O., Husain, L., and Katcoff, S., ^{12}C($\bar{p}$,$\bar{p}$n)^{11}C, ^{12}C(π^-,π^-n)^{11}C, and ^{19}F(π^-,π^-n)^{18}F Cross Sections at 2.5 GeV/c, Phys. Rev., C, 3: 1538 (1971).

03:31 COMPUTER SIMULATIONS OF HIGH- AND LOW-ENERGY NUCLEAR REACTIONS. Harp, G. D., Friedlander, G. Miller, J. M., (Columbia Univ.), Bertrand, F. E. (ORNL). (Brookhaven National Laboratory, Chemistry Department).

In parallel with the extensive experimental investigations of both high- and low-energy nuclear reactions at BNL, theoretical studies have always been carried on to aid in the systematization and understanding of the experimental results. One nuclear model that has proved exceptionally useful for this purpose is the intranuclear cascade evaporation model. This model is continually being improved as more precise experimental information becomes available. At the present time, the model is fairly successful in predicting such seemingly unrelated quantities as high-energy proton spectra and radiochemically measured cross sections.

The intranuclear cascade model has recently been extended to deal with reactions induced by 60- to 300-MeV pions. This particular model has the unique feature that it considers the participation of the unstable (3,3) isobar in the cascade process. As yet, the available experimental data are insufficient for an adequate test of the various assumptions made in the model. The predictions of this model are now being used to design experiments for this purpose. For example, recoil-range calculations are now underway that will provide quantitative information for proposed recoil-range experiments with incident pions. The model can and will serve also as a prototype for treating other unstable particles such as $T = 1/2$ isobars, ρ mesons, etc.

A different model, treating the emission of nucleons from excited nuclei prior to attainment of statistical equilibrium, has also been developed. Its predictions for proton and neutron energy spectra are in good agreement with experimental data obtained at ORNL. Further refinements of this model are under way.

PUBLICATIONS

Harp, G. D., and Miller, J. M., Precompound Decay from a Time-Dependent Point of View, Phys. Rev., C, 3: 1847 (1971).

Chen, K., Friedlander, G., Harp, G. D., and Miller, J. M., Effects of Nucleon Pair Correlations on Monte Carlo Intranuclear Cascade Simulations, Phys. Rev., C, 4: 2234 (1971).

Barashenkov, V. S., Bertini, H. W., Chen, K., Friedlander, G., Harp, G. D., Iljinov, A. S., Miller, J. M., and Toneev, V. D., Medium Energy Intranuclear Cascade Calculations: A Comparative Study, Nucl. Phys., A, 187: 531 (1972).

03:32 SOLID STATE TRACK DETECTOR STUDIES OF HIGH-ENERGY NUCLEAR REACTIONS. Katcoff, S.; Hudis, J. (Brookhaven National Laboratory, Chemistry Department.

The primary aim of high-energy nuclear reaction studies is the understanding of the complicated behavior of nuclei when they are subjected to bombardment by a variety of projectiles. Irradiations are performed in primary and secondary beams at the Brookhaven AGS and at other accelerators such as the Berkeley Bevatron, NAL, and LAMPF.

Total binary and ternary fission cross sections are best measured with solid state track detectors such as mica or Lexan. Results obtained recently for U, Bi, Au, and Ag irradiated by 29-GeV ^{14}N are being extended to include irradiations by 3.9- and 2.1-GeV ^{14}N ions. It is planned to do similar experiments with 200-GeV protons from NAL.

PUBLICATIONS

Katcoff, S., and Hudis, J., Fission of U, Bi, Au, and Ag Induced by 29-GeV ^{14}N ions, Phys. Rev. Lett., 28: 1066 (1972).

Husain, L., and Katcoff, S., *Antiproton- and Pion-Induced Fission* at 2.5 GeV/c, Phys. Rev., C, 4: 263 (1971).

03:33 STUDIES OF HIGH-ENERGY NUCLEAR REACTIONS WITH COUNTER TECHNIQUES. Remsberg, L. P., (Brookhaven National Laboratory, Chemistry Department).

The primary objective of this work is the characterization and elucidation of mechanisms of nuclear reactions induced by high-energy protons. The current emphasis is on those reactions that yield products with mass numbers between 10 and 50 from heavy element targets irradiated by 28-GeV protons.

Detailed information is obtained by measuring angular and energy distributions of a wide range of product nuclei, and also by measuring angular, energy, and mass correlations of coincident pairs of product nuclei. Pairs of semi-conductor detectors are employed as telescopes to determine the kinetic energy, nuclear charge, and mass of individual nuclear fragments recoiling out of thin targets through measurements of their specific energy loss, time-of-flight, and energy.

PUBLICATIONS

Remsberg, L. P., Plasil, F., Cumming, J. B., Perlman, M. L., *Fragment Energy and Velocity Measurements in Fission of* Bismuth by 2.9-GeV Protons, Phys. Rev., C, 1: 265 (1970).

03:34 PROTON AND ALPHA-PARTICLE CROSS SECTIONS FOR ELEMENTS PRESENT IN LUNAR TARGETS. Thompson, S. (Brookhaven National Laboratory, Chemistry Department).

Radioactivities produced in material that is on the moon for a period of a few years (e.g., artifacts left by astronauts, or targets designed specifically for this purpose) can give information about solar flares.

For this reason, light- and medium-atomic weight targets (Na, Al, Si, Ca, Ti, Cr, Zr, etc.) have been irradiated with 33- and 50-MeV protons and with 46-MeV alpha particles, in order to determine cross sections for formation of the most prominent radionuclides. This work is being continued, and the energy range of proton irradiations will be extended to 200 MeV, by use of the new LINAC facility.

03:35 NUCLEAR CHEMISTRY RESEARCH OF HIGH-ENERGY NUCLEAR REACTIONS. Caretto, Albert A. Jr. (Carnegie-Mellon University, Department of Chemistry, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).

The overall objective of this research is the determination *of the mechanism of various types of nuclear reactions using* radiochemical techniques. Specifically, the kinds of reactions under investigation include high-energy proton-, alpha-, and pion-induced reactions. The so-called simple high-energy reactions, reactions of the type (p,pn), $(\alpha,\alpha n)$, and (π^+,π^+n) will be examined in considerable detail. These reactions should be sensitive to and provide a means of examining the details of the nuclear structure of the target. The probability of these reactions should also be sensitive to the nucleon skin thickness and thus provide a probe of this peripheral nuclear region. Another area of interest involves the study of heavy-ion-induced transfer reactions. These reactions are also sensitive to the nature of the peripheral nuclear region. Reactions of the type alpha transfer and double nucleon transfer, or charge exchange, are under study.

These studies are carried out by the determination of cross sections, excitation functions, and the product recoil angular and range distributions. This work has made use of the facilities available at Argonne National Laboratory, the Zero Gradient Synchrotron, the Space Radiation Effects Laboratory 600-MeV synchrocyclotron, and the Yale University Heavy Ion Linear Accelerator. Future experiments will also make use of the meson facility at Los Alamos and the accelerator at the National Accelerator Laboratory.

PUBLICATIONS

Yu, Y–W., and Caretto, A. A. Jr., The Half-Lives of ^{84}Zr and ^{85}Zr, J. Inorg. Nucl. Chem., 33: 3233 (1971).

Kiely, F. M., and Caretto, A. A. Jr., Differential Recoil Study of the $^{25}Mg(p,2p)^{24}Na$ Reaction, Phys. Rev., C, 4: 137 (1971).

Yu, Y–W., Church, L. B., and Caretto, A. A. Jr., The Angular Distribution of Recoil Productions from Some Simple Reactions of 400 MeV Protons with ^{58}Ni and ^{197}Au, Nucl. Phys., A, 152: 295 (1970).

Nieckarz, W. J. Jr., and Caretto, A. A. Jr., Nuclear Structure Effects on (p,2 Nucleon) Reactions on the Separated Isotopes of Cadmium at 400 MeV, Phys. Rev., C, 3: 1921 (1970).

Schall, R. F. Jr., and Caretto, A. A. Jr., Nuclear Structure Effects in (p,2 Nucleon) Reactions on the Separated Isotopes of Tellurium at 300 MeV, Phys. Rev., C, 3: 1924 (1970).

03:36 NUCLEAR CHEMISTRY RESEARCH. Sugarman, Nathan; and Turkevich, Anthony. (University of Chicago, Enrico Fermi Institute, 5630 Ellis Avenue, Chicago, Illinois 60637).

The Nuclear Chemistry Research Program at The University of Chicago involves the study of the interaction of high-energy projectiles with complex nuclei, and the investigation of extra-terrestrial objects, such as meteorites, by nuclear chemical techniques. The 12-GeV Argonne ZGS Proton Synchrotron, and hopefully, the 200-GeV National Accelerator Proton Synchrotron and the Los Alamos Meson facility will provide the high-energy projectiles. The irradiated targets will be analyzed radiochemically for the yields, mass and charge distribution, and momentum transfer characteristics of products in the near-target, fission-mass, and fragment-mass regions. These data will provide information on the production mechanisms and the behavior of nuclear matter in a state of high excitation.

The cosmochemical studies involve use of ultra-low-level techniques for the determination of the radioactivity induced in meteorites by solar and galactic high-energy particles, and the interpretation of these data using measured cross sections and semi-theoretical models of the proliferation of nuclear particles in a solid body bombarded by high-energy particles. The laboratory is also cooperating in the determination, by neutron activation techniques, of trace elements, such as lead and mercury, in returned lunar samples.

PUBLICATIONS

Panontin, J. A., and Sugarman, N., Mass Yield Distribution and Charge Dispersion in 450 MeV Proton Fission of ^{238}U, J. Inorg. Nucl. Chem., 34: 1485 (1972).

Turkevich, Anthony, Reed, G. W. Jr., Heydegger, H. R., and Collister, J., Activation Analysis Determination of Uranium and ^{204}Pb in Apollo 11 Lunar Fines, in Proceedings of the Second Lunar Science Conferences, Vol. 2, p. 1565, The MIT Press, Cambridge, Mass., (1971).

Van Ginneken, A., and Turkevich, Anthony, Production of ^{54}Mn and ^{65}Zn from Copper in Thick Targets by 0.45-GeV, 1.0-GeV, and 3.0-GeV Protons, J. Geophys. Res., 75: 5121 (1970).

03:37 THE MECHANISMS OF NUCLEAR REACTIONS.

Miller, J. M.; Logan, D.; Jaffe, G.; and Zebelman; Eyal, Y. (Columbia University, Department of Chemistry, New York, New York 10027).

The general objective of this continuing study is to understand in quantitative detail the factors that determine the course of nuclear reactions. In the recent past, the investigations have been primarily directed toward the evaluation of the roles of isospin and angular-momentum conservation in reactions that proceed through the formation of a compound nucleus as well as the range of validity of Bohr's Independence Hypothesis for such reactions. As a direct outgrowth of these studies, most of which were carried out with heavy-ion projectiles, we are now mainly concerned with an investigation of the complementary reactions with heavy ions that do not proceed through the formation of a compound nucleus: stripping and pickup reactions. The current investigation utilizes both solid-state counter-telescope techniques for the determination of the identity, energy, and angular distributions of the light particles that are emitted as well as radiochemical techniques for the complementary heavy residual nuclei. This complementary study is particularly valuable for the investigation of the behavior of the particles that have been transferred from the incident to the target nucleus. It is anticipated that these studies will occupy us for the new few years.

PUBLICATIONS

Miller, J. M., The Role of Angular Momentum and Isobaric Spin in Tests of the Independence Hypothesis, in Statistical Properties of Nuclei, J. B. Garg, (Ed.), p. 505, Plenum Publishing Corporation, New York, (1972).

Kowalski, L., Zebelman, A., Kandil, A., and Miller, J. M., On the Angular Distribution of Fission Fragments from the ^{170}Yb Compound Nucleus Excited to 107 MeV, Phys. Rev., C, 3: 1370 (1971).

03:38 THIN FILM DETECTORS.

Muga, M. L. (University of Florida, Department of Chemistry, 406 Nuclear Science Bldg., Gainesville, Florida 32601).

We have applied the recently invented thin film detectors (TFD) to the study of fission decay phenomena and other heavy ion reactions. In these studies (described below) particular advantage is made of the dE/dx response characteristics of the TFD to the passage of energetic heavy ions. An experiment to study the emission of light charged particles (accompanying the fission decay of ^{252}Cf) at very acute angles (<20°) with respect to the fission fragment is now in progress. In another experiment, the TFD response to selected mass (by time-of-flight and by back-to-back coincident energy measuring techniques) groups of fission fragments is observed and indicates a very strange pattern of nuclear charge distribution for low total kinetic energy fission events. Continuation of calibration studies using accelerated heavy ions of known mass and energy is planned in order to complete our understanding of the TFD response dependence on charge, mass, and energy of the transiting heavy ion. Studies of the proton-induced fission of ^{232}Th and the fission-like break up of medium mass nuclei when bombarded with heavy ions is planned for the latter half of this year. Longer range plans would make use of the more energetic heavy-ion accelerators (if available) for the calibration of the TFD at higher energies (up to 7.5 MeV/nucleon) and for heavier mass ions (up to ^{238}U), followed by the application of TFD methods to the study of heavy ion reactions in this higher energy-heavier mass region and beyond.

PUBLICATIONS

Muga, M. L., A Versatile dE/dx Detector for Heavy Mass Nuclear Particles, Nucl. Instrum. Methods, 95: 349 (1971).

Muga, M. L., Proposed Detector Assembly for Identification of Heavy Mass Cosmic Ray Nuclei of Low Energies, IEEE (Inst. Elec. Electron. Eng.), Trans. Nucl. Sci., NS-19 (1): 384 (February 1972).

Muga, M. L., and Taylor, H. E., An Improved Charged Particle Detector, U. S. Patent No. 3,567,925, Mar. 2, 1971.

03:39 STUDIES OF THE MASSES AND DECAY SCHEMES OF LIGHT NUCLEI FAR FROM THE VALLEY OF BETA-STABILITY.

Cerny, Joseph. (Lawrence Berkeley Laboratory: Nuclear Chemistry Division).

Research in this project is directed toward characterizing the properties of nuclei that lie on the limits of nuclear stability in the lighter elements. The masses of these "exotic" nuclei are used to test theoretical mass formulas that predict nuclear properties throughout the periodic table, while their decay schemes are studied to search for new modes of radioactive decay.

Both conventional particles and heavy ions from the 88-inch cyclotron are used to induce multi-neutron and multi-proton transfer reactions capable of reaching hitherto uncharacterized nuclei and measuring their masses. Such reactions as ^{12}C(^{3}He, ^{6}He)^{9}C have been used to study neutron-deficient nuclei and reactions like ^{26}Mg(^{6}Li,^{9}C)^{23}F are under investigation to study neutron-excess nuclei. These experiments utilize electronic systems capable of determining the identity of the reaction products and their energies even though only very low yields are observed.

Nuclei far from stability often show interesting new decay modes — such as beta-delayed proton emission or true proton radioactivity — and are detected through their unique radiations. A gas transport or helium jet system is used to sweep the nuclear reaction products to a remote area where high resolution, low background data may be obtained. Studies of the decay schemes of these nuclei provide a great deal of spectroscopic information on nuclear energy levels, spins and parities; further, some of these studies permit fundamental investigations of the beta-decay process itself and its interaction with nuclear symmetry principles.

PUBLICATIONS

Mendelson, R., Wozniak, G. J., Bacher, A. D., Loiseaux, J. M., and Cerny, J., Mass of ^{13}O and the Isobaric Multiplet Mass Equation, Phys. Rev. Lett., 25: 533 (1970).

Cerny, J., Esterl, J. E., Gough, R. A., and Sextro, R. G., Confirmed Proton Radioactivity of ^{53m}Co, Phys. Lett., B, 33: 284 (1970).

Hardy, J. C., Esterl, J. E., Sextro, R. G., and Cerny, J., Isospin Purity and Delayed-Proton Decay: ^{17}Ne and ^{33}Ar, Phys. Rev., C, 3: 700 (1971).

Gough, R. A., Sextro, R. G., and Cerny, J., Beta-Delayed Proton Emission of ^{23}Al, Phys. Rev. Lett., 28: 510 (1972).

03:40 NUCLEAR REACTIONS WITH POLARIZED PROTONS AND DEUTERONS.

Conzett, H. E. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

Polarized proton and deuteron beams are used to study the spin-dependence of the interaction of these particles with nuclei. Large spin-dependent effects are generally seen in nuclear scattering and reactions involving protons and deuterons, so polarization experiments are essential for any realistic test of the theory of these processes. The polarized-ion source has resulted in polarized cyclotron beams above 15 MeV that surpass, in intensity and energy range, those few in existence at other facilities. This makes possible many more-detailed investigations of the role played by the nuclear spin in the nuclear interaction. Our present work and future plans include:

(a) Measurements of the vector-analyzing power in $\vec{d}$ – ^{4}He scattering between 15 and 45 MeV. These measurements establish ^{4}He as a standard analyzer for vector-polarized deuterons above 15 MeV, where none had previously existed.

(b) Measurements of the vector-analyzing power of various reactions induced with polarized protons and deuterons. These result in unambiguous determinations of the spins of states of the product nuclei and also provide detailed information on the reaction mechanism itself.

(c) Development of a polarized neutron beam from the ^{3}He($\vec{d}$,$\vec{n}$) ^{4}He reaction, to be used in $\vec{n}$–p scattering to answer the still outstanding questions of the T = 0 nucleon–nucleon interaction.

PUBLICATIONS

Hardy, J. C., Bacher, A. D., Plattner, G. R., Macdonald, J. A., and Sextro, R. G., Two-Nucleon-Transfer Reactions Induced by Polarized Protons, Phys. Rev. Lett., 25: 298 (1970).

Plattner, G. R., and Bacher, A. D., Absolute Calibration of Spin-½ Polarization, Phys. Lett., B, 36: 211 (1971).

Bacher, A. D., Plattner, G. R., Conzett, H. E., Clark, D. J., Grunder, H., and Tivol, W. F., Polarization and Cross-Section Measurements for p-^{4}He Elastic Scattering Between 20 and 45 MeV, Phys. Rev., C, 5: 1147 (1972).

Plattner, G. R., Bacher, A. D., and Conzett, H. E., Phase Shifts for p-^{4}He Elastic Scattering Between 20 and 45 MeV, Phys. Rev., C, 5: 1158 (1972).

de Swiniarski, R., Bacher, A. D., Resmini, F. G., Plattner, G. R., Hendrie, D. L., and Raynal, J., Determination of Deformation Parameters of ^{20}Ne and ^{22}Ne by Inelastic Scattering of Polarized Protons, Phys. Rev. Lett., 28: 1139 (1972).

03:41 HEAVY ION NUCLEAR REACTIONS.

Harvey, B. G., and Hendrie, D. L. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

Heavy ion beams from the 88-inch cyclotron (^{12}C, ^{16}O, ^{20}Ne) are energy-analyzed so that the nuclear reactions that they induce in targets can be studied with high-energy resolution in a magnetic spectrometer. The spectrometer is equipped with a unique focal plane detector that unambiguously identifies the heavy ions resulting from the nuclear reactions as to their mass and atomic numbers.

The purposes of the project are a) to study the mechanism of heavy ion nuclear reactions and b) to apply these reactions to the study of nuclear structure. With objective a) in mind, relatively simple reactions have been studied in which one nucleon (proton or neutron) is transferred to or from the target nucleus. To investigate the role of the high angular momentum in heavy ion reactions, the interaction of 150-MeV ^{20}Ne ions with ^{27}Al nuclei is under investigation.

Work on objective b) has hardly begun: it awaits a better understanding of the reaction mechanisms. For example, it has just been discovered that the proton transfer reactions ^{54}Fe(^{16}O,^{15}N)^{55}Co and ^{54}Fe(^{12}C,^{11}B)^{55}Co populate the energy levels of ^{55}Co in very different yields. Comparison of the two reactions can probably be used to assign spin values to nuclear levels.

Assuming reasonable progress in the understanding of these simple reactions, more complex transfers of several nucleons will be studied. It will need much more experimental work to gain some insight into the role of the high angular momentum.

Since the ability to identify heavier and heavier ions, and to measure their energies with high precision, is of capital importance, work will continue to be done on the focal plane detector instrumentation. The counter system that has been developed may well have valuable applications in other fields (perhaps for medical radiography).

03:42 HIGH-ENERGY NUCLEAR REACTIONS INVOLVING THE NUCLEAR SURFACE.

Markowitz, S. S. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

The purpose of this research is to study the mechanisms of high-energy nuclear reactions, with special attention directed towards understanding simple reactions that can occur at or near the nuclear surface. By use of different nuclear projectiles available at LBL at the 184-inch synchrocyclotron (protons, ^{3}He and ^{4}He ions) in the energy range of hundreds of MeV, and by selecting carefully the target nuclides, it should be possible to see effects of the recently postulated neutron-skin and/or alpha-particle clustering at the nuclear surface. The procedure experimentally involves bombardment followed by gamma and beta detection with Ge(Li) and end-window gas proportional counters. Complex gamma spectra are analyzed with the aid of appropriate computer programs following multichannel analysis. Work is in progress on the system of Ge plus high-energy protons.

A proposal to study the mechanism of pion-induced nuclear reactions (by Ph.D. Candidate, Norman P. Jacob, and Prof. S. S. Markowitz) has been approved as a formal Research Proposal at the Los Alamos Meson Physics Facility (LAMPF). The purpose is to use π^+ and π^- mesons of various energies ranging about the free-particle pion–nucleon resonance energy to study fundamental interactions between pions and nucleons within nuclear matter. Simple reactions of pions with light elements, such as carbon, fluorine, oxygen, and others, will be measured by determining the excitation functions for (π,πn) reactions. The project will get under way in the summer of 1973, using the unique high-intensity and variable-energy meson beams attained at LAMPF, and will complement research done at Berkeley.

03:43 NUCLEAR REACTIONS INDUCED BY HEAVY IONS AT THE SuperHILAC: GENERAL RADIOCHEMICAL STUDIES.

Markowitz, S. S. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division.

Nuclear reactions induced by the heavy-ion beams at the SuperHILAC are complex and varied in nature when heavy target elements like thorium or uranium are involved. Many groups will be studying these reactions with a variety of physical or radiochemical methods. In the series of experiments contemplated here targets will be bombarded at the SuperHILAC and analyzed by radiochemical separation and measurement techniques with the purpose of identification and measurement of the yield of radioactive products with half-lives of a few minutes or longer. From the pattern of products it is believed that much can be learned about the nature of nuclear reactions induced by heavy ions including such general reaction types as compound–nucleus formation, cluster–transfer, spallation, and fission.

03:44 AVERAGE NUCLEAR PROPERTIES.

Myers, William D. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

A continuing program is underway for the calculation of macroscopic attributes of nuclei such as total binding and deformation energies, density distributions, and properties of nuclear collective dynamics. The approach employed places special emphasis on the fact that many nuclear characteristics can be described in terms of an expansion in powers of $A^{-1/3}$ (where A is the nuclear mass number). This feature of nuclei, which has its origin in the saturation of nuclear forces, has allowed us to formulate a simple algebraic description of nuclei.

The name droplet model has been chosen for this description since it is a natural extension of the well-known liquid drop model. The scope of this approach is evident when one considers that the data base relevant for the comparison of these model calculations with experiment includes nuclear ground state masses and deformation energies, fission barriers and half-lives, nuclear radii, isotope shifts, and single particle potential well parameters. In addition when suitable shell effects were included, the method led to the prediction of super-heavy elements and fission isomers.

The formulation of this approach and its generalization to other features of nuclei depends heavily upon concurrent studies employing the Thomas–Fermi statistical model. The Thomas–Fermi calculations that were performed in support of the current version of the droplet model are being extended to include highly excited nuclei and nuclei in a surrounding neutron gas. These studies, which are of value in themselves, will help us to formulate a temperature-dependent droplet model and a droplet model applicable to the study of crustal properties of neutron stars.

The past emphasis on static properties is being replaced by an increased concern with dynamical properties such as nuclear viscosity and moments of inertia. The goal is to provide a unified description of the essential features of nuclei important in the various frontier fields of nuclear physics: In heavy-ion physics, a description of interaction potentials, collective dynamics, and amalgamation probabilities; in intermediate energy physics, a description of nuclear density distributions which includes predictions of a neutron skin; and in nuclear astrophysics predictions of binding energies for use in r-process calculations and calculations of stellar dynamics as well as predictions of the nature of neutron stars.

PUBLICATIONS

Myers, William D., Nucl. Phys., A, 145: 387 (1970).
The Droplet Model, in Proceedings of the 1971 Mont Tremblant International Summer School, University of Toronto Press, 1972.

03:45 NUCLEAR FRAGMENTATION INDUCED BY HIGH-ENERGY PROJECTILES AT THE BEVATRON.

Poskanzer, A. M., and Hyde, E. K. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

The aims of the work are to study the mechanism of the production of nuclear fragments by high-energy projectiles and to produce new exotic light nuclei. Targets are placed in the external beam of the Bevatron and the emitted nuclear fragments are detected and identified using thin semiconductor counters that measure their total energy, rate-of-energy loss, and time-of-flight.

Studies have been completed on the energy spectra and angular distributions of helium through argon fragments from uranium and silver targets. Extension of the work to lighter target nuclei like aluminum is in progress. Extensions to heavier projectiles are planned when the Bevalac project, which links the SuperHILAC to the Bevatron, is completed. This would allow the use of projectiles as heavy as neon. A beginning is being made with the use of the high-energy alpha particle beam which is now available at the Bevatron in sufficient intensity.

Previous searches for exotic new isotopes have produced ^{11}Li, ^{14}B, ^{15}B, and ^{17}C. Searches for other nuclei, at the limits of particle stability, are in progress.

PUBLICATIONS

Poskanzer, A. M., Butler, G. W., and Hyde, E. K., Fragment

Production in the Interaction of 5.5-GeV Protons with Uranium, Phys. Rev., C, 3: 882 (1971).

Hyde, E. K., Butler, G. W., and Poskanzer, A. M., Characteristics of Fragments Produced in the Interaction of 5.5-GeV Protons with Silver, Phys. Rev., C, 4: 1759 (1971).

Butler, G. W., Poskanzer, A. M., and Landis, D. A., Identification of Nuclear Fragments by a Combined Time-of-Flight, ΔE−E Technique, Nucl. Instrum. Methods, 89: 189 (1970).

03:46 EFFECTS OF ANGULAR MOMENTUM IN HEAVY-ION REACTIONS. Stephens, Frank S., and Diamond, Richard M. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

The use of heavy ions can bring large amounts of angular momentum into the colliding system, but so much angular momentum may be involved that a new feature can occur, namely, failure of the compound nucleus to form because the centrifugal force is too great. Even with impact parameters corresponding to somewhat smaller amounts of angular momentum that could be retained by a compound nucleus at equilibrium, non-compound nucleus products may be formed because the colliding nuclei do not hold together long enough to reach equilibrium; there are local accumulations of energy (hot spots) on the nuclei where they come into contact that evaporate particles or spall off fragments in the collision. These ideas were suggested as long as 10 years ago, but in recent years refinements in techniques have made it possible to test them more directly.

We have carried out a study of the gamma rays emitted in-beam and out-of-beam from a target of ^{27}Al irradiated by ^{20}Ne of various energies. From the Doppler shifts observed with some of the lines and from a study of the gamma yields as a function of projectile energy and of target thickness, we have been able to distinguish those transitions coming from compound nucleus products and those from direct reactions. We plan to continue these studies using other target−projectile pairs in order to try to unravel what fraction of the cross section goes to compound nucleus evaporation products, to fission products, to quasi-elastic (transfer) reactions, and to the non-equilibrium escape reactions.

03:47 GENERAL FISSION RESEARCH. Thompson, S. G., and Moretto, L. G. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

The study of fission phenomena covering a wide range of targets, projectiles, and other conditions is planned. Some specific examples are the following: 1) measurements of fission barriers for some medium-weight elements. Such data provide an important basis for checking and improving recent most reliable mass formulas; 2) the energy dependence of the fission probabilities up to high energies for a wide range of target projectile combinations; 3) contributions of high-order fission to the total fission probabilities; 4) study of total compound nucleus cross sections at moderate and high energies are an important basis for items 1, 2, and 3 above; 5) influence of angular momentum on fission probabilities — involved also in heavy ion reaction studies; 6) fission fragment angular distributions (from aligned nuclei) provides information about transition states involved when nuclei undergo fission and may also give information about the pairing gap at the saddle point; and 7) studies of nuclear viscosities and inertias as available from fission phenomena (also involved in heavy-ion reaction studies).

PUBLICATIONS

Moretto, L. G., Thompson, S. G., Routti, J., and Gatti, R. C., Phys. Lett., B, 38: 471 (1972).

03:48 STUDIES IN HEAVY-ION REACTIONS. Tsang, Chin Fu. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

With the completion of the Super-Heavy-Ion-Linear-Accelerator at Berkeley (and other heavy ion accelerators in Europe) a whole new field is opened in the study of the process of heavy-ion reactions. Thus depending on the impact parameter in the collision of heavy ions with a target nucleus, several phenomena may occur: (1) many-nucleon-transfer reactions; (2) reactions in which the projectile and the target nuclei fuse together, but fission immediately without equilibrium being attained for the fused system; (3) reactions in which the compound nucleus is formed, but is unstable toward fission; and (4) compound nucleus formation. It is the aim of this project to understand the general dynamic features of these phenomena. Such an understanding is crucial in attempts to produce super-heavy nuclei by heavy-ion reactions. Many physical effects will have to be carefully considered, including rotational effects, fusion−fission ("vibrational") inertia, competition between neutron emission and fission at high excitation energies, and viscosity of the nuclear matter flow leading to the formation of a ground state compound nucleus. The problem is being attacked in two directions. First, simple models are constructed and experimental data are analyzed to extract the physics of the processes. Correlations will be made and predictions by extrapolations may then be possible. Second, more fundamental microscopic calculations are done on the various physical effects and then incorporated in the understanding of these reactions. Thus, for example, we have made a microscopic calculation of the rotational moment of inertia, and a calculation on the vibrational inertia by means of the Hill−Wheeler generator-coordinate method is being considered. It is hoped that this project will be able to throw light on what actually is happening in heavy-ion reactions, and to suggest the optimum conditions whereby superheavy nuclei may be produced.

03:49 NUCLEAR REACTION AND FISSION STUDIES. Gordon, G. E., Viola, V. E. Jr., and Walters, W. B. (University of Maryland, Department of Chemistry, College Park, Md. 20742).

The investigation of nuclear reactions induced by intermediate-energy projectiles is being investigated with two objectives in mind: (1) to understand nuclear reaction mechanisms, especially fission, in heavy element targets, and (2) to apply the results to understanding the origin of nature's elements. In order to test theoretical models of nuclear fission at moderately high excitation energies, we are studying reactions induced in actinide element targets with 60- to 160-MeV ^{4}He ions. These studies include (1) total reaction cross section and elastic scattering measurements, from which nuclear reaction parameters are derived; (2) fission fragment angular correlation measurements, which permit the separation of compound nucleus from direct processes; and (3) fragment angular distribution measurements that provide information about the nuclear shape at fission. A related problem involves determination of the probability of producing highly neutron-deficient nuclides by means of (^{4}He,xn) and (^{3}He,xn) reactions, where x is of the order of 10 to 15. We are attempting to use a new on-line counting technique which will permit half-life measurements in the microsecond range.

We are also attempting two kinds of fission studies with the use of Ge(Li) detectors to identify and measure intensities of γ rays from specific fission product nuclides: (1) by observing fission products collected on foils placed at various angles to the beam, we will measure angular distributions of specific products from fission induced by charged particles from the cyclotron; and (2) by observing fission products collected in foils placed against a ^{252}Cf source, we will measure ranges for various mass chains to search for fine structure of kinetic energy release previously suggested in the vicinity of double-closed-shell products of mass $A \sim 132$.

In addition, we are determining the probability of producing Li, Be, and B isotopes in proton bombardments of light target nuclides. These studies are designed to test various theories for the production of these elements in nature.

PUBLICATIONS

Minor, M. M., Salwin, A. E., Viola, V. E. Jr., Bondelid, R. O., and Theus, R. B., The Use of Position-Sensitive Semiconductor Detectors in the Study of Heavy Element Nuclear Reactions, Nucl. Instrum. Methods, 99: 63 (1972).

Viola, V. E. Jr., Minor, M. M., Salwin, A. S., Theus, R. B., and Bondelid, R. O., Direct Interaction Effects in the Fission of ^{238}U with 63.5-MeV ^{4}He Ions, Nucl. Phys , A, 174: 321 (1971).

Sikkeland, T., Clarkson, J. E., Steiger-Shafrir, N. H., and Viola, V. E., Jr., Fission Excitation Functions in Interactions of ^{11}B, ^{12}C, ^{14}N, and ^{19}F with Various Targets, Phys. Rev., C, 3: 329 (1971).

03:50 FISSION. Ferguson, R. L. (Pleasonton, F., Plasil, F., Schmitt, H. W., Physics Division). (Oak Ridge National Laboratory, Chemistry Division).

Studies of fission provide insight into the properties of nuclei at extreme distortions and thus are very useful in testing the limits of theory. Experimental determinations of such features as the prompt neutron and gamma ray deexcitation of fission fragments and the total kinetic energy released in fission of very heavy nuclei afford powerful means of probing new theoretical ideas.

We have recently measured the average number and energy of gamma rays emitted within 5 nsec after fission, as a function of fragment mass, for several cases of low-excitation fission and find very interesting features that seem to be associated with the deformability of the fragments. We are measuring prompt neutron emission in the fission of ^{209}Bi bombarded by alpha particles of 40 to 50-MeV. By varying the bombarding energy we hope to test predictions of the liquid-drop theory in a mass region where it has been shown to be reasonably applicable. We plan to measure the average total kinetic energy of fragments from the fission of

^{248}Cm bombarded by ^{12}C. This will allow us to test the prediction of the "two-center model" of fission, that fission of compound nuclei somewhat heavier than uranium leads to quite high kinetic energies but that the kinetic energy released in fission of superheavy elements would again be lower.

PUBLICATIONS

Erdal, B. R., Wahl, A. C., and Ferguson, R. L., Modes of Formation of Tin Fission Products, J. Inorg. Nucl. Chem., 33: 2763 (1971).

Ferguson, R. L., Plasil, F., Alam, G. D., and Schmitt, H. W., Fission Fragment Mass Distributions and Kinetic Energies for Spontaneous Fission Isomers, Nucl. Phys., A, 172: 33 (1971).

Roche, M. F., Troutner, D. E., and Ferguson, R. L., The Independent Yield of ^{112}Ag from Thermal Neutron Induced Fission of ^{233}U and ^{235}U, Radiochim. Acta, 16: 66 (1971).

Burnett, S. C., Ferguson, R. L., Plasil, F., and Schmitt, H. W., Neutron Emission and Fission Energetics in the Proton-Induced Fission of ^{233}U and ^{238}U, Phys. Rev., C, 3: 2034 (1971).

03:51 NEUTRON CROSS SECTIONS AND OTHER NUCLEAR PROPERTIES. Halperin, J., Stoughton, R. W. (Oak Ridge National Laboratory, Chemistry Division).

It is the purpose of this program to supply information on neutron reaction rates of importance to an atomic energy program. These rates are of importance in fission reactors and in fusion devices, so that the energies covered range from thermal to thermonuclear. Although heavy element and fission product nuclides are of special concern, almost any nuclide is of potential interest as a fuel, moderator, coolant, control element, structural material, flux monitor, or any reactant or product within a reactor environment. The measurements include thermal neutron cross sections, resonance integrals, fission spectrum neutron cross sections, and cross sections for (d,t) neutrons. Measurements will also be made of fission product yields, half-lives, $\bar{\nu}$ (neutrons/fission) for spontaneously fissionable nuclides, and decay schemes where pertinent.

Activation cross section measurements are carried out largely by radiochemical or mass spectroscopic techniques, which require very much smaller samples (micrograms to picograms) than are required by other methods of measurement and yet yield integral data of comparable accuracy. They thus complement the absorption method which provides differential cross sections as a function of energy but requires much larger samples. In cases of rare or highly radioactive materials, the advantages of working with minute samples can be a decisive factor in the choice of method.

PUBLICATIONS

Bemis, C. E., Jr., Druschel, R. E., Halperin, J., and Walton, J. R., Thermal Neutron Capture Cross Section and Resonance Integral for 10.7-Year ^{85}Kr, Nucl. Sci. Eng., 47: 371 (1972).

Bemis, C. E., Jr., Druschel, R. E., and Halperin, J., Effective Capture and Fission Cross Sections for ^{253}Cf, Nucl. Sci. Eng., 41: 146 (1970).

03:52 NUCLEAR REACTIONS. Thomas, T. Darrah. (Oregon State University, Department of Chemistry and Radiation Center,. Corvallis, OR 97331).

The main objective of this program is the understanding of low- and medium-energy nuclear reactions and fission. Recent work has been primarily concerned with the initial encounter between two complex nuclei and with the emission of long-range alpha particles in fission.

In the first of these areas, we have considered the question of whether two highly charged nuclei will distort one another during the time of their interaction. The answer is important to the design of experiments for super-heavy element production. Future work will involve experiments at the SuperHILAC at Berkeley and at the University of Washington to measure elastic scattering and nuclear reaction cross sections.

We also have done theoretical calculations on the formation of so-called quasi-molecular states in the interaction of two carbon nuclei at subbarrier energies. We find little theoretical reason to believe that quasi-molecules are formed and conclude that the resonances that have been attributed to quasi-molecules arise from modified shape-elastic scattering.

Our fission research has been aimed at using the angular and energy distributions of the long-range alpha particles to determine the parameters that describe the nucleus at scission. These results provide tests of various theories of fission.

PUBLICATIONS

Rajagopalan, M., and Thomas, T. D., Angular Distribution of Alpha Particles Emitted in the Fission of ^{252}Cr, Phys. Rev., C, 5: 2064-2071 (1972).

_____, and Thomas, T. D., Emission of Alpha Particles in the Fission of ^{238}U by 16- and 42-MeV Protons, Phys. Rev., C, 5: 1402-1409 (1972).

Mosel, U., Thomas, T. D., and Riesenfeldt, P., Ion–Ion Potentials in a Two-Center Model, Phys. Lett., B, 33: 563-7(1970).

Riesenfeldt, Peter W., and Thomas, T. Darrah, Influence of Nuclear Forces on the Coulomb Barrier in Heavy-Ion Reactions, Phys. Rev., C, 2: 2448-2449 (1970).

Riesenfeldt, Peter W., and Thomas, T. Darrah, Effect of Nuclear Deformability on Reaction Cross Sections, Phys. Rev., C, 2: 711-720 (1970).

03:53 CHARGES OF IONS PRODUCED AS NUCLEAR REACTION RECOILS. Wolke, Robert L. (University of Pittsburgh, Wherrett Laboratory of Nuclear Chemistry, Department of Chemistry, Pittsburgh, Pennsylvania 15213).

The primary objective of this project is to determine the effects of nuclear reactions on the extranuclear electrons of the atoms involved. The method being used is to measure the degree of ionization of the recoiling nuclear reaction products, utilizing a spectrograph attached to the reaction chamber. Currently, some deuteron-induced reactions are being used to produce boron and carbon ions recoiling from extremely thin targets. In this way the primary distribution of ionic charges is being sought as it arises from the sudden interactions involved in the reaction itself, relatively unmodified by subsequent interactions with a medium. The work is progressing through a series of different types of nuclear reactions designed to emphasize different possible ionization-producing mechanisms: coulomb shakeoff, recoil shakeoff, and a kind of non-adiabatic coulomb disruption of the electron cloud by the incident and emitted particles.

PUBLICATIONS

Wolke, R. L., Sorbo, R. A., Volkar, M. A., Gangadharan, S., and Mason, E. V. Jr., Instantaneous Charges of Recoils from Nuclear Scattering, Phys. Rev., Lett., 27: 1449 (1971).

03:54 THERMODYNAMIC STUDIES ON HEAVY ELEMENTS AND STUDIES IN NUCLEAR CHEMISTRY. Cobble, James W. (Purdue University, Department of Chemistry, Lafayette, Indiana 47907).

When ordinary binary fission is induced in elements of atomic number higher than gold using medium excitation energies (20 to 80 MeV), it was discovered in this laboratory that ternary fission was also produced. It is the purpose of this research project to study experimentally this unusual process and to elucidate the mechanism of ternary fission. Ternary fission products observed by radiochemical means to date range in mass and charge from ^{24}Na to ^{45}Ca. The very low formation cross sections vary sharply with energy, and with the charge and mass of the compound nucleus. By low-level radiochemical procedures the lower limits of detection have been extended to fractions of nano-barns. In the heavy elements, the ternary fission cross sections are observed to increase into the microbarn range. If this trend continues, the compound nuclei that can be reached by very heavy ions on uranium may undergo ternary fission as a major decay process.

The present experimental program consists of bombarding various target elements from gold to uranium with ^{4}He, ^{12}C, and ^{0}Ne ions. A fraction of the ternary products recoil out of the arget and are trapped on collecting foils, and then radiochemically separated and counted. The bombardments are being carried out at various angles with respect to the beam in an attempt to look at angular correlations and fission anisotropy as well as to discriminate against spallation impurities.

In future research it may be possible to study the ternary process by instrumental on-line methods if the cross section increases as expected into the "super-heavy" element range. The ternary process is also a valuable probe for true compound nucleus formation when heavier and heavier ions are used as bombarding projectiles. In such bombardments, the differences between ordinary binary fission and spallation processes become diffuse.

PUBLICATIONS

Hinchey, R. J., and Cobble, J. W., Standard State Entropies for the Aqueous Trivalent Lanthanide and Yttrium Ions, Inorg Chem., 9: 917 (1970).

_____, and Cobble, J. W., The Thermodynamic Functions for Pu^{3+} (aq) and the Entropies for Some Trivalent Actinide Ions, Inorg. Chem., 9: 922 (1970).

Uhl, D. L., McDaniel, T. L., and Cobble, J. W., Search for Evidence of Ternary Fission Induced in ^{197}Au, ^{209}Bi, and ^{239}Pu by Intermediate-Energy Helium Ions, Phys. Rev., C, 4: 1357 (1971).

Roginski, T. C., Davis, M. E., and Cobble, J. W., Fission of ^{232}Th Induced by Intermediate-Energy ^{4}He Ions, Phys. Rev., C, 4: 1361 (1971).

03:55 DEEXCITATION PROCESSES IN NUCLEAR REACTIONS. Porile, Norbert T. (Purdue University, Department of Chemistry, Lafayette, Indiana 47907).

The objective of this research program is the achievement of a detailed characterization of the mechanisms of various high- and medium-energy nuclear reactions.

Several investigations concerning the formation of neutron-deficient products in the interaction of uranium with 12-GeV protons are in progress. These include a measurement of the charge dispersion and recoil properties at A = 131, a study of the isotopic yields and recoil properties of xenon nuclides, and an investigation of the energy dependence of recoil properties of neutron-deficient isobars with A = 131 between 1 and 29 GeV.

Preparatory studies for the investigation of nuclear reactions induced by previously unavailable projectiles or at heretofore unaccessible energies are in progress. The interaction of silver with 200-GeV protons from the NAL synchrotron will be studied and comparative measurements are currently being performed at 12 GeV. An experiment to study the formation of ^{24}Na from various targets irradiated by 100- to 400-MeV pions from LAMPF is in preparation.

Various projects designed to provide a detailed understanding of compound nuclear reactions induced by 10- to 20-MeV protons and α particles in medium A targets are in progress. A study of the density of highly excited levels of ^{63}Cu and ^{65}Cu populated in (α,p), (p,α), (α,α'), and (p,p') reactions is currently being performed. Studies of the independence hypothesis and of the effects on its validity due to iso-spin conservation and pre-compound emission are being performed by means of differential cross section measurements. The compound nuclei of interest in this work are ^{56}Fe, ^{64}Zn, and ^{66}Zn.

PUBLICATIONS

Chang, S. K., and Porile, N. T., Differential Range Study of the ^{65}Cu(^{3}He,α) Reaction at 32 MeV, Phys. Rev., C, 5: 1247 (1972).

Kennedy, A. J., Pacer, J. C., Sprinzak, A., Wiley, J., and Porile, N. T., Levels of ^{55}Co Populated in Compound Nuclear Reactions, Phys. Rev., C, 5: 500 (1972).

Chang, S. K., and Porile, N. T., Differential Range Study of the ^{65}Cu(α,αn) Reaction at Intermediate Energies, J. Inorg. Nucl. Chem., 34: 413 (1972).

Panontin, J., and Porile, N. T., Charge Distribution and Recoil Properties in the Fission of ^{208}Pb by 11.5 GeV Protons, J. Inorg. Nucl. Chem., 33: 3211 (1971).

Beg, K., and Porile, N. T., Energy Dependence of the Recoil Properties of Products from the Interaction of ^{238}U with 0.45–11.5 GeV Protons, Phys. Rev., C, 3: 1631 (1971).

03:56 NUCLEAR STRUCTURE STUDIES. Preiss, Ivor L. (Rensselaer Polytechnic Institute, Department of Chemistry, Troy, New York 12181).

The objectives of the research are to determine the effects of nuclear structure on nuclear reactions, and to elucidate details of structure as it relates to nuclear deformation.

We have found that the photonuclear reactions of ^{51}V between 40 and 100 MeV exhibit a character that cannot be explained by the classical dipole absorption excitation process or a statistical deexcitation. It is hoped that studies of other target and product nuclei can be undertaken to determine whether the target and residual nuclear structure influence photonuclear processes.

Isomerism has been found in ^{69}Se, ^{70}Se, ^{71}Se, and ^{154}Pm. The isomerism in selenium argues for a deformed nuclear core, while that of ^{154}Pm indicates a deformation 30% larger than anticipated. Decay scheme studies are being continued, in both mass regions to determine the magnitude of deformation for Se, and to ascertain whether ^{154}Pm is an isolated case or whether isomerism is a characteristic of the mass region. The possibility of isomerism due to a change in nuclear shape presents itself. We have begun studies of various nuclear reactions to determine whether a specific reaction mechanism may favor a specific shape in the residual nucleus.

The reaction and decay studies are carried out at Yale, NBS, and SUNY-Albany accelerator laboratories, as well as at RPI.

PUBLICATIONS

Dewanjee, M. K., and Preiss, I. L., Decay of Samarium Isotopes: ^{140}Sm, ^{141m}Sm, ^{142}Sm and $^{143(m+g)}$Sm, J. Inorg. Nucl. Chem., 34: 1105 (1972).

Collé, R. P., and Preiss, I. L., An Isopropanol Solid CO_2 Cooled Accelerator Target Assembly, J. Phys., E (London), 4: 977 (1971).

LaBrecque, J. J., and Preiss, I. L., Decay of ^{154}Pm, J. Inorg. Nucl. Chem., 35: (1972).

03:57 NEUTRON AND GAMMA EMISSION FROM HIGHLY EXCITED STATES AND STATES WITH HIGH SPIN. Sperber, Daniel. (Rensselaer Polytechnic Institute, Department of Physics, Troy, New York 12181).

The purpose of the current research is the application of the statistical model to the study of nuclear reactions in the region of highly overlapping levels. Of immediate interest is the study of (a) (α,xn) reactions for deformed nuclei, (b) heavy-ion-induced reactions and reactions in which the compound nucleus is far off the beta stability line, (c) reaction in which fission competes with particle and gamma emission, (d) the statistical study of reactions that yield information about the double-humped barrier and the inertial parameters as a function of deformation, and (e) the study of possible heavy-ion-induced reaction for the synthesis of super-heavy elements. As can be seen all problems concern themselves with the highly excited and states with high spin in heavy nuclei for which the statistical model is most appropriate. The main philosophy in the present program is to formulate the theory from first principles as far as possible and to reduce the number of adjustable parameters to a minimum. Most observable quantities depend on the population of states in all intermediate and final nuclei as a function of time, energy, and spin. Coupled integro-differential equations for the population of states are derived and solved. From the calculated population of states the observable quantities are evaluated.

PUBLICATIONS

Liggett, G., Sperber, D., Angular Distribution of Particles Evaporated in Nuclear Reactions, Phys. Rev., C, 3: 167 (1971).

______, and Sperber, D., Isomer Ratio for (b, xn, py; γ) Reactions, Phys. Rev., C, 3: 447 (1971).

Sperber, Daniel, The Compound Nucleus and Its Decay in Proceedings of the Fourth International–Polish Summer Institute on Nuclear Physics, Vol. I, pp. 102-200, University of Warsaw (1972).

03:58 NUCLEAR REACTION MECHANISMS: MECHANISMS OF HEAVY-ION REACTIONS. Blann, M. (University of Rochester, Department of Chemistry, Rochester, N. Y. 14627).

The question of describing the mechanisms of reactions between large aggregates of nuclear matter, and in particular the conditions under which they undergo nuclear fusion, is very much an open question. Our program is aimed at providing models for this process. We are proceeding along two routes. The first of these involves making highly precise experimental measurements of the cross sections for various reaction channels in heavy-ion reactions. We plan to pursue this program further at LBL Super-HILAC. The second aspect involves searches and/or development of models that will give a basis for understanding the experimental results. A gyrostatic model is presently under investigation, and calculations with this model will be used to suggest more definitive experiments.

PUBLICATIONS

Winn, W. G., Gutbrod, H. H., and Blann, M., Predicted Limits for the Production of Nuclides Far from Stability, Nucl. Phys., A, 188: 423 (1972).

Doron, T. A., and Blann, M., Decay Scheme Studies of Short Lived Isotopes of 69 ≤ A ≤ 88 Produced by Heavy Ion Bombardment, Nucl. Phys., A, 161: 12 (1971).

03:59 NUCLEAR REACTION MECHANISMS: NUCLEAR EQUILIBRATION MODELS. Blann, M. (University of Rochester, Department of Chemistry, Rochester, N. Y. 14627).

The question of the equilibration process in nuclear reactions, what happens between the initial interaction of target and projectile and the achievement of equilibrium, is both an open and an important problem. Our main thrust has been in the developing and testing of classical models that will permit prediction of these phenomena. Such models will be very useful in treating many other areas of nuclear reaction models; and indeed other applications have already been made. We are currently pursuing two paths in the development of these models. One is to evaluate the intranuclear transition rate for nucleon–nucleon interactions as a function of nuclear density and Fermi energy. The second is to develop a model based on a Thomas–Fermi approach whereby reactions induced by complex particles might be treated within a preequilibrium model formalism.

PUBLICATIONS

Blann, M., Importance of the Nuclear Density Distribution on Preequilibrium Decay, Phys. Rev. Lett., 28: 757 (1972).

———, and Mignerey, A., Preequilibrium Decay at Moderate Excitations and the Hybrid Model, Nucl. Phys., A, 186: 245 (1972).

———, Hybrid Model for Preequilibrium Decay in Nuclear Reactions, Phys. Rev. Lett. 27: 337, 700(E), and 1550(E) (1971).

Cline, C. K., and Blann, M., The Preequilibrium Statistical Model: Description of the Nuclear Equilibration Process and Parameterization of the Model, Nucl. Phys., A, 172: 225 (1971).

———, and Lanzafame, F. M., Preequilibrium Statistical Model: Analyses of Excitation Functions, Nucl. Phys., A, 142: 559 (1970).

03:60 STUDIES OF NUCLEAR FISSION, LOW-ENERGY NUCLEAR REACTIONS AND TRANSURANIC NUCLEI. Huizenga, John R. (University of Rochester, Departments of Chemistry and Physics, Rochester, New York 14627).

The work in progress and proposed for this next year includes studies of nucleon-transfer reactions (emphasizing the deformed lanthanide and actinide nuclei), nuclear fission, experimental and theoretical nuclear level densities, nuclear reaction mechanisms, and the effects of chemical environment and high pressure on electron capture. The nucleon-transfer reactions give information on the energies, spins, and parities of deformed nuclei that are used to test various theoretical models of these nuclei. The nuclear fission experiments are performed with heavy ions to gain insights into questions of angular momentum, reaction mechanism, and potential energy surfaces of highly deformed nuclei. The question of nuclear level density is fundamental in our understanding of nuclear statistical processes, and it is especially important to study the effect of nuclear shell structure on level density. Information on the change in electron density at the ^{7}Be nucleus with pressure is being investigated by observing the change in electron-capture half-life.

PUBLICATIONS

Lu, C. C., Huizenga, J. R., Stephan, C. J., and Gorski, A. J., Effects of Isospin on Statistical Nuclear Decay, Nucl. Phys., A, 164: 225 (1971).

Yuen, G., Rizzo, G. T., Behkami, A. N., and Huizenga, J. R., Fragment Angular Distributions of Neutron-Induced Fission of ^{230}Th, Nucl. Phys., A, 171: 614 (1971).

Vaz, L. C., Lu, C. C., and Huizenga, J. R., Isospin and the Bohr Independence Hypothesis, Phys. Rev., C, 5: 463 (1972).

Huizenga, J. R., Experimental and Theoretical Nuclear Level Densities, in Statistical Properties of Nuclei, J. B. Garg (Ed.), p. 425, Plenum Publishing Corporation, 1972.

Williams, F. C. Jr., Chan, G., and Huizenga, J. R., The Significance of Shell Corrections in the Parameterization of Numerical State Density Calculations, Nucl. Phys., A, 187: 545 (1972).

03:61 ANGULAR MOMENTUM EFFECTS IN NUCLEAR REACTIONS. Natowitz, Joseph B., (Texas A&M University, Department of Chemistry, College Station, Texas 77843).

Reactions induced by high-energy (~5- to 30-MeV/amu) heavy ions are being utilized to study the role of angular momentum on the production and deexcitation of highly excited nuclei. Two basic experimental techniques, the use of dielectric track detectors and the use of semiconductor detector telescopes, are employed to observe the various charged species (including recoiling product nuclei) that are produced during the reactions. Emphasis is on the investigation of upper limits to the nuclear angular momentum and on the effect of high angular momentum on the statistical deexcitation process. The study includes an exploration of rare modes of deexcitation such as heavy fragment emission and sub-barrier α particle emission which are expected to be enhanced at high angular momentum. Future emphasis will shift to the competition between various possible reaction mechanisms for reactions with high-energy heavy ions and the use of heavy-ion transfer reactions to obtain structural information.

PUBLICATIONS

Natowitz, J. B., and Chulick, E. T., Limits to the Formation of Compound Nuclei in Heavy-Ion Induced Reactions, in Proceedin of the European Conference on Nuclear Physics, Aix-en-Provence, France, June 1972, p. 52.

Natowitz, J. B., Complete Fusion Cross Sections for the Reactions of Heavy Ions with Cu, Ag, Au, and Bi, Phys. Rev., C, 1: 623 (1970).

Lewis, C. W., Natowitz, J. B., and Watson, R. L., A Precise Test of the Z^2 Dependence of X-Ray Emission Induced by Alpha Particles and Deuterons, Phys. Rev. Lett., 26: 481 (1971).

Natowitz, J. B., and Chulick, E. T., Angular Distributions of Fission Fragments in the First Chance Fission of ^{198}Hg, Nucl. Phys., A, 172: 185 (1971).

03:62 MECHANISMS OF LOW-ENERGY NUCLEAR REACTIONS. Sarantites, Demetrios G. (Washington University, Department of Chemistry, St. Louis, Missouri 63130).

The long-term goal of these research efforts is to advance our detailed understanding of the mechanism of nuclear reactions below ~100 MeV. Current efforts concentrate on experiments designed to provide quantitative information about the parameters that describe the emission of prompt γ rays from nucleon unbound states, which in turn plays an important role in determining the relative cross sections of reactions such as $(\alpha,p\gamma)$ and $\alpha,2p\gamma)$ or $(\alpha,n\gamma)$ and $(\alpha,2n\gamma)$. Some of these parameters include the mean life-times, the multipole character and the multiplicity of the γ rays in the de-exciting cascades. Experiments for this purpose employ sophisticated multiparameter $p\gamma$, $n\gamma$, $p\gamma(\theta)$, or $n\gamma(\theta)$ coincidence experiments with annular Si(Li) detectors or $(E + \Delta E) \times \Delta E$ detector telescopes, large scintillator neutron detectors and ultra high-resolution Ge(Li) γ ray detectors, including angular correlation and Doppler shift attenuation measurements. Detailed measurements of the cross sections for the production of as many as 28 individual levels in each reaction product are also being obtained in reactions induced by 12- to 30-MeV $^{4}He^{++}$ on ^{58}Ni, ^{54}Fe, and ^{60}Ni, by 7- to 14-MeV protons on ^{58}Ni and ^{61}Ni, and by 25- to 40-MeV $^{12}C^{4+}$ on ^{50}Cr and ^{46}Ti. These cross section measurements as a function of excitation energy of the γ cascade are used (a) to extract information about the energy and angular momentum dependence of the density of nuclear levels, (b) to correlate the yields with level spins, (c) to determine the line of states with lowest angular momentum ("yrast" line) and the region of the EJ diagram where γ emission dominates against neutron and proton emission for each reaction product, and (d) to determine the extent of direct reaction contribution present in some of the reactions in question.

PUBLICATIONS

Hoffman, E. J., Sarantites, D. G., and Lu, N.-H., Structure of ^{61}Cu via $^{58}Ni(^{4}He,p\gamma)$ High-Resolution Prompt Gamma-Ray Spectrometry, Nucl. Phys., A, 137: 146-176 (1971).

Hoffman, E. J., and Sarantites, D. G., De-Excitation of the ^{61}Cu Compound Nucleus via Photon Emission from Proton and Neutron Unbound States, Nucl. Phys., A, 173: 177-206 (1971).

Sarantites, D. G., and Hoffman, E. J., On the Role of Gamma-Ray Emission from Nucleon Unbound States in the Mechanism of Compound Nuclear Reactions, Nucl. Phys., A, 180: 177-207 (1972).

03:63 RADIOCHEMICAL STUDIES OF NUCLEAR FISSION. Wahl, Arthur C. (Washington University, Department of Chemistry, St. Louis, Mo. 63130).

The objectives of this investigation are to learn about the charge and mass distributions of products of low-energy fission processes and to use this information to help understand the mechanism of nuclear fission. Current studies are concerned with effects of nuclear shells, especially the 50-proton shell, on charge and mass distributions. Present evidence indicates that heavy fragments from the very probably asymmetric modes of fission have 50 or more protons, an indication that suggests that enhanced nuclear stability, and/or possibly other properties, associated with shell closure in nascent fission fragments is an important cause for the high probability of asymmetric charge and mass distributions. Further evidence concerning the importance of shell closure is being sought by measuring the cumulative yields of In fission products and the independent yields of the complementary (for U fission) Tc fission products. For possible use in the discovery and study of some of the very short-lived (half-lives $\lesssim$1 sec) indium fission products of interest, a rotating beta-recoil device has been built and will be tested with Cs → Ba decay pairs with known half-lives and yields.

PUBLICATIONS

Lin, Chien-Chang, and Wahl, Arthur C., Cumulative Yields of 40.1-Min ^{123}Sn, 9.6-Min ^{125}Sn, and ^{128}Sn from Thermal-Neutron-Induced Fission of ^{235}U, Inorg. Nucl. Chem., 34: 1479 (1972).

Erdal, B. R., and Wahl, A. C., Modes of Formation of Tin Fission Products, J. Inorg. Nucl. Chem., 33: 2763 (1971).

03:64 FISSION STUDIES ON ELEMENTS BELOW POLONIUM. Neuzil, E. F. (Western Washington State College, Department of Chemistry, Bellingham, Washington 98225).

The main objective of this research program is to determine the characteristics of the charged-particle-induced fission of elements lighter than polonium. Of concern are the probability for fission, the type of distribution of fission fragments, the change in fission probability with the change in bombarding particle energy, and the effect of different bombarding particles creating the same fissioning species. Current investigation with elements and enriched isotopes of these elements from Re to Tl indicated that the probability for fission decreases quite rapidly as the atomic number decreases for fission induced by the same particle at a constant energy. The probability for fission drops exponentially for a given isotope as the energy of the bombarding particle drops. The distribution of fission fragments is gaussian with a width at half-maximum of only two or three mass units wide for Re isotopes at a bombarding energy of 41-MeV helium ions, to about 16 mass units wide for Tl isotopes at the same bombarding energy. No consistent trend has been observed for the fission caused by different particles creating the same fissioning species with the same energy content.

PUBLICATIONS

Neuzil, E. F., and Hensley, W., Helium Ion-Induced Fission of ^{204}Pb at 65, 41, 37 and 25 MeV, J. Inorg. Nucl. Chem., 32: 1761, (1970).

ALSO SEE Nuclear Spectroscopy: 03:9, 03:11, 03:15, 03:16, 03:23, 03:26; Heavy Element Chemistry: 03:68, 03:70, 03:72, 03:74, 03:77, 03:81, 03:84, 03:89, 03:90, 03:95, 03:97, 03:99; Hot Atom Chemistry: 03:199; Analytical Chemistry: 03:397; and Miscellaneous Chemical Studies: 03:448, 03:464, 03:465.

HEAVY ELEMENT CHEMISTRY

Studies of the nuclear structure and reactions and all aspects of the chemistry of the actinide elements.

03:65 SPECTROSCOPY OF THE ACTINIDE ELEMENTS.

Carnall, W. T.; Cohen, D.; Fields, P. R.; Fried, S.; Morrison, J.; Patterson, J. H.; Rajnak, K.; Sarup, R.; and Wagner, F. Jr. (Argonne National Laboratory, Chemistry Division.)

This program is concerned with the experimental measurement of actinide and lanthanide ion absorption spectra, the theoretical interpretation of the experimental data in terms of energy level structure parameters, and the application of the results to qualitative and quantitative analysis as well as to the prediction of thermodynamic properties. Spectra both in solutions and in solid compounds are studied.

The absorption spectra of $Er^{3+}: LaF_3$ and $ErCl_3 \cdot 6H_2O$ are being investigated at low temperature and high resolution. $Er^{3+}(4f^{11})$ has energy level parameters that approximate those for U^{3+}. We have observed anomalies in the parameters determined for U^{3+} and Np^{3+} that make it difficult to extrapolate to the structures expected for the heavier actinides. The study of Er^{3+} resulted in an understanding of certain second-order interactions that are important for f^{11} (f^3) systems, and provided a basis for a more detailed interpretation of U^{3+} and Np^{3+} spectra. Experimental studies of the absorption spectra of the following systems are in progress and will extend into 1973 and 1974: Cm^{3+}(aquo), $BkCl_3$, $CfCl_3$, Sm^{3+} (several crystal matrices), $BkBr_3$. We expect the study of the low-temperature crystal spectra of the heavy actinide compounds to be of particular value in developing an understanding of their coordination chemistry.

The ab initio calculation of the corrections to the Hartree-Fock theory due to electrostatic configuration interaction for a heavy ion, Pr^{3+} ($4f^2$), represents the first attempt to derive theoretically the values of the most important class of correction terms for the theoretical model used in all of our work. The good agreement with those values determined parametrically lends strong support to the mode of approach we have taken. Further calculations in the actinide range are planned.

PUBLICATIONS

Carnall, W. T., Fields, P. R., and Poppalardo, R. G., Absorption Spectrum of $PuCl_3$, J. Chem. Phys., 53: 2922 (1970).

______, Sjoblom, R. K., Barnes, R. F., and Fields, P. R., Observation and Interpretation of Low Energy Bonds in the Solution Absorption Spectra of Bk^{3+} and Bk^{4+}, Inorg. Nucl. Chem. Lett., 7: 651 (1971).

______, Fields, P. R., and Sarup, R., Optical Absorption Spectra of $Er^{3+}: LaF_3$ and $ErCl_3 \cdot 6H_2O$, J. Chem. Phys., 56: 4750 (1972).

Morrison, J. C., Fields, P. R., and Carnall, W. T., Configuration Interaction and the Spectra of $LaCl_3 : Pr^{3+}$, Phys. Rev., B, 2: 3526 (1970).

______, and Rajnak, K., Many-Body Calculations for the Heavy Atoms, Phys. Rev., A, 4: 536 (1971).

03:66 THEORETICAL STUDIES OF NUCLEAR STRUCTURE IN THE HEAVY ELEMENTS.

Chasman, R. R. (Argonne National Laboratory, Chemistry Division.)

The purpose of this research program is to develop a good theoretical description of deformed nuclides, with particular emphasis on the heavy elements. The most important features in such a description consist of the nuclear single particle potential and the attractive two-body residual interactions. Our program is being carried out on two fronts: (1) the calculation of nuclear properties as determined by various models of the single particle potential and of the residual interactions and (2) a long-term collaborative effort with the single nucleon transfer spectroscopy program at Argonne.

Our theoretical studies of the single particle potential center on the study of shifts and changes in energy level spacings induced by variations of the nuclear single particle potential. These calculations are combined with the results obtained from the single nucleon transfer spectroscopy program to make a detailed study of the nuclear single particle potential. We are in the process of completing such an analysis of the odd-neutron actinides and are embarking on a study of the odd-proton actinides.

Residual two-body interactions lead to important nucleon correlation effects in nuclei. The most important of these residual interactions is the pairing interaction. We have recently developed a correlation method for the theoretical treatment of pairing forces. We are trying, at present, to extend the method to the treatment of more complicated residual interactions.

PUBLICATIONS

Chasman, R. R., Simple Momentum-Dependent Nuclear Central Potential, Phys. Rev., C, 3: 1803 (1971).

______, Two-Body Interactions: The Method of Correlated Quasi-Particles. I, Phys. Rev., C, 5: 29 (1972).

______, 0^+ Excited States in the Actinides, Phys. Rev. Lett., 28: 1275 (1972).

Braid, T. H., Chasman, R. R., Erskine, J. R., and Friedman, A. M., (d,p) and (d,t) Studies of the Actinides. II. ^{243}Cm, ^{245}Cm, ^{247}Cm, and ^{249}Cm, Phys. Rev., C, 4: 247 (1971).

03:67 NUCLEAR SPECTROSCOPY OF TRANSPLUTONIUM ELEMENTS.

Fields, P. R.; Ahmad, I.; Barnes, R. F.; Sjoblom, R. K.; and Wagner, F. Jr. (Argonne National Laboratory, Chemistry Division.)

The primary aim of our research program is to identify the single-particle states in the actinide region and measure alpha, beta, and gamma transition rates involving these states. These studies in conjunction with the current nuclear reaction spectroscopy at Argonne map out the Nilsson orbitals in the transplutonium region. Currently, we are investigating the decay scheme of 7-h^{251}Fm. This nuclide decays predominantly (99%) by electron capture. Because of the expected high spin ($\frac{9}{2}$) for the ^{251}Fm ground state, electron capture decay selectively populates the high-spin states in ^{251}Es. We have identified the $\frac{7}{2}$-(514) and $\frac{9}{2}$+(624) proton states in ^{251}Es. This is the first time these two states have been positively identified in any nucleus. The observed proton states will be helpful in checking the predictions about the super-heavy elements. The alpha decay of ^{251}Fm is being investigated with the help of an alpha magnetic spectrometer and high-resolution gamma and electron spectrometers. We have already identified the $\frac{5}{2}$+(622) and $\frac{9}{2}$-(734) single-neutron states in ^{247}Cf.

We recently completed the decay scheme of ^{238}Am and identified several electric monopole (E0) transitions in ^{238}Pu. With the aid of this information several 0^+ and 1^- states in ^{238}Pu were identified. The 0^+ states are of special interest to nuclear physicists because so far these are not well understood. These 0^+ states are also populated in (p,t) reactions on actinide targets. We plan to investigate the decay scheme of other low-spin odd-odd nuclides (like 2.1-h ^{250}Es) and measure the rotational constants and B(E0)/B(E2) ratios for the 0^+ bands. This information will aid us in a better understanding of nuclear structure.

PUBLICATIONS

Fields, P. R., Ahmad, I., Friedman, A. M., Lerner, J., and Metta, D. N., Alpha Decay of ^{247}Cm, Nucl. Phys., A, 160: 460 (1971).

Ahmad, I., Porter, F. T., Freedman, M. S., Barnes, R. F., Sjoblom, R. K., Wagner, F. Jr., Milsted, J., and Fields, P. R., Energy Levels in ^{251}Cf via Alpha Decay of ^{255}Fm, Phys. Rev., C, 3: 390 (1971).

———, Sjoblom, R. K., Barnes, R. F., Wagner, F. Jr., and Fields, P. R., Electron Capture Decay of ^{238}Am and Electric Monopole Transitions in ^{238}Pu, Nucl. Phys., A 186: 620 (1972).

Porter, F. T., Ahmad, I., Freedman, M. S., Barnes, R. F., Sjoblom, R. K., Wagner, F. Jr., and Fields, P. R., Energy Levels in ^{239}Pu Populated by Electron-Capture Decay of 11.9-Hr ^{239}Am, Phys. Rev., C, 5: 1738 (1972).

03:68 PRODUCTION OF ELEMENTS IN THE ACTINIDE REGION. Fields, P. R.; Ahmad, I.; Diamond, H.; Friedman, A. M.; Sjoblom, R.; Lerner, J. L.; Barnes, R.; Cohen, D.; Carnall, W. T.; Horwitz, E. P.; Fried, S.; Wagner, F. Jr.; Glendenin, L. E.; Flynn, K. F.; and Gindler, J. E. (Argonne National Laboratory, Chemistry Division.)

In recent years our efforts have been concentrated on specific nuclides of interest in the transcurium region. The primary interest has often been in their nuclear properties, and a number of scientists with diverse interests and talents may collaborate on producing a particular nuclide. Our principal production tools at Argonne are the cyclotron and the isotope separator and highly developed chromatographic techniques for the isolation of specific nuclides.

We often use accelerators located at other sites and with the advent of the Berkeley SuperHILAC we expect to participate in a major cooperative program aimed at the production of many new actinide as well as transactinide nuclides. If and when a heavy-ion accelerator becomes available, it will become one of our most important production tools.

Coordinated efforts to produce relatively large amounts of trans-californium elements for the purpose of studying fission characteristics are continuing. Studies of the spontaneous fission of ^{256}Fm have been completed and the determination of the mass yield curve for the thermal neutron-induced fission of ^{255}Fm is in progress. Studies of the neutron-induced fission of ^{253}Fm and the spontaneous fission of ^{254}Fm have been planned. It is anticipated that much of our effort in 1973-74 will be directed at developing the techniques for isolating nuclides of interest from targets irradiated in the Berkeley SuperHILAC. We will continue to investigate actinide nuclides that can be prepared in the ANL cyclotron.

03:69 CHEMISTRY OF Np, Pu AND Am. Fields, P. R.; Carnall, W. T.; Fried, S.; Cohen, D.; Barnes, R.; Sjoblom . (Argonne National Laboratory, Chemistry Division.)

The study of the physical and chemical properties of the lighter actinide elements develops an understanding of their chemical relationships to each other, to their electronic structures, and to the other elements in the periodic table.

A study of the structure of Np ions by means of the Raman spectra of Np(V), Np(VI), and Np(VII) both in acidic and basic solution is continuing. Attempts are also being made to measure the molecular weight of the Np(V) species in basic solution using ultrafiltration techniques. Preliminary studies show the molecular weight of Np(V) to be > 1000 in dilute tetramethylammonium hydroxide. Attempts to produce NpF_5 have been only partially successful. X-ray analysis of one preparation revealed a pattern isostructural with UF_5, but this pattern was not observed in other preparations. Mössbauer spectroscopy has shown that several preparations contained mixed Np(V) and Np(IV) fluorides. Further work is planned.

Investigations of the chemistry of Pu and Am in basic solution, which is particularly important to separations procedures, and in molten hydroxides, are in progress and will be extended to heavier actinides.

Mössbauer studies with U, Np, and Am compounds are continuing in cooperation with members of the Solid State Science and Physics Divisions.

PUBLICATIONS

Dunlap, B. D., Shenoy, G. K., Kalvius, G. M., Cohen, D., and Mann, J. B., Electron Densities and Isomer Shifts for Various Neptunium Ions, in Hyperfine Interactions in Excited Nuclei, Gvirol Goldring and Rafael Kalish (Eds.), Gordon and Breach, Science Publishers, Inc., New York. 1971. pp. 709-717.

03:70 NUCLEAR PROPERTIES AND REACTIONS OF HEAVY ELEMENTS. Fields, P. R.; Diamond, H.; Ahmad, I.; Wahlgren, M. A.; Barnes, R. F.; Sjoblom, R.; Wagner, F.; Gindler, J. E.; and Friedman, A. M. (Argonne National Laboratory, Chemistry Division.)

This program, in which cross sections, excitation functions, the products of nuclear reactions, and fission are studied, is aimed at producing the nuclides whose properties are to be investigated as well as determining the best methods for producing heavy and super-heavy elements.

A sophisticated gas recoil chamber has been built to collect and identify products from nuclear reactions with half-lives as short as milliseconds. The chamber will be used at Argonne and Michigan State University in studying nuclear isomers, neutron-deficient isotopes, and special delayed spontaneous fission isomers.

Investigation of the reactions of ^{249}Cf, ^{244}Cm, and ^{241,243}Am with ^{4}He and ^{3}He are in progress. We have started the measurement of electron binding energies in Am. Alpha groups associated with ^{251}Fm decay will be investigated. Major emphasis in 1973-74 will be given to heavy-ion reactions such as stripping, transfer reactions, compound nucleus formation, and fission using the Berkeley Super/HILAC. Our ultimate aim is to be able to exploit fully the great potential of this type of investigation through use of the proposed Argonne heavy-ion accelerator.

PUBLICATIONS

Ahmad, I., and Wahlgren, M. A., Long-Lived Standards for Efficiency Calibration of Ge(Li) Detectors, Nucl. Instrum. Methods, 99: 333 (1972).

Goodman, L. S., Diamond, H., Stanton, H. E., and Fred, M. S., g_j Value for the Atomic Ground State of Fermium, Phys. Rev., A, 4: 473-475 (1971).

Kato, W. Y., Armani, R. J., Larsen, R. P., Moreland, P. E., Mountford, L. A., Gasidlo, J. M., Popek, R. J., and Swanson, C. D., An Integral Measurement of ^{239}Pu and ^{233}U Alpha, Nucl. Sci. Eng., 45: 37-46 (1971).

03:71 CHEMISTRY OF THE HEAVIER ACTINIDES. Fields, P. R.; Fried, S.; Carnall, W. T.; Cohen, D.; Barnes, R.; and Sjoblom, R. (Argonne National Laboratory, Chemistry Division.)

This investigation is directed to attaining a basic understanding of the chemical reactions characteristic of the heavier actinide elements. It also seeks to examine the relationship between electronic structure, as revealed in absorption spectra, and chemical properties.

With the increasing availability of the transcurium actinides it has been possible to measure the first low-temperature absorption spectra of some of the pure halides of Bk and Cf. Preparation on a mg scale is being carried out using methods that had already been devised for the microchemical study of these compounds. The compounds are distributed as thin films over the inner wall of a quartz tube, and light transmitted through the films is analyzed. Results have so far established the energies of the lowest-lying levels in the chlorides and bromides of Bk^{3+} and Cf^{3+} and make it possible to deduce general trends in electronic structure in the transcurium elements. These studies will be extended to include observations of the fluorides and iodides. At the same time properties of the crystals produced are being examined using x-ray and infrared spectroscopy. Possible volatile fluorides of Cf and Es are also under investigation. Solution absorption spectra of Bk and Cf are being studied in acid and basic, particularly in carbonate, solutions, in conjunction with an investigation of oxidation–reduction reactions.

PUBLICATIONS

Carnall, W., Fried, S., Wagner, F. Jr., Barnes, R. F., Sjoblom, R. K., and Fields, P. R., Absorption Spectra of $BkCl_3$ and $CfCl_3$, Inorg. Nucl. Chem. Lett., 8: 579 (1972).

03:72 PRODUCTION AND STUDIES OF THE NUCLEAR AND CHEMICAL PROPERTIES OF HEAVY ACTINIDE AND TRANS-ACTINIDE ELEMENTS. Fields, P. R.; Unik, J. P.; Horwitz, P.; Wolf, K.; Friedman, A.; Ahmad, I.; Stein, L.; Fried, S.; Cohen, D.; and Bloomquist, C. A. A. (Argonne National Laboratory, Chemistry Division.)

The search for new elements has in recent years received added incentive through many theoretical calculations which indicate that a region of enhanced nuclear stability, an island of super-heavy elements, may exist as a result of predicted closed-shell configurations of 114 protons and 184 neutrons. Studies of the nuclear and chemical properties of this entire new class of elements could contribute a great deal to our understanding of the nucleus and its electronic configurations. Unfortunately, the high-energy heavy-ion projectiles that are needed to produce the neutron-rich isotopes on this island of stability have not been available from existing accelerators. We have attempted to produce very heavy elements using secondary reactions induced by irradiating large quantities of heavy targets such as tungsten and uranium with GeV protons. By bombardment of ^{238}U with 12- and 28-GeV protons, secondary products as heavy as ^{248}Cf were observed to be produced. The effective cross sections for producing heavier elements are unfortunately so low as to prove impractical using existing GeV proton accelerators. However, the powerful chemical separation and detection methods, as well as the expertise developed during these earlier studies, will be applied to searches for super-heavy elements produced using the LBL SuperHILAC Accelerator in collaboration with the staff of LBL.

03:73 HEAVY ELEMENT REACTION SPECTROSCOPY PROGRAMS. Friedman, A. M.; Chasman, R.; Erskine, J.; and Braid, T. (Argonne National Laboratory, Chemistry Division.)

The major purpose of this program is to understand the structure of actinide nuclei. For this purpose we have been engaged in an experimental study of the properties of actinide energy levels as seen by reaction spectroscopy at the tandem Van de Graaff accelerator and the cyclotron. We have also utilized information obtained by decay scheme experiments and have tried to correlate the results of all of these experiments with theoretical developments in nuclear structure.

We have recently completed a survey of the properties of neutron states in the actinides and tested the more important properties of these states against current theories. We are now engaged in a study of the properties of proton states in this region and of beta and pairing vibrational states. We have also begun a survey of two quasiparticle states of both neutron pairs and proton neutron pairs.

It is hoped that the results of the first of these investigations will allow us to test the theoretical predictions for proton states. We will use these and past results to find a theoretical description of the more complex collective states that we are now studying.

After completing these experiments in order to extend these studies to more complex nuclear properties of the actinides, we would require access to beams of heavier ions for transfer reactions, since it will be only by use of these heavier ions that one can excite more collective nuclear properties or states of higher angular momentum.

PUBLICATIONS

Braid, T. H., Chasman, R. R., Erskine, J. R., and Friedman, A. M., (d,p) and (d,t) Reaction Studies of the Actinide Elements. I. ^{235}U, Phys. Rev., C, 1: 275-289 (1970).

______, Chasman, R. R.; Erskine, J. R., and Friedman, A. M., (d,p) and (d,t) Studies of the Actinide Elements. II. ^{243}Cm, ^{245}Cm, ^{247}C, and ^{249}Cm, Phys. Rev., C, 4: 247-261 (1971).

Maher, J. V., Erskine, J. R., Friedman, A. M., Schiffer, J. P., and Siemssen, R. H., Unexpected Strong Pair Correlations in Excited O^+ States of Actinide Nuclei, Phys. Rev. Lett., 25: 302-306 (1970).

______, Erskine, J. R., Friedman, A. M., Schiffer, J. P., and Siemssen, R., Population of O^+ States in Actinide and $A \simeq 190$ Nuclides by the (p,t) Reaction, Phys. Rev., C, 5: 1380 (1972).

03:74 RADIOCHEMICAL AND PHYSICAL STUDIES OF NUCLEAR FISSION. Glendenin, L. E.; Gindler, J. E.; and Flynn, K. F. (Argonne National Laboratory, Chemistry Division.)

The thrust of this program is to investigate systematically both by radiochemical and physical methods the spontaneous fission, low-energy neutron-induced fission, and medium-energy (<50-MeV) charged particle and photon-induced fission of available heavy element nuclides. These studies include the distributions of mass, nuclear charge, and kinetic energy of the fission fragments: the emission of γ and x rays by the fragments; and angular momentum effects. The objective of such measurements is to provide a basis of information for the elucidation of the fission process. A more practical objective is to provide information germane to the development and operation of nuclear reactors.

Currently we are examining the kinetic energy and mass distributions for nuclides that fission either spontaneously or with thermal neutrons. These include nuclides over a wide range from ^{229}Th through ^{256}Fm, including isotopes of Es and Fm that are near the edge of what appears to be a new and interesting region of symmetric fission.

The radiochemical and physical studies of the fission process will be continued for the heaviest nuclides available. In addition, plans are being made to investigate the fission of any "superheavy" elements that may be produced by heavy ion reactions at the Berkeley SuperHILAC.

PUBLICATIONS

Flynn, K. F., Horwitz, E. P., Bloomquist, C. A. A., Barnes, R. F., Sjoblom, R. K., Fields, P. R., and Glendenin, L. E., Distribution of Mass in the Spontaneous Fission of ^{256}Fm, Phys. Rev., C, 5: 1725 (1972).

Reisdorf, W., Unik, J. P., Griffin, H. C., and Glendenin, L. E., Fission Fragment K X-ray Emission and Nuclear Charge Distribution for Thermal Neutron Fission of ^{233}U, ^{235}U, and ^{239}Pu and Spontaneous Fission of ^{252}Cf, Nucl. Phys., A, 177: 337 (1971).

Von Gunten, H. R., Flynn, K. F., and Schmid, A., The Thermal-Neutron Cross Section of ^{227}Th, J. Inorg. Nucl. Chem., 32: 3441 (1970).

Aumann, D. C., and Gindler, J. E., The Ratio of ^{111}Pd Isomers Formed in Charged-Particle and Photon-Induced Fission of Several Heavy Nuclides, J. Inorg. Nucl. Chem., 32: 731 (1970).

Gindler, J., Munzel, H., Buschmann, H., Christaller, G., Michel, F., and Rohde, G., Fragment Angular Distributions in the Fission of Heavy Nuclei by 103 MeV Helium Ions and 51.5 MeV Deuterons, Nucl. Phys., A, 145: 337 (1970).

03:75 ATOMIC BEAM MAGNETIC RESONANCE MEASUREMENTS OF THE ACTINIDES. Goodman, L. S.; Diamond, H.; and Stanton, H. E. (Argonne National Laboratory, Chemistry and Physics Divisions.)

Atomic beam magnetic resonance measurements of transitions between Zeeman levels of neutral atoms can yield atomic and nuclear magnetic dipole moments and nuclear (electric) quadrupole moments. The values of these fundamental properties of atoms and nuclei can be used to test and guide theoretical descriptions of atomic and nuclear structures. The apparatus is sensitive to radioactivity and can cope with the large quantities of radioactivity required. It has been used to establish the electronic ground-state configuration of fermium, which is inaccessible to optical spectroscopy and is now being used to study einsteinium and fermium isotopes. Plutonium, neptunium, berkelium, curium, and francium studies are under consideration.

PUBLICATIONS

Goodman, L. S., Diamond, H., Stanton, H. E., and Fred, M. S., g_j Value for the Atomic Ground State of Fermium, Phys. Rev., A, 4: 473 (1971).

03:76 DYNAMIC CHEMICAL BEHAVIOUR OF SOME ACTINIDE COMPOUNDS IN AQUEOUS SOLUTION. Sullivan, J. C. (Argonne National Laboratory, Chemistry Division.)

Kinetic investigations of oxidation–reduction reactions in aqueous solution compose a fundamental class of time-dependent phenomena. The specific chemistry of the 5f transition elements provides important information necessary for the development of analytical and separation procedures as well as providing significant results within the framework of relevant theoretical descriptions.

Two systems currently under investigation are the equilibrium and kinetic studies of the reactions

$$Ru(NH_3)_6^{3+} + Np(III) = Np(IV) + Ru(NH_3)_6^{2+} \qquad (1)$$

$$Ru(NH_3)\ _5H_2O^{3+} + Np(III) = Ru(NH_3)\ _5H_2O^{2+} + Np(IV) \qquad (2)$$

and the kinetic study of the reaction

$$2Np(VI) + C_6H_4(OH)_2 = 2Np(V) + O:C_6H_4:O. \qquad (3)$$

Reactions (1) and (2) are the first studies of a redox reaction with the neptunium ions where the process is constrained to proceed by an outer-sphere mechanism. Such reactions are significant for understanding the importance of relevant parameters in the Marcus theory. Reaction (3) provides an opportunity to assess the reactivity patterns of Np(VI) with a reductant of use in analytical separation schemes.

The reactions of Np(VI) with the biologically significant R-SH compounds are scheduled for early investigation. The kinetic study of the reaction of Np(VI) with cysteine should yield information on the kinetic parameters that characterize the formation of cysteine with an oxidant that reacts via an outer-sphere path. Comparison with such kinetic parameters obtained in the well-documented Fe(III) oxidation should contribute to a theoretical understanding of the process.

PUBLICATIONS

Hindman, J. C., and Sullivan, J. C., Chap. 7, in Vol. 1, A. E. Martell (Ed.), Van Nostrand Reinhold Company, New York, Coordination Chemistry, 1971.

03:77 STUDIES OF NUCLEAR FISSION USING CHARGED-PARTICLE NUCLEAR REACTIONS. Unik, J. P.; Wolf, K.; and Gorski, A. (Argonne National Laboratory, Chemistry Division.)

Charged-particle nuclear reactions are currently being used to produce a wide variety of fissioning systems with different angular momentum and excitation energy distributions in order to study the properties of the nuclear deformation potential energy surfaces, the fission scission point and the transition states. Studies of scission-point properties now in progress are yielding information on how the initial protons, neutrons, and excitation energies of fissioning nuclei are partitioned between the two fission fragments. For example, studies of neutron emission from a wide variety of different fissioning systems will provide information on the partition of excitation energy between the fragments and the deformation of fission fragments at the moment of scission. Research on the transition states and the potential energy barriers are providing important information on the motion of nucleons in extremely deformed nuclei (only achieved in the fission process) and the influence these parameters have on the final properties of the fission fragments. Current studies of spontaneously fissioning isomers are providing detailed information on the properties of secondary minima existing in these fission deformation potential energy surfaces. Recently seven new isomers have been discovered and studied extensively in the neptunium through berkelium region and these measurements are now being extended to even heavier elements.

PUBLICATIONS

Wolf, K. L., and Unik, J. P., Fissioning Isomers of Americium, Curium, and Berkelium Isotopes, Phys. Lett., B, 30: 405 (1972).

03:78 RESEARCH IN NUCLEAR CHEMISTRY. Choppin, Gregory R. (Florida State University, Department of Chemistry.)

The principal objective in this research is the study of the structural, thermodynamic, and kinetic parameters of the complexation of the trivalent lanthanide and actinide elements in aqueous solution. The gradual change in cationic radii provides a unique opportunity to investigate cation charge density and size effects in hydration and complexation. Correlation of data from optical spectroscopy, potentiometry, calorimetry, and solvent extraction has supported a model of ionic bonding with large coordination and hydration numbers. A correlation between the basicity of the ligand and the inner vs outer sphere nature of the complexes has been noted. A series of fluoro- and chloro-substituted acetate ligands varying from weakly to strongly basic are being studied with Am(III) and Eu(III) to define the variation of complex type with basicity more precisely. The complexes formed with several dibasic organic ligands such as squarate and croconate are under investigation to evaluate the steric effects of the ligands upon the thermodynamics of complexation.

A kinetic study of actinide exchange in EDTA complexes indicates that the amino groups are not involved in the complexes but play a role in the kinetics via protonation. The tetracarboxylate analog of EDTA in which methylene replaces the amino groups is being synthesized to study the thermodynamics and kinetics of its complexation with the lanthanides and actinides as a test of the models of the EDTA complexes.

PUBLICATIONS

Choppin, G. R., and D'Olieslager, W., The Kinetics of Exchange Between Lanthanide Ions and Lanthanum EDTA, J. Inorg. Nucl. Chem., 33: 127 (1971).

——, Structure and Thermodynamics of Lanthanide and Actinide Complexes in Solution, XIII International Conference on Coordination Chemistry, Plenary Lectures, Butterworth & Co. (Publishers) Ltd., London, 1970.

——, and Dadgar, A., The Thermodynamics of Lanthanide Complexing by Acetylacetonate, J. Coord. Chem., 1: 179 (1972).

——, and Stampfli, R., Thermodynamics of Kojate Complexes of the Lanthanides, J. Coord. Chem., 1: 173 (1972).

——, and Stampfli, R., The Thermodynamics of Lanthanide Hexacyanoferrate(III) Complexation, J. Inorg. Nucl. Chem., 34: 205 (1972).

03:79 MASS SPECTROMETRIC SEARCH FOR ^{244}Pu IN NATURE. Mewherter, J. L.; and Rourke, F. M. (Knolls Atomic Power Laboratory.)

Small traces of ^{244}Pu may occur in natural material, either as residual amounts of primordial ^{244}Pu (half-life 8.3 × 10^7 years) or possibly as a minor component of the cosmic ray flux.

In conjunction with chemists at Los Alamos Scientific Laboratory who isolated the plutonium fraction from a large mineral deposit of bastnaesite ore we recently were able to further purify and detect 2 × 10^7 atoms of ^{244}Pu using the KAPL three-stage (tandem magnetic plus electrostatic) mass spectrometer. Current work includes an attempt to confirm the presence of ^{244}Pu from considerably larger amounts of the same deposit and in addition to also search for ^{244}Pu in recently obtained lunar material, as well as more recent terrestrial minerals that might incorporate ^{244}Pu from a steady-state cosmic ray origin.

PUBLICATIONS

Hoffman, D. C., Lawrence, F. O., Mewherter, J. L., and Rourke, F. M., Detection of ^{244}Pu in Nature, Nature, 234: 132 (1971).

03:80 ACTINIDE AND LANTHANIDE CHEMISTRY. Edelstein, N. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division.)

The basic purpose of this project is to increase substantially the knowledge of the chemical and physical properties of the actinide elements and their compounds, and (for purposes of comparison) of the lanthanide elements and their compounds. These studies are intended to clarify and extend the relationship between electron configuration and the chemical, magnetic, and optical properties of the elements and their ions, particularly in the solid state.

Magnetic and electronic spectral data of actinide compounds have been principally interpreted on the basis of a model of point charges. Direct evidence for the inadequacy of this model is seen from the appearance of extra structure (superhyperfine structure) in the electron paramagnetic resonance spectra of some actinide ions diluted in a cubic lattice, CaF_2. This structure arises from the interactions of these ions with the fluorine ions. Electron nuclear double resonance (ENDOR) measurements have shown much larger ligand interactions in the 5f actinide series than in the 4f lanthanide series due to the more extended nature of the 5f orbitals. These types of measurements will be extended to other transition ions in various host crystals.

Another type of compound in which it is believed covalent (or bonding) effects are predominant is the bis(cyclooctatetraenyl) actinide(IV) complexes. So far it has been shown that Th^{4+}, U^{4+}, Np^{4+}, and Pu^{4+} form a "sandwich" complex with two eight-membered planar cyclooctatetraenyl rings similar to the structure of ferrocene. The available magnetic evidence indicates f orbital participation in the π bonding predominating in these complexes. Synthetic magnetic and optical spectral work are being continued to elucidate the bonding in this unique type of complex.

There has been much speculation on the role of f electrons in the bonding of actinide metals. It now appears that beyond atomic number 94 the 5f electrons become localized. With the present availability of milligram quantities of the heavy actinides through Cf a program to synthesize very pure metals of Am, Cm, Bk, and Cf has been initiated. X-ray crystallographic studies and magnetic susceptibility measurements from 2 to 300°K will be made on these samples. It is hoped this information will provide a better understanding of the bonding properties of the actinide metals.

PUBLICATIONS

Cunningham, B. B., Coordination Chemistry and Physical Properties of Transplutonium Actinide Compounds, Pure Appl. Chem., 27: 43 (1971).

Marei, S. A., and Cunningham, B. B., Magnetic Measurements of Curium Metal, CmF_3, and CmOCl, J. Inorg. Nucl. Chem., 34: 1203 (1972).

Kolbe, W., and Edelstein, N., Electron–Nuclear Double Resonance of Pu^{3+} in CaF_2, Phys. Rev., B, 4: 2869 (1971).

Edelstein, N., Lamar, G. N., Mares, F., and Streitwieser, A. Jr., Proton Magnetic Resonance Shifts in Bis(cyclooctatetraenyl) Uranium (IV), Chem. Phys. Lett., 8: 399 (1971).

Streitwieser, A. Jr., Dempf, D., LaMar, G. N., Karraker, D. G., and Edelstein, N., Bis(1,3,5,7 tetramethylcyclooctatetraene) Uranium (IV) Bis(1,3,5,7 tetramethylcyclooctatetraene) Neptunium (IV). Proton Magnetic Resonance Spectrum and the Question of f-orbital Covalency, J. Amer. Chem. Soc., 93: 7343 (1971).

03:81 SEARCH FOR SUPERHEAVY ELEMENTS BY ON-LINE IDENTIFICATION IN SASSY SYSTEM. Ghiorso, A. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division.)

To expedite the quest for the hypothesized super-heavy elements that are expected to be made as the result of heavy ion reactions at the Berkeley SuperHILAC, we have developed a very efficient apparatus to which we have given the name SASSY, an acronym that stands for Small Angle Separator System. The aim of the system is a separation of the desired recoil products according to their velocity, mass, and nuclear charge. SASSY should accomplish this separation with good enough resolution to allow the first sensitive survey of the possibilities of super-heavy element production by means of heavy-ion bombardment.

The instrument works in the following way. After a super-heavy recoil atom has been ejected (for example, let us assume a 100-MeV recoil from the interaction of ^{76}Ge with ^{232}Th), it passes undeflected through a velocity separator in vacuum while the impinging heavy ion beam is bent completely into a faraday cup. The super-heavy particle then passes through a thin-window multiwire proportional counter into a gas-filled magnetic field region. The counter records for each particle the x- and y-positions, the time within a couple of nanoseconds, and an approximate value of its dE/dz in the counter gas. Within the gas-filled region the recoil undergoes a very large number of charge-changing collisions so that its behavior in the magnetic fields is defined by its mean charge state and thus is the same as every particle with the same nuclear charge, velocity, and mass. The recoil is thus focused and bent by quadrupole and homogeneous magnetic fields, and it passes through a second transmission counter into a region where its final detection can be accomplished by solid state devices. The two proportional counters measure the velocity of each recoil and its magnetic radius of curvature. The solid detectors measure the recoil energy and any subsequent radioactive decay by alpha emission or spontaneous fission. Alternative detection methods include the use of nuclear emulsions and characteristic x-ray measurements.

03:82 NEW-ELEMENT CHEMISTRY—ELEMENTS-104, -105, AND BEYOND. Ghiorso, A.; Nurmia, M.; Nitschke, J. M.; and Hulet, E. K. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division.)

Elements-104 and -105 can at present be produced only at a rate of a few atoms per hour. In addition, the half-lives of even the longest-lived known isotopes of these elements are only a few tens of seconds. Thus it has been necessary to develop an entirely new type of instrument—a computer-controlled chemistry machine—to perform the hundreds of repetitive experiments needed to determine the chemical behavior of a sufficient number of the newly synthesized atoms. This machine was partially tested with element-104, and its first main task will be to study the so far unknown chemical characteristics of element-105, hafnium It can automatically perform a complicated chemical separation and study the radiations from a number of different fractions under direct computer control. The experimenter can give directions to the computer and change the procedures by means of a teletypewriter terminal.

Using this apparatus, present plans envision a comprehensive investigation of the chemical properties of elements-104 and -105 in collaboration with members of the Nuclear Chemistry Division of the Lawrence Livermore Laboratory. Both ion exchange and hydrolysis types of experiments will be performed. Depending on the success of the first experiments the future chemical studies can be extended as needed. The question of heavier element chemical research will depend on yields and half-lives.

03:83 QUANTUM MECHANICAL DESCRIPTION OF PARTICLE TRANSFER BETWEEN HEAVY IONS. Glendenning, Norman K. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division.)

There is a rapidly developing body of experimental data on reactions between heavy ions. Such reactions in which several nucleons are transferred makes possible, in principle, a detailed study of the correlations between nucleons in the nucleus. In the collision between ions of large Z, Coulomb excitation may become very important, so that states whose parentage is based very largely on collective excited states should be populated with greater probability than in transfer reactions involving light nuclides that have been most intensively studied in the past. It might be thought that a quantum mechanical calculation of the transfer reaction under conditions where Coulomb excitation is important would entail the usual difficulties associated with the long range of the Coulomb field, and semi-classical descriptions have been formulated. However, these difficulties do not in fact arise in the transfer process, because a close collision is required in order to transfer neutrons. A fully quantum mechanical treatment is therefore feasible. It is clearly a prerequisite that the reaction mechanism involved in heavy-ion transfer reactions be understood before they can be used effectively in the study of nuclear correlations. It is the aim of this project to investigate by means of appropriate model calculations what role the Coulomb excitation process will play in transfer reactions.

PUBLICATIONS

Ascuitto, R. J., Glendenning, N. K., and Sorensen, B., Nucl. Phys., A, 170: 65 (1971).

____, Glendenning, N. K., and Sorensen, B., Nucl. Phys., A, 183, 60 (1972).

03:84 SPONTANEOUS FISSION STUDIES. Thompson, S. G.; and Moretto, L. G. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division.)

Studies of spontaneous fission in which the isotope ^{252}Cf is used will be continued. Measurements of the prompt radiations, e.g., neutrons, γ rays, and x-rays, associated with events in which the energies of both fragments are also measured, provide information concerning the fission process itself and the decay properties of neutron-rich nuclei produced only in the fission process. Examples of experiments to be done in the near future are given below. 1) More-accurate measurements of the lifetime of the prompt fragments for γ decay should give, for example, more precise information concerning the extraordinarily large deformations of fragment nuclei in the region near mass 100. 2) Measurements of g-factors of 2+ states of even–even fission fragments by observing perturbed angular correlations of gamma transitions from fragments recoiling into magnetized iron will be made. 3) More accurate measurements of the number of neutrons emitted by fragments of known masses and kinetic energies will be made using a large liquid scintillator. This apparatus will also be used to measure $\bar{\nu}$, the number of neutrons per fission for several heavy nuclei. 4) Studies will be made of fission events in which two or more long range particles, e.g., two alpha particles, are emitted. Such data may provide information on the times associated with the division of nuclei. 5) Studies will be conducted on the decay properties of odd-mass fission fragments. If certain relationships can be discovered by studying the γ spectra, it may be possible to work out decay schemes just as was done successfully for more than 30 even–even fission fragment nuclei. 6) Fission properties of super-heavy nuclei (if produced) will be studied. Measurements will be made of kinetic energies of fragments and the number of neutrons, $\bar{\nu}$, emitted per fission event.

PUBLICATIONS

Cheifetz, E., Jared, R. C., Thompson, S. G., and Wilhelmy, J. B., Phys. Rev. Lett., 25: 38 (1970).

______, Jared, R. C., Thompson, S. G., and Wilhelmy, J. B., in International Conference on the Properties of Nuclei Far from the Region of Beta Stability, Leysin, Switzerland, 1970, Report CERN-70-30, Vol. 2, p. 883, 1970.

______, Wilhelmy, J. B., Jared, R. C., and Thompson, S. G., Phys. Rev., C, 4: 1913 (1971).

Wilhelmy, J. B., Thompson, S. G., Jared, R. C., and Cheifetz, E., Phys. Rev. Lett., 25: 1122 (1970).

03:85 STUDIES OF THE MACROSCOPIC PROPERTIES OF LARGE NUCLEI BY MEANS OF HEAVY-ION REACTIONS. Thompson, S. G.; and Moretto, L. G. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division.)

A large variety of heavy ions will be available at the SuperHILAC. These complex projectiles will allow us to study the macroscopic dynamic properties of very large nuclear systems, as they can be described for instance by the liquid drop model. a) The experimental determination of Coulomb barriers will give information regarding the initial phase of the interaction. The effects of the ground state deformation and the deformation induced by the mutual repulsion can be studied in such a fashion. b) As the two nuclei come in contact, the system will tend to equilibrate both in shape and in charge-to-mass ratio. The measurement of the mass and charge distribution of the fragments produced at this stage will give information about the different relaxation times involved and possibly about viscosity. It will also be possible to test some hydrodynamic predictions, already verified in different liquids, like "splash back" reactions. c) As the relaxation processes terminate, a compound nucleus is formed. Heavy ions make possible the study of the equilibrium properties of compound nuclei not only as a function of excitation energy but as a function of angular momentum as well. For small angular momenta, the compound nucleus should flatten. Above a critical angular momentum, the compound nucleus should become very elongated. The shape of the evaporation spectra of charged particles should confirm such predictions. d) The compound nucleus can decay in various ways. Some modes involve large displacement of nuclear matter, for example fission or the emission of complex particles. These processes can also be studied as a function of excitation energy and angular momentum, and they provide valuable data concerning the static and dynamic properties of nuclear matter.

03:86 "EFFECT OF NUCLEAR SHAPE ON ELECTRONIC ORBITALS OF SUPER-HEAVY ELEMENTS." Waber, James T. (Northwestern University, Department of Materials Science, Technological Institute.)

Precise calculation of the x-ray transition energies has been investigated as one means of identifying super-heavy elements. It appears to be feasible. However, various relativistic quantum electrodynamic corrections that are difficult to calculate accurately reduce the present reliability.

One interaction between electronic orbitals and the nucleus, namely, the hyperfine splitting, has been investigated using multi-configurational relativistic Hartree–Fock wave functions. The new treatment has resulted in improved agreement with experimental results.

Another interaction, the isomer shift in Mössbauer spectroscopy, has been reformulated more precisely in terms of the difference between four relativistic integrals.

There are plans to investigate chemical compounds of super-heavy elements using the α-cluster method modified to include relativistic effects.

PUBLICATIONS

Fricke, B., and Waber, J. T., Theoretical Predictions of the Chemistry of Superheavy Elements; Continuation of the Periodic Table Up to Z = 184, Actinides Rev., 1: 433 (1971).

______, A Phenomenological Calculation of Vacuum Fluctuation in Electronic and Muonic Atoms, Lett. Nuovo Cim., 2(6): 293 (1971).

______, and Waber, J. T., Atomic and Ionic Radii of Superheavy Elements, J. Chem. Phys., 56: 3246 (1972).

______, and Waber, J. T., The Atomic Ground State Configuration of Elements E159 and E160, J. Chem. Phys., 56: 3726 (1972).

______, Desclaux, J. P., and Waber, J. T., Precise Calculations of Atomic Electron Binding Energies in Fermium, Phys. Rev. Lett., 28: 714 (1972).

03:87 TRANSURANIUM ELEMENT CHEMISTRY. Baybarz, R. D.; and Haire, R. G. (Oak Ridge National Laboratory, Chemical Technology Division.)

Now that significant quantities of transuranium elements are available, a systematic study of actinide element chemistry and of comparative lanthanide element chemistry is being carried out. These studies will materially increase our basic understanding of the actinide series. This program includes solution chemistry (with particular emphasis on complex formation) and the preparation of solid actinide compounds and their characterization by x-ray diffraction, electron microscopy, thermogravimetry, differential thermal analysis, and metallographic examination. Experimental work on the hydroxides is nearing completion. Phase changes for sesquioxides of the actinides, americium through einsteinium, have been investigated from room temperature to the melting points. Metals of the actinide elements, americium through einsteinium, were prepared by reduction of the oxide with lanthanum. Crystal structures of the metals were studied by electron-diffraction techniques from 20 to 1000°C; phase transitions and melting points were determined. At the present time, emphasis is given to preparation and identification of compounds containing divalent and tetravalent actinides. Comparative studies of the lanthanides and actinides will include preparation, identification, and hydrolysis of carbides.

PUBLICATIONS

Baybarz, R. D., Knauer, J. B., and Peterson, J. R., New Encapsulation Techniques for the Fabrication of ^{252}Cf Neutron Sources, Nucl. Technol., 11: 609 (1971).

______, Stokely, J. R., and Peterson, J. R., Absorption Spectra of Bk(III) and Bk(IV) in Several Media, J. Inorg. Nucl. Chem., 34: 739-746 (1972).

Fahey, J. A., Peterson, J. R., and Baybarz, R. D., Some Properties of Berkelium Metal and the Apparent Trend Toward Divalent Character in the Transcurium Actinide Metals, Inorg. Nucl. Chem. Lett., 8: 101 (1972).

Stokely, J. R., Baybarz, R. D., and Peterson, J. R., The Formal Potential of the Bk(IV–Bk(III) Couple in Several Media, J. Inorg. Nucl. Chem., 34: 392-393 (1972).

Nugent, L. J., Baybarz, R. D., Burnett, J. L., and Ryon, J. L., Electron-Transfer and f → d Absorption Bands of Some Lanthanide and Actinide Complexes and the Standard (III–IV) Oxidation Potentials for Each Member of the Lanthanide and Actinide Series, J. Inorg. Nucl. Chem., 33: 2503 (1971).

03:88 PREPARATION AND PROPERTIES OF ACTINIDE OXIDES. McBride, J. P.; Haire, R. G.; and Morse, L. E. (Oak Ridge National Laboratory, Chemical Technology Division.)

The purpose of this program is to investigate the properties and reactions of lanthanide and actinide oxides and hydroxides, the oxides being both as dispersed, hydrated colloids and as ceramics. The studies include the conversions to ceramic carbides and nitrides and their reactions, including determination of reaction rates and identification and control of stable and metastable phases. The colloids studied range from concentrated sols as utilized in sol–gel processing to extremely dilute dispersions significant to waste streams, etc. Colloid electrical double-layer barriers and the dispersion–aggregation behavior they control are being studied both theoretically by computer modeling and experimentally by chemical methods including electrophoresis, streaming current, conductimetry, diffraction, and microscopy.

Crystal structures of the transplutonium oxides and hydroxides are being examined by electron diffraction, more suitable than x-ray diffraction for the high-specific-activity isotopes. Controlled oxidation of urania sols is being correlated with degree of crystallinity, zeta potential, and degree of aggregation of the colloidal particles. These studies, together with flow and stability studies of various mixed sols, are coordinated with theoretical modelling studies. Current studies of carbothermic and nitrogen-carbothermic reactions and products, e.g., for use in reactor fuels, will be extended to hydrolysis of lanthanide and actinide carbides to produce synthetic hydrocarbon fuels.

PUBLICATIONS

Baybarz, R. D., Haire, R. G., and Fahey, J. A., On the Californium Oxide System, J. Inorg. Nucl. Chem., 34: 557 (1972).

McBride, J. P., McCorkle, K. H., Pattison, W. L., and Finney, B. C., The CUSP Process for Preparing Concentrated, Crystalline Urania Sols by Solvent Extraction, Nucl. Technol., 13: 148 (1972).

______, McCorkle, K. H., and Pattison, W. L., Production of Predominantly Crystalline Sols of Urania, U. S. Patent No. 3,629,133, Dec. 21, 1971.

Haire, R. G., Lloyd, M. H., Beasley, M. L., and Milligan, W. O., Aging of Hydrous Plutonium Dioxide, J. Electron Microsc. (Tokyo), 20: 8 (1971).

Lindemer, T. B., and Bradley, R. A., Kinetic Models for the Synthesis of $(U,Pu)O_{2-y}$ by Hydrogen-Reduction and Carbothermic Techniques, J. Nucl. Mater., 41: 293 (1971).

03:89 NUCLEAR STRUCTURE STUDIES IN THE HEAVY ELEMENT REGION. Bemis, C. E. Jr., Silva, R. J.; Dittner, P. F.; (Ford, J. L. C. Jr.; McGowan, F. K.; Stelson, P. H.; Milner, W. T.; and Robinson, R. L.; Physics Division). (Oak Ridge National Laboratory, Chemistry Division.)

The behavior of nuclear matter is determined to a large extent by level structure and shape effects. Thus, particle scattering and Coulomb excitation experiments on those heavy nuclei that shed light on these properties are being pursued; for example, single proton states in ^{249}Bk were obtained from the energies of the deuterons and tritons emitted in the ^{248}Cm(^{3}He,d) and (^{4}He,t) reactions. Similarly, nuclear levels of ^{236}U are being obtained via inelastic deuteron-scattering experiments. Also, knowledge of ground-state deformations, static and transition electric quadrupole and hexadecapole moments, and lifetimes of excited nuclear states are being obtained for a number of even–even transuranium isotopes from Coulomb excitation studies.

Investigation of states in the first potential well (but connected to states in the second well) gives further insight into the states at large deformation. The products of fission isomerism via Coulomb excitation will provide an exact description of these states, and we plan to extend our studies to the production of spontaneously fissioning isomers via Coulomb excitation, e.g., ^{242m}Am.

As high-atomic-number projectiles become available, studies of multiple Coulomb excitation, angular momentum limits, and direct Coulomb-induced fission will be possible.

PUBLICATIONS

Ford, J. L. C. Jr., Stelson, P. H., Bemis, C. E. Jr., McGowan, F. K., Robinson, R. L., and Milner, W. T., Precise Coulomb Excitation B(E2) Values for First 2^+ States of the Actinide Nuclei, Phys. Rev. Lett., 27: 1232 (1971).

McGowan, F. K., Bemis, C. E. Jr., Ford, J. L. C. Jr., Milner, W. T., Robinson, R. L., and Stelson, P. H., Equilibrium Quadrupole and Hexadecapole Deformation in ^{230}Th and ^{238}U, Phys. Rev. Lett., 27: 1741 (1971).

03:90 A STUDY OF COMPLEX NUCLEAR REACTION MECHANISMS INVOLVING HEAVY IONS AND HEAVY TARGET NUCLEI. Hahn, R. L., and Dittner, P. F., (Toth, K. S., Physics Division), Keller, O. L. (Oak Ridge National Laboratory, Chemistry Division.)

The use of heavy ions allows experimenters to progress to new frontiers in nuclear interactions. As the complexity of the bombarding ion increases, the number and complexity of reaction paths increase thus leading to a large variety of product nuclei. The study of heavy-ion reactions provides important information to our understanding of the interaction of nuclear matter and, at the same time, aids in the discovery of new and better methods of production of the heaviest elements and isotopes.

The effects of projectile mass and atomic number, angular momentum, and shell structure upon such quantities as the total reaction cross section, Coulomb barrier height and shape, and the probabilities for fission and complex emission are being measured for the ions ^{12}C, ^{14}N, ^{16}O, and ^{20}Ne. The excitation functions, energies, and angular distributions of the light-ion products (i.e., ^{4}He, ^{8}Be, etc.) produced in the bombardment of ^{238}U with ^{12}C and ^{16}O are being determined with an $E-\Delta E$ particle identification system. In addition, the energy and angular distributions of ^{244}Cf and ^{245}Cf nuclei produced in the reactions $^{238}U(^{12}C,5n$ and $6n)$ and $^{239}Pu(^{12}C,\alpha 2n$ and $\alpha 3n)$ are being determined by alpha counting of collected recoils.

These studies will be extended to other heavy element targets, e.g., ^{208}Pb and ^{241}Am, and to more complex projectiles (Ne to Ar). For this, improvements in the ORIC ion source will be necessary, so that the heavier ions will have sufficient energy to penetrate the Coulomb barrier.

03:91 SEARCH FOR SUPER-HEAVY ELEMENTS BY NEUTRON MULTIPLICITY COUNTING. Halperin, J., Stoughton, R. W and Druschel R. E. (Oak Ridge National Laboratory, Chemistry Division.)

An unexpected stability has recently been predicted for nuclides near closed shells at $Z = 114$ and higher. If such nuclei were formed in stellar nucleosynthesis, the half-lives predicted suggest that detectable amounts would remain in nature.

Since such super-heavy elements (or their daughters) are expected to decay by spontaneous fission and since the number of neutrons per fission ($\bar{\nu}$) is calculated to be very high (~10), we have assembled a neutron multiplicity counter to search for such nuclides. The counter accepts samples of about 50 kg and has a sensitivity of about 1 spontaneous fission (of high $\bar{\nu}$) per day.

This technique has two main advantages over others. The large sample size allows measurements without prior chemical separation (which entails possible loss of an element of imperfectly known properties), and the insensitivity to γ rays allows study of rather hot accelerator targets.

With this counter, we are examining a wide range of natural samples, and intend to examine accelerator targets as they become available. A growing number of accelerators is able to provide heavy-ion beams of adequate energy and intensity to test the possibility of synthesizing such super-heavy nuclides.

PUBLICATIONS

Macklin, R. L., Glass, F. M., Halperin, J., Roseberry, R. T., Schmidt, H. W., Stoughton, R. W., and Tobias, M., Neutron Multiplicity Counter, Nucl. Instrum. Methods, 102(1): 181-187 (July 1, 1972).

03:92 INVESTIGATIONS OF THE ACTINIDE ELEMENTS AND THEIR COMPOUNDS BY ELECTRON SPECTROSCOPY. Krause, M. O. (Oak Ridge National Laboratory, Chemistry Division.)

Electron spectroscopy offers a powerful approach to the determination of binding energies of electrons in atoms. The host atoms can be located in gases or in solids so that environmental effects can be pinpointed. Two aspects of the binding energy are particularly interesting in the actinide region because they can only be studied there. One is the second-order relativistic corrections that enter into the calculation of binding energies from first principles, and the second is the behavior of the 5f electrons with chemical binding.

An evaluation of inner shell binding energies and x-ray energies of the actinides is being made to test such theoretical predictions. Further, photoelectron spectrometry is to be used to measure binding energies with high accuracy in free Am atoms, where solid state and chemical effects are eliminated.

In the lanthanide region, electron spectroscopic studies on compounds such as the fluorides have already yielded fruitful results in the determination of the location of the 4f electrons, their spin-splitting, and their energy shifts as a function of atomic number through the series. Similar information will be most helpful in the development of an understanding of the bonding in the actinide region since the data are expected to be amenable to theoretical treatments already developed in our laboratory.

PUBLICATIONS

Krause, M. O., and Wuilleumier, F., Electron Binding Energies in Americium, in Electron Spectroscopy, D. A. Shirley (Ed.), North Holland Publishing Company, Amsterdam, Holland, 1972, p. 759.

_____, and Wuilleumier, F., X-Ray Analysis by Photoelectron Spectrometry, in Proceedings of the International Conference on Inner Shell Ionization Phenomena, Atlanta, Apr. 14, 1972.

03:93 PHYSICAL CHEMISTRY OF THE ACTINIDE ELEMENTS. Nugent, L. J., (K. L. Vander Sluis, Physics Division). (Oak Ridge National Laboratory, Chemistry Division.)

In the actinide region the direct determination of such quantities as oxidation potentials, heats of sublimation, ionization potentials, and heats of solution, has proceeded slowly because of manifold experimental and theoretical difficulties. Recently, however, we have been making considerable progress in the theoretical prediction of unknown oxidation potentials in the heavy elements, and these predictions have been instrumental in directing new experimental efforts. For example, guided by these predictions, we have just prepared the first compounds of divalent actinides (californium dibromide and americium diiodide), and a polarographic determination of the II-III oxidation potential of californium has just been completed.

The techniques used to predict oxidation potentials have now been extended to allow the estimation of heats of sublimation and solution in the actinide region. These estimates indicate that some presently accepted data are in error. Although interest in thermodynamic properties at the end of the actinide series is high, such properties for elements 100 (fermium) and beyond will be available only from theory because the quantities potentially available are so small. This points up the value of our theoretical approach and also indicates the importance of obtaining experimental values for all the elements possible, so that the theoretical values will have as much experimental validation as possible.

PUBLICATIONS

Nugent, L. J., and Vander Sluis, K. L., Theoretical Treatment of the Energy Difference Between $f^q d^1 s^2$ and $f^{q+1} s^2$ Electron Configurations for Lanthanide and Actinide Atomic Vapors, J. Opt. Soc. Amer., 61: 1112 (1971).

_____, Baybarz, R. D., Burnett, J. L., and Ryan, J. L., Electron-Transfer and f → d Absorption Bands of Some Lanthanide and Actinide Complexes and the Standard (III-IV) Oxidation Potentials for Each Member of the Lanthanide and Actinide Series, J. Inorg. Nucl. Chem., 33: 2503 (1971).

_____, Laubereau, P. G., Werner, G. K., and Vander Sluis, K. L., Noncovalent Character in the Chemical Bonds of the Lanthanide(III) and Actinide(III) Tricyclopentadienides, J. Organometal. Chem. (Amsterdam), 27: 365 (1971).

Vander Sluis, K. L., and Nugent, L. J., Energy Difference Between $f^q p s^2$ and $f^{q+1} s^2$ Electron Configurations for Lanthanide and Actinide Neutral Atoms, J. Opt. Soc. Amer., 61: 50 (1971).

03:94 SOLID STATE AND SOLUTION CHEMISTRY OF THE TRANSURANIUM ELEMENTS. Peterson, J. R. (Consultant from University of Tennessee), Burns, J. H., Baldwin, W. H., (Baybarz, R. D., Chemical Technology Division). (Oak Ridge National Laboratory, Chemistry Division.)

A major interest in the transuranium elements is the bonding exhibited in solution and in crystals. Our studies of bonding range from the metals themselves through binary compounds, such as oxides and halides, to relatively complex compounds that sometimes include organic moieties. We aim to establish the bonding of the various transuranium elements in a variety of states of combination by structural, thermodynamic, spectroscopic, and magnetic measurements on appropriate elemental or compound samples.

Our studies of the metallic state have been directed to berkelium. It was first prepared here, and its melting point and the structures of its two modifications were determined. We plan to study magnetic properties of the two modifications and to obtain the heat of solution of the element.

Neptunium was first coerced into the oxidation state of VII in the USSR, through a complex ion of only guessed-at identity. We have worked out a crystal-growing technique to obtain single crystals of compounds such as $LiCo(NH_3)_6Np_2O_8(OH)_2 \cdot 2\ H_2O$ which we have shown by x-ray diffraction to contain the square planar NpO_4^- ion. This suggests that $NpO_4(OH)_2^{3-}$ may occur in strongly alkaline solution, and we are planning to examine its structure spectroscopically. We also plan to see whether fluorine can be substituted for oxygen while maintaining the neptunium in the VII state.

PUBLICATIONS

Peterson, J. R., Fahey, J. A., and Baybarz, R. D., The Crystal Structures and Lattice Parameters of Berkelium Metal, J. Inorg. Nucl. Chem., 33: 3345 (1971).

———, and Baybarz, R. D., The Stabilization of Divalent Californium in the Solid State: Californium Dibromide, Inorg. Nucl. Chem. Lett., 8: 423 (1972).

Fahey, J. A., Peterson, J. R., and Baybarz, R. D., Some Properties of Berkelium Metal and the Apparent Trend Toward Divalent Character in the Transcurium Actinide Metals, Inorg. Nucl. Chem. Lett., 8: 101 (1972).

Laubereau, P. G., Ganguly, L., Burns, J. H., Benjamin, B. M., Atwood, J. L., and Selbin, J., Preparation and Properties of Triindenylthorium Chloride and Triindenyluranium Chloride, Inorg. Chem., 10: 2274 (1971).

03:95 SEARCH FOR NEW TRANSURANIUM ELEMENTS AND ISOTOPES. Silva, R. J.; Bemis, C. E. Jr.; Dittner, P. F.; Eichler, E.; Hahn, R. L.; Keller, O. L.; and Mallory, M. L.; D. C. Hensley and C. D. Goodman, Physics Division). (Oak Ridge National Laboratory, Chemistry Division.)

The heavy actinide and transactinide elements lie at the presently known limit of nuclear matter. The investigation of their stability and structure provides important information for nuclear theories and suggests directions for improved stability calculations. The study of alpha, gamma, and fission properties can lead to more detailed knowledge of the nuclear energy levels of the heaviest elements and to a better understanding of these nuclear decay processes.

Currently, we are attempting to produce the new element-106 via *the ^{249}Cf(^{18}O,4n)^{263}106 reaction. Because of the half-lives (millisec.)* and low product rates (a few atoms per day), a large fraction of our effort is directed toward the development of techniques for the fast isolation of product nuclei and the identification of atomic numbers and mass numbers. For example, on-line energy, velocity and mass analysis systems as well as fast gas-phase chemical separations are being developed. In addition, the alpha–x-ray technique for Z identification, developed for element-102 (^{255}No), is being applied to element-104 (^{257}104). A gas-jet capillary system is being developed for rapid transport of product atoms in high yield over a distance of several feet to a shielded area. The alpha–x-ray technique can then be used for decay studies of nuclides with sub-second half-lives. We will continue our search for and study of long-lived isotopes of known elements as well as, e.g., the recently discovered isotope ^{259}No ($T_{1/2}$ = 54 minutes).

PUBLICATIONS

Dittner, P. F., Bemis, C. E. Jr., Hensley, D. C., Silva, R. J., and Goodman, C. D., Identification of the Atomic Number of Nobelium by an X-Ray Technique, Phys. Rev. Lett., 26: 1037 (1971).

———, and Bemis, C. E. Jr., K-Series X-Ray Energies and Intensities for Curium, Berkelium, Californium, and Einsteinium, Phys. Rev., A, 5: 481 (1972).

Chu, Y. Y., Perlman, M. L., Dittner, P. F., and Bemis, C. E. Jr., Electron Binding Energies, X-Ray Spectra, and L Shell Fluorescence Yields in Curium (Z = 96), Phys. Rev., A, 5: 67 (1972).

03:96 CHEMICAL STUDIES OF ACCELERATOR-PRODUCED ELEMENTS IN THE ACTINIDE, TRANSACTINIDE, AND SUPERHEAVY REGIONS. Silva, R. J.; Keller, O. L.; Baybarz, R. D.; and Peterson, J. R. (University of Tennessee). (Oak Ridge National Laboratory, Chemistry Division.)

The great correlative and predictive power of the Periodic Table of the Elements rests on the periodicity with atomic number of the electronic configurations, which, in turn, rests on the fundamental laws of quantum mechanics. As the elements get heavier, however, relativistic effects become more and more important, and they could change the familiar periodicity significantly. Such relativistic effects are now seen as important in the calculation *of certain atomic properties, but they may soon be seen in the test* tube as an actual change in chemical properties away from those expected on the basis of systematics alone. Although predictions made here and elsewhere indicate that such large changes will not occur until around elements-111 and -115, it is important now to be studying the heaviest elements available, namely those in the range of 102 through 105. These elements are important in themselves because they occur at the end of the actinide (5f) series and at the beginning of the transactinide (6d) series of elements. Mapping out the structure of the periodic table in this critical region is therefore the next important step at the frontier of inorganic chemistry.

Collaborative experiments have already been carried out with researchers at the Berkeley HILAC on the aqueous chemistry of elements-102 and -104. The construction of an automated system is now nearing completion for the first aqueous chemical separation of element-105 (using ^{262}105, $T_{1/2} \cong 40$ seconds). Also, at the Oak Ridge Isochronous Cyclotron, we have initiated studies of the chemistry of lawrencium, element-103, using the three-minute isotope of mass 260. Since element-103 is the last member of the actinide series, and element-104 the first member of the transactinides, these experiments are looking at a point where the chemistry should change drastically with a change of one in atomic number.

PUBLICATIONS

Silva, Robert, James Harris, Matti Nurmia, Kari Eskola, and Albert Ghiorso, Chemical Separation of Rutherfordium, Inorg. Nucl. Chem. Lett., 6: 871 (1970).

Keller, O. L. Jr., Burnett, J. L., Carlson, T. A., and Nestor, C. W. Jr., Predicted Properties of the Superheavy Elements. I. Elements 113 and 114, Eka-Thallium and Eka-Lead, J. Phys. Chem., 74: 1127 (1970).

03:97 STUDIES OF LOW-ENERGY-INDUCED NUCLEAR FISSION. Loveland, Walter D. (Oregon State University, Chemistry Department.)

The main objectives of this research program are:

(a) An attempt to search experimentally for evidence of a connection between the transition nucleus and the fission mass distribution.

(b) Measurements of the fragment angular momentum in fission for fissioning systems of different (Z,A) and as a function of the fragment mass asymmetry in a given fissioning system.

(c) A study of the details of the energy balance in fission.

Research toward objective (a) is being carried out by measuring and analyzing the fragment angular distributions and cross sections as a function of excitation energy for ^{226}Ra (n,f). Isomer ratio measurements and fragment γ-ray angular correlations are used to study fragment angular momentum. Current studies of the fission energy balance involve measurement of γ-ray-energy release in ^{239}Pu (n,f). Research on unusual aspects of fission such as short-range α particle emission and ternary fission is being carried out as well as studies of the nuclear structure of fragments near A = 132.

PUBLICATIONS

Loveland, W., and Shum, Y. S., Fission Fragment Angular Momen*tum in Charged Particle Induced Fission I.* ^{134}Cs and ^{95}Nb Isomer Ratios, Phys. Rev., C, 4: 2282 (1971).

———, A Laboratory Experiment on the Statistical Theory of Nuclear Reactions, Amer. J. Phys., 39: 627 (1971).

———, Nuclear Fission, in American Institute of Physics Handbook of Physics, 3rd ed., D. Gray (Ed.), McGraw-Hill Book Company, Inc., New York, 1971.

03:98 "SPECTROSCOPIC STUDIES OF ACTINIDE IONS IN CRYSTALLINE SOLIDS". Gruber, John B. (Washington State University, Department of Physics.)

Our research objectives are the detailed evaluation and analysis of the optical and magnetic properties of actinide ions incorporated into single-crystal insulator, semiconductor, and superconductor lattices. Single crystals are either procured or grown in our laboratory for these studies. The optical absorption, fluorescence, and Zeeman spectra provide data that (1) identify the electronic states of actinide ions, (2) indicate mechanisms of coupling between the ion and the lattice through evaluation of optical transition line widths, and (3) provide actinide ion–ion interactions through additional observed lines as a function of actinide ion concentration.

Magnetic studies in the form of EPR and NMR experiments indicate the nature of the ground state level of the actinide ion in the crystal, the actinide nucleus coupling to the 5f electrons, and the degree to which the 5f electrons are involved in chemical bonding.

Actinide ions "doped" into various semiconductors and superconductors act as optical and magnetic probes in understanding the electrical properties of these materials.

Lasers are used to induce optical harmonics and multiphoton absorption in all these materials. Optical harmonic generation allows us to continue the search for useful optical parametric oscillators. Multiphoton absorption allows us to study states of actinide ions not observed using ordinary spectroscopy techniques. We can induce ultraviolet laser action by internal pumping through the actinide ions themselves when such actinide ion states are not excited by single photon flash-lamp techniques.

PUBLICATIONS

Stoner, T. R., and Gruber, J. B., Closure Procedure for Two-Photon Absorption Intensities, J. Chem. Phys., 52: 1508 (1970).

Gruber, J. B., Two-Photon Spectroscopy: Rare Earth and Actinide Ions in Single Crystals, in Proceedings of the Ninth Rare Earth Research Conference, USAEC Report CONF-711001, Vol. II, pp. 475-477, 1971.

Olsen, D. N., Stöhr, J., and Gruber, J. B., Use of Pseudopotential for Crystal-Field Splitting of J Levels of $TmCl_3 \cdot 6H_2O$, J. Chem. Phys., 55: 4471 (1971).

Berringer, B. W., Gruber, J. B., Loehr, T. M., and O'Leary, G. P., Far-Infrared and Raman Spectra of Hexachloro Salts of Tetravalent Neptunium, J. Chem. Phys., 55: 4608 (1971).

Richardson, R. P., and Gruber, J. B., Paramagnetic Resonance of Tetravalent ^{237}Np in Single Crystals of ThO_2, J. Chem. Phys., 56: 256 (1972).

03:99 SEARCH FOR ELEMENT-118 (EKA-RADON). Wahl, Arthur C. (Washington University, Department of Chemistry.)

The objectives of this investigation are to discover nuclides with atomic number 118, to study the decay properties of these nuclides and of their probable descendants (isotopes of elements-116, -114, -112, and -110), and to look for very short-lived (half-lives $\sim 10^{-8}$ sec) spontaneously fissioning products of heavy-ion reactions. Heavy targets (^{209}Bi, ^{238}U) will be bombarded with heavy ions (^{136}Xe, ^{204}Hg, ^{238}U) from the Berkeley SuperHILAC to try to form compound nuclei that fission to give a broad spectrum of products including isotopes of element-118. Fission fragments will be stopped in strontium stearate, from which only inert gas atoms will escape into an evacuated space lined with plastic and/or mica track detectors, which will register the passage of a fragment from a spontaneously fissioning descendant formed by several alpha decay steps from an 118 isotope. The heavy-ion beam and some reaction products will pass through a hole in the stearate collector and down a tube containing baffles over track detectors to register fragments from decay by spontaneous fission of reaction products in flight. Construction of the equipment is nearing completion; it will be tested at the Washington University cyclotron before experiments are undertaken at the SuperHILAC.

PUBLICATIONS

Lin, Chien-Chang, and Wahl, Arthur C., Cumulative Yields of 40.1-Min ^{123}Sn, 9.6-Min ^{125}Sn and ^{128}Sn from Thermal-Neutron Induced Fission of ^{235}U, J. Inorg. Nucl. Chem., 34: 1479 (1972).

Erdal, B. R., and Wahl, A. C., Modes of Formation of Tin Fission Products, J. Inorg. Nucl. Chem., 33: 2763 (1971).

ALSO SEE Nuclear Spectroscopy: 03:1, 03:2, 03:15, 03:18; Nuclear Reactions: 03:27, 03:28, 03:30, 03:32, 03:38, 03:47, 03:49, 03:50, 03:51, 03:52, 03:54, 03:58, 03:60, 03:63; Chemical Spectroscopy; 03:237, 03:256, 03:257, 03:261; Thermodynamics: 03:308, 03:311, 03:316, 03:321; High-Temperature and Inorganic Chemistry: 03:340, 03:359, 03:363; Structural Chemistry: 03:371, 03:372, 03:373; Analytical Chemistry: 03:407; Separations Chemistry: 03:412, 03:414, 03:415, 03:418; Engineering Chemistry: 03:437; Miscellaneous Chemical Studies: 03:448, 03:455, 03:456.

RADIATION CHEMISTRY: AQUEOUS

Studies of the interactions of ionizing radiation with water and aqueous solutions.

03:100 RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS. Hart, E. J.; Matheson, M. S.; Schmidt, K. H.; Jonah, C.; Martin, J.; and Miller, J.: (Argonne National Laboratory, Chemistry Division).

The primary processes taking place in irradiated water and the reactions of hydrated electrons (e^-_{aq}), H atoms, and OH radicals are being investigated by pulse radiolysis techniques. The pulse length of our new high-current, L-Band (1300 MHz) Linac has been decreased from about 1×10^{-9} sec to near 50×10^{-12} sec by the recent installation of a new prebuncher. This single 50-picosecond pulse delivers a dose of 2 to 3 kilorads. Reactions of subnanosecond duration may now be studied with equipment consisting of a pulsed laser, a fast photodiode, and a multichannel analyzer having a time resolution of about 90 picoseconds. Work is in progress to settle the controversy regarding the primary hydrated electron yield. $G(e^-_{aq})$ is presently reported as ranging from 3.4 to 5.0. The absolute value of $G(e^-_{aq})$ as well as the decay rate of e^-_{aq} at subnanosecond time intervals will provide information regarding "spur" size and e^-_{aq} distribution. Our picosecond pulse will also be used to study pre-hydration reactions of e^-.

Studies involving subexcitation electron-, e^-_{aq}-, OH-, and H-atom reactions with scavengers at high concentrations, such as those in living cells, are under investigation. Other pulse radiolysis studies utilizing standard spectrophotometric and conductimetric techniques, and γ irradiation will continue on aqueous oxygen and methane solutions. The excitation of $RH(CN)_6^{3-}$, Ru $(bipyridyl)_3^{2+}$, and electron tunnelling in aqueous glasses and other inorganic and organic ions are also being studied along with fluorescent reactions of tritiated water and chemiluminescent reactions of e^-_{aq}.

PUBLICATIONS

Bjergbakke, E., and E. J. Hart, Oxygen Formation in the Gamma-Ray Irradiation of $Fe^{2+}-Cu^{2+}$ Solutions, Radiat. Res., 45: 261-273 (1971).

Gupta, B. L., and E. J. Hart, Radiation Chemistry of Some Sulfonaphthalein Dyes, Radiat. Res., 48: 8-19 (1971).

Koulkes-Pujo, A. M., B. D. Michael, and E. J. Hart, Scavenger Studies of Electron Pulse Irradiated Solutions at Hydrated Electron Half-Lives in the Range 35 to 0.35 Nanoseconds, Int. J. Radiat. Phys. Chem., 3(3): 333 (1971).

Michael, B. D., E. J. Hart, and K. H. Schmidt, The Absorption Spectrum of e^-_{aq} in the Temperature Range −4 to 390°, J. Phys. Chem., 75: 2798-2805 (1971).

03:101 EFFECTS OF MERCAPTANS AND DISULFIDES IN PHOTOCHEMICAL AND HIGH-ENERGY-RADIATION-INDUCED REACTIONS. Cohen, Saul G. (Brandeis University. Department of Chemistry. Waltham, Massachusetts 02154).

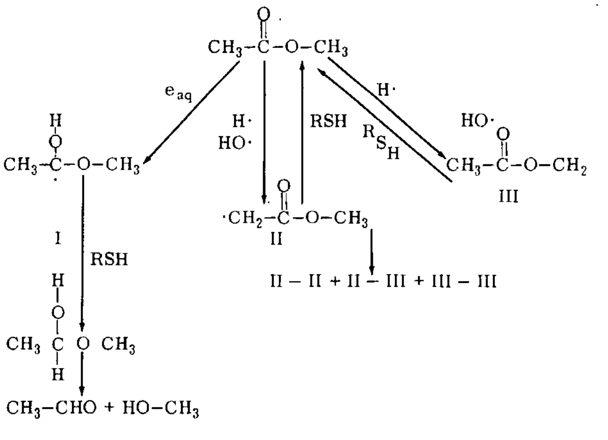
The objective of this program is to establish the factors that allow mercaptans to either inhibit or accelerate the chemical consequences of γ and ultraviolet radiation.

The radiation- and light-induced reactions that we study are those in which fragments or excited species abstract or donate a hydrogen atom, and the radicals so formed lead to the products

$$A\cdot + BH \rightarrow AH + BH\cdot \rightarrow HBBH \text{ or } B + BH_2$$
$$A + BH_2 \rightarrow AH\cdot + BH\cdot \rightarrow HBBH + HAAH, \text{ etc.}$$

We have shown that mercaptans may act alone or as the mercaptan-thiyl radical hydrogen atom donor–acceptor couple. They inhibit and enhance reactions by the same mechanism, by reaction with radical intermediates, donating or abstracting hydrogen. They inhibit if these reactions restore the intermediates to the initial states. They accelerate if these reactions carry intermediates on to products, that may not be formed at all in the absence of mercaptans.

We are currently studying γ radiolysis of esters in dilute water solution, Scheme A. The radicals are formed as indicated and in the absence of mercaptans lead to dimeric products. This is inhibited by mercaptans, which restore the radicals to the starting ester. However, mercaptan accelerates reductive cleavage. Extension of this to polymeric systems indicates that mercaptans would prevent cross-linking but enhance chain rupture. This study will be extended to γ and ultraviolet irradiation of ethers, amines, amides, and polymeric systems. Inhibition of formation of dimeric products by other additives, sodium formate, carbon monoxide, 2-propanol, and nitrous oxide, which react directly with H and OH, is also being studied.



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PUBLICATION

Cohen, S. G., and F. L. Lam, Repair and Damage by Mercaptans in ^{60}Co Gamma-Ray Irradiation of Organic Compounds in Aqueous Solution, Radiat. Res., 45: 462 (1971).

03:102 RADIATION CHEMISTRY OF CYANIDE ION. Allen, A. O. and Bielski, B. H. J. (Brookhaven National Laboratory, Chemistry Department).

The effects of radiation on aqueous solutions of most of the common ions have been studied extensively, but an adequate study of cyanide has not yet been made. There is reason to believe that action of free radicals on cyanide ions may have been important in the chemistry that led to the origin of life in the primitive oceans.

Irradiation of KCN solutions by γ rays in the absence of oxygen yields a variety of products: NH_3, CO_3^{2-}, CNO^-, CH_2O, $HCOO^-$, cyanamide, urea, glycine, and others not yet identified. As irradiation continues, still more complex compounds are built up. The main primary chemical action of the radiation is to produce OH radicals and solvated electrons; the latter do not react with cyanide, but convert the products of the reaction of OH with cyanide to a variety of forms. Addition of N_2O converts the solvated electrons to OH radicals and simplifies the chemistry; the main initial stable product then is CNO^-, though more complicated products build up in time. To determine the reaction mechanisms in more detail, quantitative studies of product yields and pulse radiolysis studies of cyanide solutions under various conditions are being made.

03:103 STUDY OF ENZYMATIC MECHANISMS BY PULSE RADIOLYSIS. Bielski, B. H. J. (Brookhaven National Laboratory, Chemistry Department).

Basic experimental methods are being developed for the application of pulse radiolysis to the study of enzyme mechanisms. Pulse radiolysis offers a method of introducing substrate into the system in microseconds. Its advantage over flow-mixing techniques that operate in the millisecond range is apparent. The onset and course of an entire enzymatic cycle have been demonstrated on the ascorbic acid–horseradish peroxidase (HRP) systems, after the substrate (H_2O_2) was formed during a 10-microsecond pulse. A new transient absorbing light at 370 nm was discovered by this technique. Subsequently this transient was also seen in flow experiments when H_2O_2 and HRP were mixed alone. At present the transient is being studied in the presence of tert-butyl alcohol, a convenient radical scavenger.

Preliminary experiments with the lactate–pyruvate–L-lactic dehydrogenase system have shown that the substrate (pyruvate) can be produced easily from D-lactic acid by radiation. The D-lactic acid does not react with L-lactic dehydrogenase and hence is a good source for rapid synthesis of pyruvate via the lactic acid radical. Future plans include a systematic study of this system including the cofactor nicotinamide adenine dinucleotide (NAD^+). The free lactate radical is found to bring about conversion of the reduced form NADH to NAD^+ in the presence of molecular oxygen.

PUBLICATION

Bielski, B. H. J., D. A. Comstock, and R. A. Bowen, Ascorbic Acid Free Radical. I. Pulse Radiolysis Study of Optical Absorption and Kinetic Properties, J. Amer. Chem. Soc., 93: 5624 (1971).

03:104 PULSE RADIOLYSIS OF DNA AND DNA CONSTITUENTS. Holroyd, R. A. (Brookhaven National Laboratory, Chemistry Department).

The technique of pulse radiolysis is being utilized to follow the chemical alterations that DNA in aqueous solution undergoes following a pulse of radiation. Both solvated electrons and hydroxyl radicals react rapidly with DNA to form radicals. The subsequent reactions of these DNA radicals are being explored. Two of the most important changes of interest are protection and sensitization. The conversion of a DNA base radical back to the intact base is classified as a type of protection. Current studies are concerned with the mechanism of sensitization of DNA by bromouracil. It is known from molecular studies that electron transfer from thymine to bromouracil occurs in a diffusion-controlled reaction. The electron on bromouracil causes dissociation of bromide, leaving a very reactive uracil radical which, it is postulated, will abstract from the deoxyribose to cause strand breaks. The results obtained for a solution of DNA in which all the thymine has been replaced by bromouracil are very similar to the results obtained with DNA. In both cases the electron reacts with the DNA to form free radicals that have lifetimes in the range of seconds; however, the anticipated rapid electron transfer to bromouracil is not observed. Further investigation will elucidate the nature and reactions of DNA radicals formed by electron attachment.

03:105 ESR STUDIES OF INORGANIC RADICALS. Fessenden, R. W.; Behar, D.; Samuni, A.; and Chawla, O. P. (Carnegie-Mellon University, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).

ESR methods are being used to study inorganic radicals in aqueous solution with both radiolysis and photolysis for radical generation. Emphasis is upon kinetic and mechanistic aspects and parallel pulse radiolysis experiments are being carried out where profitable. Direct observation of the radical intermediates is preferred as has been possible with $\dot{S}O_3^-$, $\dot{P}O_3^{2-}$, $H\dot{P}O_2^-$, and several other radicals that can be formed both from radiolytically produced OH and photolytically. Where such direct experiments are not possible, radical trapping with $CH_2{=}NO_2^-$ is used to convert the radicals (R) to a more readily observed form ($RCH_2\dot{N}O_2^-$). A large number of radicals, including the interesting species $\dot{N}_3$ formed from azide, have been studied in this way. Other studies include those of the peroxy radicals formed from transition metal–H_2O_2 complexes and the reactions of CN^- and HCN in irradiated solutions. Extensions of these studies are in progress.

PUBLICATIONS

Behar, D., and Richard W. Fessenden, An Investigation of Radicals Produced in the Photolysis of Thiosulfate Solutions by ESR, J. Phys. Chem., 75: 2752 (1971).

———, and Richard W. Fessenden, ESR Studies of Inorganic Radicals in Irradiated Aqueous Solutions. I. Direct Observation, J. Phys. Chem., 76: 1706 (1972).

———, and Richard W. Fessenden, ESR Studies of Inorganic Radicals in Irradiated Aqueous Solutions. II. Radical Trapping with Nitromethane, J. Phys. Chem., 76: 1710 (1972).

03:106 ESR STUDIES OF RADIATION-PRODUCED RADICALS. Fessenden, R. W.; Schuler, R. H.; and Neta, P. (Carnegie-Mellon University, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).

Previous work in these laboratories has shown that the in situ radiolysis of flowing aqueous solutions is a practical and convenient means of producing radicals for ESR studies. Current applications emphasize mechanistic and structural aspects. The specificity of ESR spectra is being used to provide radical identifications for those studying related systems by other means such as pulse radiolysis. Examples are the reactions of e_{aq}^- with nitriles to form $R\overset{H}{C}{=}\dot{N}$ and with olefinic and aromatic compounds to form anion radicals. Because minor changes in radicals are readily detected by their effect on the spectra, studies of the equilibria and kinetics of acid dissociations are possible and are receiving considerable attention. This radiolytic method of radical generation has also been used to produce radicals for structural studies by means of ^{13}C hyperfine splittings both in enriched compounds and at the natural abundance level.

PUBLICATIONS

Eiben, K., and Richard W. Fessenden, ESR Studies of Transient Radicals in Aqueous Solutions, J. Phys. Chem., 75: 1186 (1971).

Neta, P., and Richard W. Fessenden, Reaction of Nitriles with Hydrated Electrons and Hydrogen Atoms in Aqueous Solution as Studied by ESR, J. Phys. Chem., 74: 3362 (1970).

———, and Richard W. Fessenden, Electron Spin Resonance Study of Radicals Produced in Irradiated Aqueous Solutions of Amines and Amino Acids, J. Phys. Chem., 75: 738 (1971).

———, and Richard W. Fessenden, Electron Spin Resonance Study of Radicals Produced in Irradiated Aqueous Solutions of Thiols, J. Phys. Chem., 75: 2277 (1971).

Laroff, Gary P., and Richard W. Fessenden, ^{13}C Hyperfine Interactions in Radicals from Some Carboxylic Acids, J. Chem. Phys., 55: 5000 (1971).

03:107 APPLICATION OF ESR METHODS TO REACTION KINETIC STUDIES. Fessenden, R. W.; Schuler, R. H.; Neta, P.; and Behar, D. (Carnegie-Mellon University, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).

Both steady state and time-resolved ESR methods are being developed to examine the reaction kinetics of radical intermediates present in the radiolysis of aqueous solutions. To date attention has been focused on determining the rate constants for reaction of H atoms with various organic substrates. The method used involves a comparison of the signal intensity at steady state in the presence and absence of solute with the relative signals being controlled by the rate of the chemical reaction and decay of the chemically induced electron spin polarization. Some 200 rate constants have been measured and general patterns established for H atom reactions that allow predictions of reactivity to be made. These rate constants are, of course, of considerable importance in the design of any experiment involving H atoms. Work is in progress toward extending aspects of this approach toward measurements of other small radicals such as CF_3. Parallel work is being carried out toward direct measurements of reaction rates via time-resolved ESR spectrometry.

PUBLICATIONS

Neta, P., and Robert H. Schuler, Rate Constants for Reaction of Hydrogen Atoms with Aromatic and Heterocyclic Compounds. The Electrophilic Nature of Hydrogen Atoms, J. Amer. Chem. Soc., 94: 1056 (1972).

———, and Robert H. Schuler, Rate Constants for Reaction of Hydrogen Atoms with Compounds of Biochemical Interest, Radiat. Res., 47: 612 (1971).

———, Richard W. Fessenden, and Robert H. Schuler, An Electron Spin Resonance Study of the Rate Constants for Reaction of Hydrogen Atoms with Organic Compounds in Aqueous Solution, J. Phys. Chem., 75: 1654 (1971).

03:108 RADIATION CHEMICAL STUDIES ON SYSTEMS OF BIOCHEMICAL INTEREST. Neta, P. (Carnegie-Mellon University, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).

Both electron spin resonance and pulse radiolysis techniques have been applied to the study of the radiolysis of compounds of biological significance, including amino acids and peptides, sulfur compounds, pyrimidine bases, halouracils, pyridinium compounds, and others. ESR studies have identified the radicals produced by the reaction of amino acids and dipeptides with e_{aq}^- (causing deamination), with H and OH (resulting in H abstraction from CH), and with O^- (abstracting H from NH also). Pyrimidine bases have been found to add OH to either position 5 or 6. The initial adducts undergo consequent changes, which in the latter case result in ring opening. Some electron adducts of the pyrimidines have been observed by ESR, but the electron adducts of 5-bromo- and 5-chlorouracils have been found to undergo rapid dehalogenation. Dehalogenation of bromo-, chloro-, and fluorouracils is efficiently caused by the radiation of OH with these compounds, the yields being determined by product analysis, the kinetics followed by pulse radiolysis and the resulting radicals identified by ESR. Pulse radiolysis and ESR studies have also revealed the difference in reaction mechanism of O^- as compared to OH and the unique use of O^- for the production of some specific radicals has been pointed out and is being explored. Radicals produced from pyridine and pyridinium derivatives, including NAD^+, are currently being studied by ESR.

PUBLICATIONS

Neta, P., and Richard W. Fessenden, Electron Spin Resonance Study of Deamination of Amino Acids by Hydrated Electrons, J. Phys. Chem., 74: 2263 (1970).

———, Electron Spin Resonance Study of Radicals Produced in Irradiated Aqueous Solutions of Uracil and Related Pyrimidines, Radiat. Res., 49: 1 (1972).

———, Morton Z. Hoffman, and M. Simic, Electron Spin Resonance and Pulse Radiolysis Studies of the Reactions of OH and O^- Radicals with Some Organic Compounds, J. Phys. Chem., 76: 847 (1972).

03:109 MICELLES AS SIMPLE MODEL SYSTEMS FOR RADIATION AND PHOTOCHEMISTRY IN BIOLOGICAL ENVIRONMENTS. Patterson, L. K. (Carnegie-Mellon University, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).

In order to study some effects of the biological environment on various kinetic processes in radiation and photochemistry we have chosen to consider micelles as appropriate preliminary model systems. These systems provide regions of quasi-ordered hydrocarbon environments as well as interfacial regions between the hydrocarbon and aqueous phases. Distribution of a substrate among these regions and the aqueous phase has been shown to strongly affect reactivities of the substrate toward the primary radicals e_{aq}^-,·OH, and ·H. Both enhancement and retardation of rate constants relative to measurements in aqueous solution have been observed. Present investigations are directed at relating such effects to specific interaction between micelles and various functional groups. Also, it has been found that several radiation-induced chain reactions are affected by the presence of micelles even when initial radical formation is not. For example, formation of micelles from a surfactant having $(CH_3)_3N^+$ as a surface active group may be shown to enhance chain reactions involving cytosine and cytodine.

Micellar studies have also been conducted on kinetics of excited hydrocarbon singlet states. These also show that specific micelle–hydrocarbon interactions affect reactivity toward quenchers in the bulk aqueous phase as well as energy transfer and excimer formation. This work, in which simple substrates have been used, is meant to provide a basis for understanding effects observed as we move to incorporate more complex molecules of biological importance into the micellar systems.

PUBLICATIONS

Fendler, J. H., E. J. Fendler, G. Bogan, L. K. Patterson, and K. M. Bansal, Steady State and Pulse Radiolysis Studies of Cl_2^-. Reactivity in Micellar Systems, Chem. Commun., 14 (1972).

Fendler, Janos H., and Larry K. Patterson, Micellar Effects on the Reactivity of Hydrated Electron with Benzene, J. Phys. Chem., 74: 4608 (1970).

Bansal, K. M., E. J. Fendler, J. H. Fendler, and L. K. Patterson, Reactions of Hydrated Electrons, Hydrogen Atoms, and Hydroxyl Radicals in Micellar Systems, Int. J. Radiat. Phys. Chem., 3: 321 (1971).

Patterson, L. K., Krishan M. Bansal, and J. H. Fendler, Pulse Radiolytic Investigations of Hydroxyl Radical Reactivities in Micellar Solutions, Chem. Commun., 152 (1971).

03:110 PULSE RADIOLYSIS STUDIES. Patterson, L. K.; Behar, D.; and Schuler, R. H. (Carnegie-Mellon University, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).

A conventional pulse radiolysis apparatus capable of observing intermediates on the time scale of 0.1 μsec and longer has been interfaced with a PDP-8 data processor for data accumulation, data processing and feedback control of the experiment. Automatic scan of spectra is provided. Detailed studies are being carried out on the intermediates present during radiolysis of aqueous solutions of both inorganic and organic solutes. In many instances it is possible to correlate these pulse radiolysis studies with related ESR work being carried out in these same laboratories. For example, examination of the spectrum resulting from OH attack on 5-fluoro-, 5-chloro-, and 5-bromouracil shows the production of a common radical as is confirmed by the ESR observations. It is suggested that this radical is rapidly produced from the initial OH adduct by loss of HX. The capability of data accumulation as provided by the direct interface with the processor greatly enhances the versatility of this equipment and this versatility will be enhanced even more in the near future by the acquisition of a Biomation 2000 channel sample and hold unit. Many different types of systems are being examined with emphasis being on studies involving the nature and reaction kinetics of intermediates produced by ·OH and e_{aq}^- reactions.

PUBLICATION

Behar, D., Pulse Radiolysis Studies on Br^- in Aqueous Solution: The Mechanism of Br_2^- Formation, J. Phys. Chem., 76: 1815 (1972).

03:111 RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS OF ORGANIC HALIDES. Schuler, R. H. (Carnegie-Mellon University, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).

Both ion selective electrode and pulse conductivity methods provide a very sensitive way of examining the radiation chemistry of aqueous solutions of organic halides. Direct determination of halide ion production by the former method makes available information on the overall chemical reaction whereas the pulse approach makes it possible to examine intermediate production on the microsecond to millisecond time scale. It has been shown, for example, that methyl chloride reacts rapidly with e_{aq}^- to produce a Cl^- ion within microseconds and that CF3Cl undergoes a similar reaction followed by hydrolysis of the CF_3 radical on a time scale longer than milliseconds. Reaction of e_{aq}^- with $CF_2ClCOOH$ initially produces the radical $\cdot CF_2COOH$ (which can be seen in related ESR studies), and this radical also subsequently hydrolyzes completely. Currently we are exploring the reaction of OH with halogen-substituted olefinic compounds.

PUBLICATIONS

Balkas, Turgut I., J. H. Fendler, and Robert H. Schuler, The Radiation Chemistry of Aqueous Solutions of $CFCl_3$, CF_2Cl_2, and CF_3Cl, J. Phys. Chem., 75: 455 (1971).

———, J. H. Fendler, and Robert H. Schuler, Radiolysis of Aqueous Solutions of Methyl Chloride: The Concentration Dependence for Scavenging Electrons Within Spurs, J. Phys. Chem., 74: 4497 (1970).

Asmus, K.-D., W. Grunbein, and J. H. Fendler, Conductometric Pulse Radiolysis of SF_6 in Aqueous Solutions; Rate of Hydrolysis of SF_4, J. Amer. Chem. Soc., 92: 2625 (1970).

03:112 APPLICATION OF LIQUID CHROMATOGRAPHIC METHODS TO THE STUDY OF THE RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS. Schuler, R. H. and Bhatia, K. (Carnegie-Mellon University, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).

To date chromatographic methods have been applied only sporadically to studies of the radiation chemistry of aqueous solutions, largely as a result of limitations imposed by sensitivity requirements. The recent development of very sensitive high-speed liquid chromatographic methods offers considerable promise for the examination of radiation products produced in dilute solutions of organic substrates. We have demonstrated that, in appropriate systems, products can be resolved and are quantitatively measurable on the submicromolar level. For example, studies of the radiation chemistry of 10^{-4} M solutions of p-bromophenol can be readily carried out at dose levels of ~100 rads. It has been shown that in this system reaction of the hydrated electrons provides a source of the p-hydroxyphenyl radical. A detailed study of the rates for reaction of this radical with various secondary solutes is in progress and should provide very much needed basic information on the reactivity of aromatic radicals. Adaptation of the chromatographic methods currently being developed is expected to provide information on the formation of products in systems that cannot be examined by more conventional approaches.

03:113 RADIATION CHEMISTRY OF ORGANIC COMPOUNDS OF NITROGEN. Garrison, W. M. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

The purpose of this program is to determine the detailed reaction mechanisms involved in the action of high-energy radiation on organic compounds of nitrogen in aqueous solution and in the solid state. The radiation chemistry of such systems is of considerable intrinsic interest from the strictly physicochemical standpoint and also has important applications in other areas of radiation research such as: radiation-chemical synthesis and modification of nitrogenous organic chemicals and fibers, radiation preservation of foods and drugs, and in the elucidation of the basic mechanisms of radiobiology.

Primary emphasis in the present program is given to organonitrogen compounds of biochemical interest. Substances under investigation include: amines, acylamines, amino acids, peptides, polypeptides, pyrimidines, and purines. The experimental approach is based on the concept that detailed reaction stoichiometries are required in the elucidation of the complete reaction mechanisms. Numerous microanalytical procedures have been developed over the past years for the determination of inorganic and organic products formed in the radiolysis of organonitrogen compounds. The methods include techniques of mass spectrometry, infrared spectrometry, gas and vapor phase chromatography, ion-exchange chromatography, solvent chromatography, ESR spectroscopy, and radiometric procedures involving the use of ^{14}C-labeled organic compounds. Through applications of these techniques we are determining the respective roles of ionic, free radical, and excited-molecule reactions that are involved in the radiolysis of the organic compounds of nitrogen.

PUBLICATIONS

Makada, H. A., and W. M. Garrison, Radiolytic Oxidation of Peptide Derivatives of Glycine in Aqueous Solution, Radiat. Res., 50: 48 (1972).

———, and W. M. Garrison, Radiolysis of Liquid N-Ethylacetamide, Int. J. Radiat. Phys. Chem., 3: 179 (1971).

Garrison, W. M., Radiation-Induced Reactions of Amino Acids and Peptides, Radiat. Res. Rev., 4: 28 (1972).

Rodgers, M. A. J., H. A. Sokol, and W. M. Garrison, Radiolytic Cleavate of the Peptide Main Chain in Concentrated Aqueous Solution, Biochem. Biophys. Res. Commun., 40: 622 (1970).

Garrison, W. M., M. Kland-English, H. A. Sokol, and M. E. Jayko, Radiolytic Degradation of the Peptide Main Chain in Dilute Aqueous Solution Containing Oxygen, J. Phys. Chem., 74: 4506 (1970).

03:114 ELECTRONIC PROCESSES IN PULSE-IRRADIATED AQUEOUS AND ALCOHOLIC SYSTEMS. Hamill, W. H.; Fisher, M. M.; and Khorana, S. (University of Notre Dame, Radiation Laboratory).

The objective of this work is to test the dry electron model for the radiolysis of water by observations at times $\geq 10^{-8}$ s to support inferences applicable to times $\leq 10^{-14}$ s. The primary species are considered to be H_2O^*, H_2O^+, and e^-, which quickly generate H, OH, $H_3O^+_{aq}$, and e^-_{aq}, which then react further. Alcoholic systems are rather analogous. High concentrations of anions are used to transfer an electron to H_2O^+ before hydration, and this prevents formation of H_3O^+, H, and OH. An increased yield of hydrated electrons is expected by the theory and we have observed such an increase. The hypothetical dry electron, e^-, should be physically and chemically distinguishable from the hydrated electron, e^-_{aq}, and this is supported by experimental evidence as follows. The yield of Cl_2^- in $\geq$1M NaCl is increased at 5×10^{-8} s in solutions to which N_2O has been added. We interpret this as indicating a production of Cl^{-*}, which has H_2O^* as precursor, and the observed yield is $G \cong 1$. At concentrations of I^- and $Br^- \geq$ 1M, appreciable yields of I_3^- and Br_3^- are found at 10^{-8} s, indicating spur reactions, but in 4 to 8M LiI and LiBr aqueous glasses at 77°K the trihalides are formed in very small yields. Since the spur reaction is decreased in the glasses, it can be taken as an indication of an increase in spur size brought about by efficient positive hole migration in the solid state. This hypothesis will be investigated more fully. Further effort is required to substantiate the existence of H_2O^*.

PUBLICATIONS

Hamill, W. H., and T. Sawai, Evidence for Very Early Effects in the Radiolysis of Water, J. Phys. Chem., 74: 3914 (1970).

———, and S. Khorana, Electronic Processes in the Pulse Radiolysis of Aqueous Solutions of Halide Ions, J. Phys. Chem., 75: 3081 (1971).

03:115 RADIOLYSIS OF LIQUIDS AT HIGH PRESSURES. Hentz, R. R.; Farhataziz; and Hansen, E. M. (University of Notre Dame, Radiation Laboratory).

The radiolysis of liquids produces transient species (electrons, ions, excited states, free radicals) the elementary reactions of which determine the radiation chemistry of the liquid. An insight into the nature and behavior of such transient species is obtainable by study of the pressure dependence of their reaction rates and spectra. For such a purpose, earlier studies of the γ radiolysis of liquids at high pressures are being extended with a recently developed system for study of the pulse radiolysis of liquids with optical detection at pressures up to 7 kbar. The system has been used for determination of the pressure dependence of (1) the optical absorption spectrum of the hydrated electron, (2) the absolute specific rates of eleven diffusion-controlled reactions of the hydrated electron, and (3) absolute specific rates of six hydrated electron reactions not controlled by diffusion. The results give definitive values for the partial molal volume and cavity volume of an electron in water and provide evidence for compressibility of the cavity. A similar study of H atom reactions in water that are and are not diffusion-controlled is in progress, and a study of OH reactions is planned. Pressure dependence of optical absorption spectra and specific reaction rates of solvated electrons in ammonia and other liquids will be examined in future work. Comparison of the results with those obtained for the hydrated electron should contribute to the elucidation of electron solvation.

PUBLICATIONS

Hentz, R. R., and D. W. Brazier, Gamma Radiolysis of Liquids at High Pressures. X. The Reaction H + OH^- and the Partial Molal Volume of the Hydrated Electron, J. Chem. Phys., 54: 2777 (1971).

———, Farhataziz, and E. M. Hansen, Pulse Radiolysis of Liquids at High Pressures. I. Absorption Spectrum of the Hydrated Electron at Pressures Up to 6.3 kbar, J. Chem. Phys., 55: 4974 (1971).

———, Farhataziz, and E. M. Hansen, Diffusion-Controlled Reactions of the Hydrated Electron, J. Chem. Phys., 56: 4485 (1972).

03:116 RADIATION AND PHOTOCHEMICAL STUDIES ON THE KINETIC EFFECTS OF MICELLE SOLUBILIZATION. Thomas, J. K.,and Wallace, Stephen C. (University of Notre Dame, Radiation Laboratory).

Laser flash photolysis and pulse radiolysis techniques have been used to study the effect of solubilization in the micellar pseudophase on the kinetic behavior of ionic and neutral species. Typically, a selected polyacene, such as pyrene, is solubilized in water by means of a surface active agent, in which the hydrophilic group may be cationic, anionic, or nonionic (such as polyoxyethylene derivatives). In the laser studies, the pyrene is excited with a short pulse of light to give the singlet excited state, which is observed by nanosecond emission or absorption spectroscopy. Specific rates of quenching are dramatically affected by the charges on both surfactant and quencher or, in the case of a neutral quencher, by its hydrophilic or hydrophobic tendencies. At the high intensities of exciting light available in these laser photolysis studies, a significant photoionization of the solubilized hydrocarbon is observed, producing hydrated electrons in the bulk of the liquid. A comparison of the rates of fluorescence quenching and electron scavenging following excitation provides additional information on the mechanism of fluorescence quenching.

In the pulse radiolysis studies hydrated electrons are produced directly in the aqueous phase, and are then observed to react with the solubilized hydrocarbon. Measurements have been made on the rate of formation of the anions of pyrene and biphenyl in these systems, these rates showing acceleration or inhibition compared to the bimolecular rate measured in pure water itself, depending on the charge of the surfactant.

03:117 THE RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS. Sworski, T. J. (Oak Ridge National Laboratory, Chemistry Division).

The primary objective is to determine the elementary processes in the spur (the region of concentrated energy deposition) when ^{60}Co gamma radiation interacts with aqueous solutions. The general approach is a determination of the yield of products that escape by diffusion from the spur into the bulk of the solution as a function of solute concentration. The approach is indirect; the nature and reactions of the intermediates are induced by chemical intuition through the use of chemical kinetics. Currently, advanced computational methods are being used to solve the kinetic equations for the radiolysis of cerium(IV)–cerium(III)–formic acid mixtures in 4.0M sulfuric acid solutions to determine both G_{OH} and $G_{SO_4^-}$ and in 4.0M nitric acid solutions to determine both G_{OH} and $G_{NO_3^-}$. G_{OH} is proportional to the electron fraction of water. The high values for G_{HNO_2} and $G_{NO_3^-}$ in 4.0M nitric acid solutions suggest the possible role of excited states of nitrate ion and/or water. Therefore, the studies in nitric acid solutions will be extended to include the determinations of G_{HNO_2}, $G_{H_2O_2}$, G_{OH}, and $G_{NO_3^-}$ as a function of nitric acid concentration. Concomitant studies in the photolysis of cerium(IV)–cerium(III)–formic acid mixtures in nitric acid solutions will be conducted to reveal the role of excited states of nitrate ion. Studies in concentrated halide ion solutions are planned.

PUBLICATIONS

Matthews, R. W., H. A. Mahlman, and T. J. Sworski, Elementary Processes in the Radiolysis of Aqueous Sulfuric Acid Solutions. Determinations of Both G_{OH} and $G_{SO_4^-}$, J. Phys. Chem., 76: 1265 (1972).

———, H. A. Mahlman, and T. J. Sworski, Kinetic Evidence that G_{OH} in the Radiolysis of Aqueous Sulfuric and Nitric Acid Solutions Is Proportional to Electron Fraction Water, J. Phys. Chem., 74: 3835 (1970).

———, H. A. Mahlman, and T. J. Sworski, Kinetics of the Oxidation of Cerium(III) by Peroxysulfuric Acids Induced by ^{60}Co Gamma Radiation, J. Phys. Chem., 74: 2475 (1970).

Mahlman, H. A., R. W. Matthews, and T. J. Sworski, Reduction of Cerium (IV) by Hydrogen Peroxide, Dependence of Reaction Rate on Hammett's Acidity Function, J. Phys. Chem., 75: 250 (1971).

ALSO SEE Radiation Chemistry: Other: 03:135, 03:156; Hot Atom Chemistry: 03:199; Chemical Spectroscopy: 03:249; Theoretical Chemistry: 03:281, 03:288; High-Temperature and Inorganic Chemistry: 03:348; Analytical Chemistry: 03:408.

RADIATION CHEMISTRY: GASEOUS

Studies of the interactions of ionizing radiation with gases.

03:118 PULSE RADIOLYSIS OF GASES. Gordon, S.; Sauer, M. Jr.; Mulac, W.; Cooper, R.; and Cummings, J. (Argonne National Laboratory, Chemistry Division).

Using fast reaction techniques (principally spectrophotometric) and pulsed radiolysis, we are engaged in assessing the role of ions, excited states, and radical species in reactions produced by irradiating gases with high-energy electrons. Specific investigations include:

1. We are continuing our studies of ion recombination and excited state formation in the pulse radiolysis of gaseous systems (M. Sauer and W. A. Mulac). Emphasis is currently being placed on the determination of chemical yields (G-values) of excited states. These measurements are of fundamental significance since they will experimentally establish the extent of direct excitation by high-energy electrons and might provide information on the importance of sub-excitation electrons. Measurement of these G-values is also important with respect to the production of excited states in ion-recombination processes. In addition to its interest to radiation chemistry, this information should be of value to plasma physics studies.
2. The formation of OH radicals produced in the pulse radiolysis of water vapor and the subsequent reaction of this radical with various inorganic and organic gases is being studied (S. Gordon, W. A. Mulac). In addition to their importance in radiation chemistry, these studies are of interest in the general field of reaction kinetics and air pollution.
3. Reactions of H atoms produced by the pulse radiolysis of mixtures of hydrogen and inorganic gases are being investigated by observing the growth of the hydrogen-containing intermediate produced using fast spectrophotometric techniques (R. Cooper and J. Cummings).

PUBLICATIONS

Sauer, M. C., and W. A. Mulac, Studies of Light Emission in the Pulse Radiolysis of Gases: Electron Recombination in Nitrogen, J. Chem. Phys., 56: 4995-5004 (1972).

———, and W. A. Mulac, Ion–Electron and Ion–Ion Recombination Coefficients in Gases Studied by Pulse Radiolysis, J. Chem. Phys., 55: 1982 (1971).

Gordon, S., W. Mulac, and P. Nangia, Pulse Radiolysis of Ammonia Gas. II. Rate of Disappearance of the $NH_2(X^2B_1)$ Radical, J. Phys. Chem., 75: 2087 (1971).

Warman, J. M., and M. C. Sauer, Jr., The Temperature Dependence of Electron Attachment to CCl_4, $CHCL_3$, and $C_6H_5CH_2Cl$, Int. J. Radiat. Phys. Chem., 3: 273-282 (1971).

Bullock, G. E., and R. Cooper, Reactions of Cyanogen Radicals with Hydrocarbons, Trans. Faraday Soc., 67(Pt. II): 3258-3264 (1971).

03:119 PHYSICAL AND CHEMICAL FACTORS INVOLVED IN AEROSOL FORMATION. Hart, E. J.; Matheson, M. S.; and Schmidt, K. H. (Argonne National Laboratory, Chemistry Division).

An apparatus for studying the physical and chemical processes occurring in water-saturated polluted atmospheres has been devised. After irradiation of the gases by light or ionizing radiations, aerosol particles develop from the sub-microscopic condensation nuclei formed from the pollutants during a 0.5- to 1.0-second expansion cycle. The density of the cloud of particles formed during the expansion is monitored by a photomultiplier sensing the intensity of scattered light. This technique offers a method for obtaining the size and number distribution of the condensation nuclei in the range below 100 Å diameter. Pollutants such as carbon monoxide and hydrocarbons have a profound effect on the number of condensation nuclei formed as well as on the rate of development of the resulting aerosol. The effect of physical variables such as temperature, humidity, gas pressure, expansion rate, and time of reaction on aerosol formations in SO_2 and organically polluted atmospheres is now under study. The chemical factors will be investigated by studying the effects of the primary pollutants (SO_2, NO, NO_2, CO, O_3, CH_4, and other organic molecules) on the size and number of particles formed. Tritiated water, pulsed 600-Kv electrons, light, and ozone will be used to generate the condensation nuclei. For selected systems an analysis of products will also be made.

03:120 INFRARED SPECTRA OF RADIOLYTIC INTERMEDIATES IN THE GAS PHASE. Schwarz, H. A. (Brookhaven National Laboratory, Chemistry Department).

This program is designed to measure infrared spectra of ions and radicals produced by electron irradiation of argon containing small amounts of various additives. Infrared spectra would be useful for identification of intermediates and for unraveling their structures. The primary action of the radiation will be on the argon and subsequent collisions will produce ions and radicals from the additives. The technique to be used is similar to the photochemical molecular modulation method developed by H. S. Johnston. The sample will be irradiated with a repetitively pulsed electron beam and the infrared transmission will be measured for a few hundred microseconds before and after the pulse. The signals from a large number of pulses will be averaged to obtain the absorption at each wavelength. The signal averaging will allow measurement of absorbance changes as small as one part in 10^5 and, in combination with a 50-meter light path, should allow measurement of spectra of the longer-lived ions. At present, the optical components and infrared detector have been ordered and the irradiation cell is being designed.

03:121 ELECTRON REACTIONS IN THE GAS PHASE. Fessenden, R. W. (Carnegie-Mellon University, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).

A microwave conductivity detector is being used in conjunction with pulse radiolysis for studies of electron reaction with various attaching gases. Data taking is facilitated by the use of an on-line digital computer. Studies of the kinetics of both three-body and two-body attachment have been made. Examples of compounds displaying the former behavior are O_2 and N_2O, both pure and in the presence of various additives, while the latter behavior is generally found for halides. The wide range of attachment rates is reflected by the rate constants for CF_4 ($<10^{-16}$) and cyclo-C_4F_8 (10^{-7} cm^{-3} molecule^{-1} sec^{-1}). Studies are underway to determine what structural features are correlated with high rate constants and of molecules such as perfluoropropylene which show a transition from three- to two-body behavior as a function of added buffer gas.

PUBLICATIONS

Warman, John M., Krishan M. Bansal, and Richard W. Fessenden, On the Pressure Dependence of Electron Attachment to O_2, Chem. Phys. Lett., 12: 211 (1971).

Fessenden, Richard W., and Krishan M. Bansal, Direct Observation of Electron Disappearance in Pulse Irradiated Fluorocarbon Gases, J. Chem. Phys., 53: 3468 (1970).

03:122 RADIATION CHEMISTRY OF HYDROCARBON AND ALKYL HALIDE SYSTEMS. Hanrahan, Robert J. (University of Florida, Department of Chemistry, Gainesville, Florida 32601).

Research in progress in the Radiation Chemistry Laboratory at the University of Florida is directed toward the identification and characterization of the primary physical and chemical processes, as well as the secondary chemical reactions, which lead to formation of the observed stable products in the radiolysis of simple chemical systems. An additional goal is the investigation of the relationship between the decomposition mechanism of chemical substances initiated by gamma radiolysis and by other types of activation including photolysis, glow discharge reactions, and electron bombardment in the mass spectrometer. The systems under investigation include hydrocarbons and alkyl halides (especially perfluorocarbons) as well as their binary mixtures. Investigations in progress include the radiolysis of pure ethyl bromide in the gas phase, the radiolysis of gaseous mixtures of ethane and hexafluoroethane, and the rare-gas-sensitized decomposition of perfluorocarbons, using He and Ar metastable atoms generated in a glow discharge. Further studies are concerned with the gamma radiolysis of gaseous perfluorocyclobutene, with the high-pressure mass spectrometry of perfluoroalkyl iodides, and with ion–molecule reactions in fluorocarbon–hydrocarbon mixtures as studied by mass spectrometry. We expect to undertake studies of the vacuum ultraviolet photochemistry of fluorocarbons and of fluorocarbon–hydrocarbon mixtures in the near future.

PUBLICATIONS

Marcotte, R. E., and R. J. Hanrahan, Fast Flow Microwave Discharge Studies of the System CF_4–CCl_4, J. Fluorine Chem., 1: 87 (1972).

Donovan, J. Marie, and Robert J. Hanrahan, The Radiation Chemistry of Methyl Iodide in the Gas Phase, Int. J. Radiat. Phys. Chem., 3: 491 (1971).

Buchanan, J. W., and R. J. Hanrahan, A Comparative Study of the Gas Phase Radiation Chemistry of Phosphine and Ammonia, Radiat. Res., 42: 244 (1970).

———, and R. J. Hanrahan, The Radiation Chemistry of Phosphine–Ammonia Mixtures in the Gas Phase, Radiat. Res., 44: 296 (1970).

———, and R. J. Hanrahan, The Use of Phosphine as a Free Radical Scavenger in the Radiolysis of Methyl Iodide, Radiat. Res., 44: 305 (1970).

03:123 THE RADIOLYSIS OF WATER IN A WIDE-RANGE RADIOLYSIS SOURCE. Melton, Charles E. (University of Georgia, Chemistry Department, Athens, Georgia 30601).

Many chemical and physical changes are produced by the interaction of ionizing radiation with a system. The present research program was initiated to obtain detailed experimental and theoretical results that would provide a basis for understanding these radiation-induced changes. The experimental technique for studying elementary reactions involved the use of a wide-range radiolysis source attached to a research mass spectrometer. With this apparatus, a step by step analysis of the elementary reactions can be made beginning at the time the individual molecules absorb energy from ionizing radiation and continuing until the final changes occur. Water was selected for study because of its importance in biological and aqueous systems. Electrons (β particles) and α particles were used as the ionizing medium. Theoretical models were to be formulated to explain the experimental results.

The primary, secondary, and tertiary stages of the gas phase reaction mechanism involving negative ions (anions) have been studied. Some results have been obtained for positive ions (cations) and free radicals of the primary stage. The tertiary stage of the anion process involves the formation of OH^-H_2O which has a bond dissociation energy of 1.1 eV and an intermolecular distance of 1.21 Å. Future studies will involve the subsequent reactions of OH^-H_2O with H_2O to form $OH^-(H_2O)_n$ where n = 1, 2, . . .? Trace amounts of radiolysis products such as O_2 and H_2 and scavengers such as NO will be introduced to determine the effect on the negative ionic complexes.

The second aspect of future work will involve a study of the charge neutralization reactions of the type $H_3O^+ + e \rightarrow$ products.

PUBLICATIONS

Melton, Charles E., Radiolysis of Water Vapor in a Wide Range Radiolysis Source of a Mass Spectrometer. I. Individual and Total Cross Sections for the Production of Positive Ions, Negative Ions, and Free Radicals by Electrons, J. Phys. Chem., 74: 582 (1970).

———, Molecular Theory of Energy Conversion and of Initiation of Chemical Reactions in Solids, Can. J. Chem., 49: 1407 (1971).

———, and George A. Neece, Cross Sections for Capture of Low Energy Electrons in H_2O Vapor, J. Chem. Phys., 55: 4665 (1971).

———, W. Massey, and B. N. Abels, The Isotopic Abundance of Neon, Argon, and Krypton, Z. Naturforsch., A, 26: 1241 (1971).

———, and George A. Neece, Rate Constants and Cross Sections for the Production of OH^- from O^- and H^- in Water, J. Amer. Chem. Soc., 93: 6757 (1971).

03:124 CHEMICAL EFFECTS AND PHYSICAL PARAMETERS IN HEAVY ION AND FISSION RECOIL TRACKS. Meisels, G. G. (University of Houston, Department of Chemistry, Houston, Texas 77004).

The chemical effects of heavy ions and particulary those brought about by fission recoils are usually expected to be similar to those induced by gamma rays or by high-energy electrons. However, the physical conditions within the heavy ion track are poorly understood, and effective concentrations of reactive intermediates and particularly track temperatures are not known. We are attempting to provide this information by using competition kinetics with cognizance of the complications introduced by diffusion out of the inhomogeneous distribution of primary species in the track. The first objective is the assignment of effective radical and ion concentration in gases as a function of density; this is achievable through analysis of products formed by free radical reactions in ethylene in the presence of radical scavengers, and of products arising from charge transfer which compete with ion–molecule addition reactions. A further step will be the determination of effective temperatures by investigating competitive reactions where the difference in activation energies is known. An important aspect of the investigation is the variation of gas density; at very low densities the system should simulate a conventional, low-dose-rate homogeneous experiment, while at higher pressures diffusion and track effects, as well as association, quenching and other pressure-dependent reactions, should set in. A simple model based on average concentration has been developed and is proving to be a good guide to further analysis.

PUBLICATION

Meisels, G. G., C. T. Chen, B. G. Giessner, and R. H. Emmel, Energy Deposition Functions in Mass Spectrometry, J. Chem. Phys., 56: 793 (1972).

03:125 MECHANISM OF ION FORMATION BY HIGH-ENERGY RADIATION FROM PRECISE MEASUREMENTS OF W. Meisels, G. G. (University of Houston, Department of Chemistry, Houston, Texas 77004).

Attempts to extrapolate the results of radiation chemical studies at low pressures to densities of greater interest in potentially practical systems require knowledge of the effect of collision frequency on competitive first order reactions. While the pressure dependence of fragmentation processes at low internal energies is relatively well understood, the effect of pressure on the fate of species excited to energies beyond the lowest ionization potential is not well known. Yet these are the predominant primary intermediates in radiation chemistry. We are attempting to obtain evidence for the competition between autoionization and dissociation of deactivation of superexcited states by making highly precise measurements of energies required to form an ion pair in gases at temperatures up to 200°C and pressures to about 20,000 torr. At the same time, precise values of a fundamental physical quantity important to the interpretation of radiation chemistry, W values, are provided. In simple hydrocarbons up to heptanes, there is no evidence for the participation of autoionizing states with lifetimes in excess of 10^{-10} sec; in alcohols only an upper limit of 1% can be set because of the existence of severe experimental complications and artifacts. We expect to pursue this problem by providing precise measurements in other systems over a similar range of conditions, and by construction of a new device that should permit a reduction in artifacts and the use of higher pressures.

PUBLICATION

Stoneham, T. A., D. R. Ethridge, and G. G. Meisels, Precise Measurements of W, the Mean Energy Required for Ion-Pair Formation in Gases. I. Alkanes, J. Chem. Phys., 54: 4054 (1971).

03:126 YIELDS AND REACTIONS OF IONS PRODUCED BY HIGH-ENERGY RADIATION. Meisels, G. G. (University of Houston, Department of Chemistry, Houston, Texas 77004).

The formation of ions in large abundances is one of the most unusual aspects of radiation chemistry; the ensuing ion chemistry is therefore of greatest interest. Consequently, we are investigating the modes of formation, the individual reactions, and the final products formed by reactions of ions in the gas phase. We produce ions using a 1.5-MeV electron accelerator, and vacuum ultraviolet radiation at 8.6, 10.0, and 11.6 eV, and attempt to elucidate the structure and reactions of ions produced from hydrocarbons and, in the future, from polar molecules, by measuring end products analyzable by gas chromatography and mass spectrometry. Charge transfer, hydride transfer,proton transfer, and electron attachment are used as diagnostic tools. At the same time, rate constants for individual reactions of relatively stable ions are evaluated as a function of kinetic energy in a mass spectrometer capable of operating at pressures of over 1 torr in the ion source. A pulsed electron beam is employed and reaction times are determined directly using a coincidence technique. Among the current aims are an association of ion reactivity with ion structure and the energy dependence of ion–polar molecule reaction rates. We hope that energy-dependent competition between dipole orientation and randomization in a reaction can be employed to assess effective track temperatures in heavy-ion radiolysis.

PUBLICATIONS

Meisels, G. G., The Radiolysis of Olefins, in The Chemistry of Alkenes, Vol. II, Jacob Zabicky (Ed.), Wiley-Interscience, Inc., New York, 1970.

Gill, P. S., Y. Inel, and G. G. Meisels, Collisional Deactivation of Intermediate $C_4H_8^+$ Ion in the Photolysis of Ethylene at 1048–1067 Å, J. Chem. Phys., 54: 2811 (1971).

Inel, Y., A. Siddiqi, and G. G. Meisels, On the Photolysis of Ethylene at 1216 Å, J. Phys. Chem., 75: 1317 (1971).

Chang, C., G. J. Sroka, and G. G. Meisels, Arrival Time Distributions in High-Pressure Mass Spectrometry. II. Reactions of $(H,D)_3^+$ in Hydrogen–Deuterium Mixtures, J. Chem. Phys., 55: 5154 (1971).

Sroka, G., C. Chang, and G. G. Meisels, Arrival Time Distributions in High-Pressure Mass Spectrometry. I. Residence Times of Reactant Ions in Chemical Ionization and the Measurement of Reaction Rate Constants, J. Amer. Chem. Soc., 95: 1052 (1972).

03:127 MASS SPECTROMETRY AND MOLECULAR EXCITATION. Newton, Amos S. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

This project is a study of the excited states of ions and molecules and the immediate fates of these states when various molecules are irradiated with ionizing radiations. Low-energy electrons are used for excitation since, with most ionizing radiations such as γ rays or fast electrons, a majority of the excitation arises from the action of low-energy secondary electrons. Long-lived highly excited states and high-kinetic-energy ions are formed in all radiolysis systems. At present their fates in such systems have not been elucidated.

Recent work has been carried out on the metastable dissociation of the CH^+ ion. This ion is of great interest in fields as diverse as radiation chemistry and astrophysics. Because of the great difficulty of obtaining excited states of this ion for spectrographic studies, only a few of the lower-lying excited states have been experimentally identified. The appearance potential of the metastable ion, its kinetic energy, and its kinetic energy release on dissociation are each measured and these identify the dissociation limit and the level of the intersystem crossing point above the limit at which the predissociation occurs. These results can be interpreted in terms of theoretical calculations of the expected excited states of the ion.

Other states of ions that have been studied are those leading to fast fragment ions with high initial kinetic energy. Most of these arise from the fragmentation of doubly charged states of the ion but some arise from excited singly charged states. A recent study of the occurrence of H_3^+ ions in the mass spectra of a wide variety of organic compounds shows H_3^+ to arise both from doubly and singly charged states. The appearance potential of each of these states can be determined. At present too little is known about the higher energy levels of complex molecules to assign states to the processes involved.

A second type of study is one in which long-lived excited neutral states of small molecules are investigated. These can be investigated with an electron beam crossed by a molecular beam. The neutral excited states or their dissociation products (including high-energy photons) can be detected by Auger electron formation when de-excitation of the states occurs at a metal surface.

PUBLICATIONS

Newton, A. A., and G. E. Thomas, Electron Impact Excitation Functions of Radiating and Metastable States of Carbon Monoxide, Chem. Phys. Lett., 11: 171 (1971).

______, A. F. Sciamanna, and G. E. Thomas, The Occurrence of the H_3^+ Ion in the Mass Spectra of Organic Compounds, Int. J. Mass Spectrom. Ion Phys., 5: 465 (1970).

______, and A. F. Sciamanna, Metastable Dissociation of the Doubly Charged Carbon Monoxide Ion, J. Chem. Phys., 53: 132 (1970).

______, and A. F. Sciamanna, Metastable Peaks in the Mass Spectra of N_2O and NO_2. II, J. Chem. Phys., 52: 327 (1970).

03:128 CHEMICAL EFFECTS OF HIGH-ENERGY RADIATION. Ausloos, P. and Sieck, L. W. (National Bureau of Standards, U. S. Department of Commerce, Radiation Chemistry Section, A-265 Chemistry Building, Washington, D. C. 20234.

The objective is to study ionic and neutral phenomena occurring in the high-energy radiation of organic and inorganic molecules; to measure rates of ion–molecule reactions and of neutralization reactions; to determine the mechanism of homogeneous neutralization of positive ions to establish modes of fragmentation of parent ions and neutral excited molecules formed by electron impact and by photon absorption.

Present and future topics to be considered are: (a) clustering reactions of polar and nonpolar molecules with cations using a mass spectrometric technique; (b) neutralization mechanisms involving low-molecular-weight hydrocarbon ions; (c) determinations of rate coefficients for ion–molecule interactions using a pulse radiolysis method; (d) unimolecular fragmentation mechanisms in ions and superexcited molecules using helium and neon resonance light sources; and (e) the effects of structure, internal energy, and density on the rates and mechanisms of ion–molecule reactions using a combination of radiolytic, photolytic, and mass spectrometric techniques.

PUBLICATIONS

Gorden, R., Jr., and P. Ausloos, The Solid Photolysis and Radiolysis of Ethylene at 20 to 77°K, J. Res. Nat. Bur. Stand., A, 75: 141 (1971).

Sieck, W.; L. Hellner, and R. Gorden, Jr., Kinetic Mass Spectrometric Determination of the Absolute Rate Coefficient for the Reaction NH_3^+ (ν = 0) + $NH_3 \rightarrow NH_4^+ + NH_2$ at Thermal Kinetic Energies, Chem. Phys. Lett., 10: 502 (1971).

______, and P. Ausloos, Ion-Molecule Reaction Chains in Isobutene, J. Chem. Phys., 56: 1010 (1972).
Rebbert, R. E., and P. Ausloos, Pulse Radiolysis of Neopentane in the Gas Phase, J. Res. Nat. Bur. Stand., A, 76: 329 (1972).
Ausloos, P., Far Ultraviolet Photolysis of Alkanes, Mol. Photochem., 4(1): 39 (1972).

03:129 STUDIES OF TRANSIENTS BY MEANS OF PULSE RADIOLYSIS AND FLASH PHOTOLYSIS. Ghormley, J. A.; Hochanadel, C. J.; Boyle, J. W. (Oak Ridge National Laboratory, Chemistry Division).

To establish mechanisms of radiation-induced chemical changes it is necessary to determine the identity, yield, and chemistry of intermediate species. We use pulse radiolysis, and generally follow the intermediates by absorption spectroscopy, although, as in the N_2-O_2 system, we sometimes use light emission. Because our accelerator (Febetron) provides pulses of very high intensity, we can work with gases, and devote most of our effort to such *small molecules as O_2 or NO. We are now studying the mechanisms* of O_3 formation, including sensitization by N_2, Ar, and He and inhibition by H_2O, NH_3, and SF_6.

We also employ flash photolysis which sometimes offers simpler conditions for the study of an intermediate. Thus, we are looking at reactions of $O(^1D)$ and $O_2(^1\Delta)$ produced by flash photolysis of O_3.

An important goal in our work is the accurate measurement of rate constants of important elementary reactions, and pulse techniques often can provide the desired reactant in a system simple enough for quantitative study. We have recently done this for the HO_2 radical in the reactions $HO_2 + HO_2 = H_2O_2 + O_2$ and $HO_2 + OH = H_2O + O_2$.

Although our interest in basic information dictates the use of simple systems, we are influenced in our choice of molecules by the demands of technology, particularly reactors, fusion, energy conversion, atmospheric modeling, and related areas.

PUBLICATIONS

Hochanadel, C. J., J. A. Ghormley, and P. J. Ogren, Absorption *Spectrum and Reaction Kinetics of the HO_2 Radical in the Gas* Phase, J. Chem. Phys., 55: 4426 (1972).
Ghormley, J. A., and C. J. Hochanadel, Production of H, OH, and H_2O_2 in the Flash Photolysis of Ice, J. Phys. Chem., 75: 40 (1971).

03:130 KINETICS OF IONIZING-RADIATION-INDUCED REACTIONS. Firestone, Richard F. (The Ohio State University, Department of Chemistry, Columbus, Ohio 43210).

Current activity includes studies of fast reactions in the pulsed-*electron-beam* radiolysis of rare gases and of liquid solutions of alcohols in alkane solvents and of the beta-ray-induced decomposition of water vapor.

Objectives of the rare gas studies include elucidation of mechanisms of decay of excited rare gas atoms and formation of excited metastable diatomic rare gas molecules and measurement of the near infrared absorption spectra of these molecules. The molecule-forming mechanism is complicated and involves competition between radiative decay and collisional steps. Crude molecular absorption spectra have been recorded.

Objectives of the work with liquid alkane–alcohol solutions include determination of effects of solvent–solute interactions on the absorption spectrum and decay time of solvated electrons. Electrons are selectively solvated by microscopic domains of alcohol molecules. The solvated electron spectrum is unaffected by the presence of solvent at ethanol concentrations above a few mole percent. Effects of solvent character and of solvent–solute interactions on the spectrum decay rates and electronic yield are of particular interest.

Objectives of the water vapor work include determination of the mechanism for hydrogen atom and molecule formation. Evidence to date indicates that hydrogen atoms are the only immediate precursors of HD in $HOH-D_2$ and $DOD-H_2$ and that $G_D = G_H =$ 13.1 molec./100 eV. Rate constants and Arrhenius parameters for reactions of D and H atoms with DOD, HOH, TOD, and TOH have been determined recently.

PUBLICATIONS

Bibler, N. E., and R. F. Firestone, Exchange Mechanism and Arrhenius Parameters of Elementary Steps in Reactions of Hydrogen Atoms with Water Vapor in Irradiated Mixtures of Hydrogen and Water Vapor, J. Phys. Chem., 76: 621 (1972).
Firestone, R. F., and L. M. Dorfman, Pulse Radiolysis of Gases, in Actions Chimiques et Biologiques des Radiations, Quinzième Séire, M. Haissinsky (Ed.), Masson et Cie, Paris, 1971.
Dickey, L. C., and R. F. Firestone, The Radiolysis of Chloroform Vapor. Effects of Phase on Arrhenius Parameters of the Hydrogen Atom Abstraction Reaction of Dichloromethyl Radicals with Chloroform, J. Phys. Chem., 74: 4310 (1970).
Bishop, W. P., and R. F. Firestone, The Radiolysis of Liquid n-Pentane, J. Phys. Chem., 74: 1425 (1970).

03:131 THE RADIATION CHEMISTRY AND MASS SPECTROMETRY OF SILANES AND GERMANES. *Lampe, F. W. (The* Pennsylvania State University, Department of Chemistry, University Park, Pennsylvania 16802).

The objectives of this program are to obtain: (1) an understanding of the radiolytic behavior of silanes, germanes, and their alkyl derivatives; (2) a mechanistic description of this radiolytic behavior in terms of the elementary free radical and ionic reactions making up the overall conversion; (3) a mechanistic understanding of the elementary free radical and ionic reactions in terms of specific reaction rates, reaction cross sections, reaction energetics, and the dependence of these parameters on reactant energy; (4) thermochemical information pertaining to silanes, germanes, and their alkyl derivatives.

High-pressure mass spectrometry and tandem mass spectrometer studies of the ionic reactions occurring in SiH_4, Si_2H_6, SiH_3CH_3, GeH_4, and in their admixtures with CH_4, NO, H_2O, N_2, C_2H_4, and C_2H_2 are planned for the immediate future. Mass spec*trometric studies of the reactions of SiH_3, Si_2H_5, and CH_3SiH_2* free radicals with themselves and with NO, H_2O, CO, CO_2, and unsaturated hydrocarbons are being conducted concurrently. Also being examined concurrently are the γ radiolyses of SiH_4-CH_4 and SiH_4-NO mixtures.

PUBLICATIONS

Potzinger, P., and F. W. Lampe, Ion-Molecule Reactions in Dimethylsilane, Trimethylsilane, and Tetramethylsilane, J. Phys. Chem., 75: 13 (1971).
______, and F. W. Lampe, Thermochemistry of Simple Alkylsilanes, J. Phys. Chem., 74: 719 (1970).
______, and F. W. Lampe, *Ionic Reactions in Methylsilane*, J. Phys. Chem., 74: 587 (1970).
Kamaratos, E., and F. W. Lampe, A Mass-Spectrometric Study of the Mercury-Photosensitized Reactions of Silane and Methylsilane with Nitric Oxide, J. Phys. Chem., 74: 2267 (1970).

ALSO SEE Radiation Chemistry: Other: 03:140, 03:162; Hot Atom Chemistry: 03:201; Chemical Spectroscopy: 03:247; Engineering Chemistry: 03:435.

RADIATION CHEMISTRY: OTHER

Experimental and theoretical studies of the radiation chemistry of condensed phases including liquids (except water and aqueous solutions), polymers, glasses, and crystals.

03:132 ELDOR INVESTIGATIONS OF RADIATION PROCESSES. Kispert, Lowell D. (The University of Alabama, Department of Chemistry, University, Alabama 35486).

It is the objective of this research to examine the role of a host lattice in determining the type and yield of radicals produced by x-irradiation of single crystals or polycrystalline material using electron–electron double resonance (ELDOR), electron spin resonance (ESR), and heavy atom substitution techniques. Irradiated single crystals of various bromo, chloro, and fluoro derivatives of acetamide and acetic acid have been used as models *for trapped radical–lattice interactions. Through ESR investiga*tions it has been possible to obtain evidence for cluster formation of radicals and to detect radical decay schemes that are dependent on the local lattice environment around each cluster. Although the presence of chlorine and bromine nuclei as substituents in the radical precursors is mainly responsible for the observed lattice dependence, these substituents have also made it difficult to determine the complete radical decay scheme as a function of host lattice by ESR methods. However, current investigations have shown that the ELDOR spectrum of oriented radicals is *extremely sensitive to, enhanced by, and made simpler with the* presence of intramolecular motion, quadrupole interactions, hyperfine anisotropy, and low observing temperatures, features which are present for chloro-, bromo-, and fluoro-substituted radicals. Therefore, by measuring the same radicals with ELDOR as were previously measured by ESR, it is expected that the complete radical decay scheme can be determined, and thus the radiation processes occurring in solids can be obtained.

PUBLICATIONS

Kispert, Lowell D., and Jane Pearson, Irradiated Single Crystal Clathrate of Dianin's Compound and 1,2-dibromo-1,1-difluoroethane: Electron Spin Resonance Observation of the Br_2^- Radical, J. Phys. Chem., 76: 133 (1972).

______, and F. Myers, Jr., ESR Study of the Chlorofluoroacetamide Radical in Irradiated Dichlorofluoroacetamide Single Crystals, J. Chem. Phys., 56: 2623 (1972).

03:133 EFFECTS OF RADIATION UPON OPTICAL ISOMERS OF TRIS-(ETHYLENEDIAMINE)COBALT(III) SALTS.

Martin, Don S. (Ames Laboratory, Chemistry Division).

Samples of the chloride, bromide, iodide, and nitrate of D, L, and D–L tris-(ethylenediamine)cobalt(III) are being radiated with Mo–Kα radiation and the gamma rays from spent fuel elements of the Ames Laboratory Research Reactor. The rate of racemization of the optical isomers is being measured together with the rate of decomposition to yield Co(II). For comparison with radiation-induced reactions the thermal rates of racemization of the samples are being determined. Moderate irradiation levels appear to cause racemization of the optical isomers before significant decomposition of the salts. The nitrates explode above 220°C and radiation-induced changes in the sensitivity to detonation are being observed. Furthermore, the x radiation produces an organic decomposition product.

Mass spectrometry identifies this component as $C_2N_2H_6$; however, there are no stable well-characterized reasonable organic compounds with this formula so work on its identification is underway. In any event there appears to be some rearrangement of the amine groups in the ethylenediamine. Because of the reactions of the ethylene ligands under irradiation it is planned to study the behavior of complexes with propylene groups as well.

03:134 POLYMER STRUCTURE AND FREE RADICAL DECAY.

Dole, Malcolm. (Baylor University, Department of Chemistry, Waco, Texas 76703).

One major industrial use of radiation is to improve the resistance of polyethylene to deformation at elevated temperatures by creating crosslinks in the polyethylene by radiation. The crosslinking reaction occurs in the recombination (decay) of free radicals. Polyethylene can exist in a number of physical forms, single crystals, extended chain crystals, mixed amorphous, and crystalline phases, etc., and it is of interest to determine the amounts and rates of free radical reactions in the different forms. The decay reaction is also catalyzed by molecular hydrogen; in order to study quantitatively the latter effect we have developed a new semimicro method for determining hydrogen solubilities in polyethylene. By interfacing a small computer with the ESR spectrometer we can automatically integrate the ESR signals and determine relative spin concentrations. Many data are now being collected for polyethylene irradiated at liquid nitrogen temperature and then allowed to warm to room temperature where the free radicals frozen in at the low temperature react rapidly, mostly to form crosslinks, but some to form allyl-type free radicals. We are trying to determine the location of the free radicals (i.e., whether in the crystalline or amorphous regions), effect of hydrogen, and kinetics decay. Data collection is almost completed, and definite conclusions should be forthcoming soon.

PUBLICATIONS

Roberts, G. P., M. Budzol, and Malcolm Dole, Radiation Chemistry of Poly(propylene oxide), J. Polym. Sci., Part A-2, 9: 1729-1745 (1971).

Waterman, David C., and Malcolm Dole, The Infrared Spectrum of Polyethylene Irradiated at 4°K, J. Phys. Chem., 75: 3988-3992 (1971).

______, and Malcolm Dole, The Radiation Chemistry of Polyethylene. X. Kinetics of the Conversion of Alkyl to Allyl Free Radicals, J. Phys. Chem., 74: 1913 '70).

______, and Malcolm Dole, Ultraviolet and Infrared Studies of Free Radicals in Irradiated Polyethylene, J. Phys. Chem., 74: 1906 (1970).

Budzol, M., and Malcolm Dole, The Radiation Chemistry of Polyethylene. XI. The Molten State, J. Phys. Chem., 75: 1671-1676 (1971).

03:135 RADIATION-INDUCED GAS–SOLID REACTIONS IN SOLIDS CAPABLE OF FORMING MONOLAYERS.

Metz, D. J., and G. Adler. (Brookhaven National Laboratory, Department of Applied Science).

There is an important class of compounds that consists of molecules with a long hydrocarbon backbone and a relatively large polar group at one end. Many of these substances can form monolayers on the surface of water. In the crystal, these molecules associate—polar group to polar group—to form similar layers. These layers, in turn, associate in pairs—hydrocarbon to hydrocarbon—to form a bilayer structure similar to that postulated for cell membranes. The crystal structure consists of stacks of these bilayers. Examples of these compounds are fatty acids and some of their derivatives, lecithins, many surfactants, etc.

As expected, free radicals can be found in these solids after irradiation. It is a peculiarity of these systems that reactive gases, such as NO, SO_2, and O_2, can diffuse into and through the lattice and react with these radicals. The kinetics of the reaction seem to be diffusion controlled, and the diffusion seems divisible into three components: (1) along defects, (2) parallel to the layer; and, (3) orthogonal to the layer. By using gases of different molecular sizes it appears to be possible to react selectively with free radicals near defects and thus determine the distribution of radicals in the crystal. After reaction, the shape of the ESR spectrum will give information on the freedom of motion of molecules and thus give some insight into defect structure. The relative ease of diffusion parallel to the layer compared with that orthogonal to the layer has suggested some new ideas on transport in ultrathin membranes which will be explored.

If, after reaction, these compounds are spread as monolayers on water, large changes in properties are observed. Stearamide irradiated and treated with SO_2 shows a large decrease in break pressure of the monolayer, followed by a subsequent increase as radiation dose is increased. Oleamide shows a decrease in area per molecule at break after irradiation and treatment with O_2. The effects seem rather sensitive to dose. Since, presumably, the packed monolayer has a structure similar to the layer in the crystal, it is expected that study of these reactions in the monolayer will give some insight into the orthogonal diffusion component and, by analogy, into transport mechanisms in ultrathin membranes.

PUBLICATIONS

Adler, J., The Reaction of Gases with Solids Having a Bilayer Structure, Israel J. Chem., 10: 133 (1972).

Adler, G., Some Implications of Organic Solid State Reactions for the Study of Phase Change Mechanisms, Trans. Amer. Crystallogr. Ass., 7: 55 (1971).

Faucitano, A., and G. Adler, The Role of Oxygen in Solid State Polymerizations 11, The Effect of Oxygen and Other Reactive Gases on the Polymerization of Methacrylamide, J. Macromol. Sci., Part A, 4: 1471 (1970).

03:136 PROPERTIES OF ELECTRONS IN DIELECTRIC LIQUIDS.

Holroyd, R. A., and A. O. Allen. (Brookhaven National Laboratory, Chemistry Department).

Studies of radiation-induced conductivity of dielectric liquids have shown that details of molecular structure have an unexpectedly large effect on the number of free ions formed by the radiation and on the mobility of electrons in the liquids. To further understand this effect we are studying the photoinjection of electrons into liquids from metal surfaces. This study enables us to measure V_0, the energy of the excess electron state, relative to the free electron in vacuo. V_0 is close to zero for n-alkanes and approximately −0.5 eV for the symmetrical molecules neopentane and tetramethylsilane. This study also provides information about thermalization distances of low-energy electrons in these liquids. The results show that most of the range of "hot" electrons is attained at near-thermal energies. Knowledge of V_0 is necessary to a theoretical understanding of the excess electron, and the magnitude of this term can be correlated with mobility. The results also lead to the interesting hypothesis that the threshold for photoionization of solutes will be different for various solvents, being considerably red-shifted for solvents having symmetrical molecules. Experiments are underway to test this idea. The chemical reactions of electrons formed in liquids by ionizing radiation are controlled by these physical parameters. Experiments are planned for study by conductivity methods of reaction rates of electrons with active solutes in a range of nonpolar solvents.

PUBLICATION

Holroyd, R. A., and M. Allen, Energy Excess Electrons in Nonpolar Liquids by Photoelectric Work Function Measurements, J. Chem. Phys., 54: 5014 (1971).

03:137 THEORY OF EXCESS ELECTRON STATES IN HYDROCARBON LIQUIDS. Nielsen, S. O. (Danish Atomic Energy Commission), and A. O. Allen. (Brookhaven National Laboratory, Chemistry Department).

The theory of excess electron states in liquid argon is well worked out, and the mobility of the electrons has been quantitatively explained. The recently discovered high-mobility electrons in liquid hydrocarbons differ from those in argon in that the mobility falls off with increasing electric field in argon but remains constant to very high fields in the hydrocarbons. This difference indicates that effective scattering centers are more numerous in the hydrocarbon liquids, resulting in shorter effective mean free paths, which suggests in turn that the single-scattering approximation which worked well for argon, but is valid only if the free path is longer than the electron wavelength, should not be used for hydrocarbons. The scattering depends on the distribution of potentials, which depends on the shapes and relative orientations of the molecules. A theory is therefore being worked out in two parts. First, the distribution of electric potentials in a hydrocarbon is calculated. The true potential is too difficult to calculate, but, as in solid state studies, it may be approximated by a synthetic "pseudopotential" that is made to give the right results for low-energy electron scattering in hydrocarbon gases. Second, the potential distribution is fitted into a multiple scattering theory that will lead to a calculation of energies and mobilities for comparison with experiment. Computer calculations of the pseudopotential are under way.

PUBLICATION

Schmidt, W. F., and A. O. Allen, Mobility of Electrons in Dielectric Liquids, J. Chem. Phys., 52: 4788 (1970).

03:138 RADIATION CHEMISTRY AND PHOTOCHEMISTRY IN THE ADSORBED STATE. Wong, P. K. (Queensboro Community College), and A. O. Allen. (Brookhaven National Laboratory, Chemistry Department).

When a heterogeneous system is irradiated, energy deposited in one phase may, by various means, transfer to another phase and produce changes there. The principles of such energy transfer must be understood to explain and predict radiation effects in real systems, including biological ones. Extensive work has been done on model systems, in which gases or vapors are adsorbed on high-surface-area mineral supports. At present, effects of ultraviolet light (uv) and gamma rays are being compared, the particular system used being CH_3Br adsorbed on porous Vycor glass and irradiated at liquid nitrogen temperature. The uv energy is absorbed by the glass and not by the CH_3Br. The yield of free CH_3 radicals, determined by electron spin resonance spectroscopy, varies with CH_3Br concentration in a different way when the system is irradiated with uv than when it is irradiated with gamma rays. The results suggest that the less energetic excitons produced by uv do not travel as far through the glass as the separated electric charges or Wannier excitons produced by the gamma rays.

PUBLICATIONS

Wong, P. K., and A. O. Allen, Charge Transfer to Molecules on the Surface of Irradiated Glass, J. Phys. Chem., 74: 774 (1970).

______, An ESR Study of Trapped Radicals Produced by the Radiolysis of Hydrogenous Materials on Porous Glass, J. Phys. Chem., 75: 201 (1971).

03:139 IONIC REACTIONS IN HYDROCARBONS. Schuler, R. H., S. J. Rzad and G. W. Klein. (Carnegie-Mellon University, Radiation Research Laboratories, Pittsburgh, Pennsylvania 15213).

Studies of the concentration dependence for the scavenging of radiation-produced ions in hydrocarbons have provided a model that can be used to correlate and interpret a very wide variety of ionic phenomena. With certain assumptions, predictions of time-dependent phenomena can be made. These predictions indicate that in pure hydrocarbons most ionic processes occur on a very short time scale ($<10^{-8}$ sec), a time scale that is just now becoming accessible to direct observation. Chemical methods provide an important probe of details of these ionic processes. We are currently exploring ion-trapping methods particularly with a view toward examining changes in the positive ion mobility which may be an important consequence of secondary positive ion reactions. Such studies are, of course, basic to obtaining an understanding of the radiation chemical behavior of all nonpolar media.

PUBLICATIONS

Infelta, Pierre P., and Robert H. Schuler, Competitive Electron Scavenging Experiments in the Radiolysis of Hydrocarbons. Kinetics of the Reactions of Secondary Ions, J. Phys. Chem., 76: 987 (1972).

Bansal, Krishan M., and Robert H. Schuler, The Effect of Ion and Radical Scavengers on the Cyclohexyl Radical Yield in the Radiolysis of Cyclohexane, J. Phys. Chem., 74: 3924 (1970).

______, and Stefan J. Rzad, Electron Scavenging in the Gamma Radiolysis of Liquid Diethyl Ether, J. Phys. Chem., 74: 2888 (1970).

Rzad, Stefan J., Pierre P. Infelta, John M. Warman, and Robert H. Schuler, The Kinetics of Electron Scavenging and Ion Recombination in the Radiolysis of Hydrocarbon Solutions, J. Chem. Phys., 52: 3971 (1970).

03:140 RADIATION-INDUCED EFFECTS IN ORGANIC SYSTEMS. Johnsen, Russell H. (Florida State University, Department of Chemistry, Tallahassee, Florida 32306).

This research program is aimed at elucidating the mechanisms for the transformation of high-energy radiation into chemical responses in organic systems. Of specific interest are the early reactions of ions, free radicals, and excited neutrals. The following aspects of this problem are currently under investigation. (1) the kinetics of recombination of free radicals in crystalline solids: Quantitative EPR studies are being conducted on amino acids in order to gain further understanding of the processes responsible for the decay of trapped free radicals. At present, evidence points toward a defect-controlled bulk diffusion process at 25°C, while at higher temperatures other processes seen to intervene; (2) ion–molecule and ion–atom reactions with emphasis on charge exchange processes at high kinetic energies. Of special interest are the cross sections for reactions of diatomic molecular ions in excited electronic states with noble gas atoms; (3) reactions of molecular ions at metal electrodes. In an effort to better understand the effect of collecting electrodes in radiolytic studies in the gas phase a tandem mass spectrometer has been constructed, and mass-selected, energy-controlled molecular ions can be directed against a metal target, with subsequent energy and mass analysis. Both neutralization and fragmentation processes have been detected and are being studied; (4) the behavior of thermal hydrogen atoms in organic solids. The role played by hydrogen atoms and possible precursors in irradiated organic materials remains ambiguous. Under investigation presently are the reaction rates of H atoms with a variety of organic solids as a function of phase, temperature, and molecular structure. Of special interest is the role played by diffusional processes as compared to surface reactions; and (5) the chemical effects of low-energy electrons. Thin films of organic solids are being subjected to electron bombardment in the 5- to 100-eV energy range—the roles of electron trapping and mobility are currently being investigated.

PUBLICATIONS

Fromont, M., and R. H. Johnsen, A Study of Charge Exchange Reactions in a Time-of-Flight Mass Spectrometer, Int. J. Mass Spectrom. Ion Phys., 4: 235 (1970).

Johnsen, R. H., Ionizing Radiation, Instrumentation, and Methods, in The Creation and Detection of the Excited State, Marcel Dekker, Inc., New York, 1971.

______, and A. K. E. Hagopian, The Effect of Phase on the Reactions of Hydrogen Atoms with Solid Propene, in Problems and Progress in Contemporary Radiation Chemistry, Prague, 1971, pp. 409-413.

Stentz, F., and R. H. Johnsen, Radical Decay Kinetics in Crystalline Amino Acids, Radiat. Res., 48: 124 (1971).

03:141 RADIATION CHEMISTRY OF MONOSUBSTITUTED AROMATIC COMPOUNDS. Knight, James A. (Georgia Institute of Technology, Nuclear and Biological Sciences Division, Atlanta, Georgia 30332).

The objective of this research program is to investigate the radiation chemistry of monosubstituted benzenes with nonhydrocarbon substituents. The approach is that of a detailed product analysis of the γ-irradiated pure compound and the compound with electron, free radical, and positive-ion scavengers and with additives that are expected to interact with excited states. Gas chromatography is the main analytical technique for product analysis. Nitrobenzene and aniline were the first compounds investigated, and the results of the studies are in press. Currently, the radiation chemistry of benzonitrile is being investigated. Products identified from the γ-irradiation of benzonitrile are hydrogen, hydrogen cyanide, the isomeric dicyanobenzenes, the isomeric cyanobiphenyls, and the isomeric dicyanobiphenyls. Irradiations of pure benzonitrile and of benzonitrile with different additives will be carried out in an effort to determine the role that reactive species, such as free radicals, ionic, and excited species, have in product formation.

PUBLICATIONS

Knight, J. A., Arylation of Nitrobenzene Induced by Gamma Radiation, Radiat. Res., 44: 50-58 (1970).

______, Gas Chromatographic Analysis of Gamma Irradiated Nitrobenzene for Biphenyl and Nitroaromatic Products, J. Chromatogr., 48: 526-529 (1970).

______, Gas Chromatographic Analysis of Gamma Irradiated Aniline for Aminoaromatic Products, J. Chromatogr., 56: 201-208 (1971).

03:142 MECHANISM OF THE DECOMPOSITION OF INORGANIC OXYANIONS. Johnson, Everett R., William Holtzscheiter, Arnold Francis, and Richard Rossmassler. (University of Maryland, Department of Chemical Engineering, College Park, Maryland 20742).

The research is directed primarily toward developing an understanding of the mechanism of the decomposition of inorganic oxyanions. A fruitful research approach has been the study of the isotope effect in the decomposition of these salts. Currently we are investigating the oxygen isotope effect in the radiation-induced decomposition of sodium nitrate. The G value ratio G(^{16}O)/G(^{18}O) for sodium nitrate decomposition as a function of temperature appears to be relatively constant over a wide range of temperature; however, G(decomposition) is quite sensitive to temperature changes. Isotope effect studies as a function of temperature and pressure are in progress.

Most mechanisms postulated for the decomposition of the oxyanions include a back reaction involving the oxygen liberated during the decomposition and the decomposition products. If this mechanism is really operable, then it would appear that it should be possible to demonstrate an oxygen exchange reaction. Various salts (nitrates, halates, etc.) are irradiated in the presence of ^{18}O and the resulting product examined by Raman spectra to determine whether ^{18}O has been incorporated into the salt. The results to date indicate that an exchange reaction can be realized in the nitrates, chlorates, and perchlorates.

PUBLICATIONS

Khare, M., and E. R. Johnson, J. Phys. Chem., 74: 4085 (1970).

Melveger, A. J., E. R. Johnson, and E. N. Ladov, J. Inorg. Nucl. Chem., 32: 337 (1970).

Johnson, Everett R., Radiation Induced Decomposition of Inorganic Molecular Ions, Gordon and Breach, Science Publishers, Inc., New York, 1970.

03:143 RADIATION-INDUCED EFFECTS IN POLYMERS AND RELATED COMPOUNDS. Silverman, Joseph. (University of Maryland, Laboratory for Radiation and Polymer Science, College Park, Maryland 20742).

Viscosity effects are measured in the grafting of vinyl monomers to polymers. Results show that grafting under high viscosity conditions near the glass transition temperature maximizes the graft yield and minimizes the yield of occluded homopolymer. Measurements show that reduced homopolymer content means superior mechanical properties. The methods have practical value in optimizing industrial grafting processes. They have fundamental value in determining conditions where grafted propagating radicals can be measured; ESR measurements are in progress.

The mechanism of the radiation polymerization of styrene in the solid state is studied by measurements of the kinetics and molecular weight distribution. A very large yield of polymerized dimers and trimers suggests intraspur termination.

LET studies on polymers and single crystals of alkanes are in progress. Our principal interest is pair radical formation.

Measurements of radiation-induced conductivity in vinyl monomers and alkanes are in progress to determine the yields and drift mobilities of charge carriers and to determine recombination kinetics of the ions.

PUBLICATIONS

Machi, S., I. Kamel, and J. Silverman, Effect of Swelling on Radiation-Induced Grafting of Styrene to Polyethylene, J. Polym. Sci., Part A-1, 8: 3329 (1970).

______, and J. Silverman, Mechanical Properties of Radiation-Induced Graft Copolymers of Styrene to Polyethylene, J. Polym. Sci., Part A-1, 8: 3529 (1970).

______, J. Silverman, and D. Metz, Radiation-Induced Polymerization of Pure Styrene at Low Temperatures, J. Phys. Chem., 76: 930 (1972).

Kamel, I., S. Machi, and J. Silverman, Radiation-Induced Grafting of Styrene Vapor to Polyethylene, J. Polym. Sci., Part A-1, 10: 1019 (1972).

03:144 ELECTRON SPIN RESONANCE STUDIES OF RADIATION EFFECTS. Rogers, Max T. (Michigan State University, Department of Chemistry, East Lansing, Michigan 48823).

Radiation damage in solid materials is being studied using electron spin resonance to identify the paramagnetic fragments produced. A variety of new and unusual molecular species are prepared in this way and the ESR parameters (g tensors and nuclear hyperfine splitting tensors) provide detailed information concerning the molecular and electronic structures of the radicals. Molecular orbital calculations are carried out to assist in interpreting the ESR parameters. Systematic studies are underway that will help in devising general rules for predicting the results of radiation damage in molecular crystals. Time and temperature variations of the ESR spectra are aids in revealing the motions and reactions of the paramagnetic species.

Organic materials being studied include carboxylic acids, amides, halocarbon derivatives, and organometallic compounds. Inorganic materials include hydrazinium salts and a variety of fluorides and oxyanions, particularly those leading to excess-electron radicals. An effort to observe triplet states of some new carbenes has been started and ESR studies of radiation damage in sugars is contemplated. A major objective has been to obtain nuclear hyperfine splitting data for common nuclei in a variety of radicals to provide a basis for interpreting new spectra.

Computer programs for analysis of spectra and their simulation are being developed, including a general method for obtaining second-rank tensors from single-crystal data.

PUBLICATIONS

Rogers, M. T., and L. D. Kispert, ESR Study of $\cdot CF_2COO^-$ Radicals in Irradiated Single Crystals of Sodium Chlorodifluoroacetate, J. Chem. Phys., 55: 2360 (1971).

Kispert, L. D., and M. T. Rogers, Temperature Dependence of the *ESR Spectrum of* $CO_2^-CF_2CFCO_2^-$ *in Irradiated Sodium Perfluoro*-succinate, J. Chem. Phys., 54: 3326 (1971).

Subramanian, S., and M. T. Rogers, An Electron Spin Resonance Study of the IO_2F^- Radical in Gamma-Irradiated Single Crystals of Potassium Oxyfluoroiodate, J. Phys. Chem., 75: 3479 (1971).

Root, K. D. J., and M. T. Rogers, ESR Spectra of Inorganic Radicals and Radical Ions, in Spectroscopy in Inorganic Chemistry, J. R. Ferraro and C. N. R. Rao (Eds.), Vol. II, pp. 115-174, Academic Press, Inc., New York, 1971.

03:145 INVESTIGATION OF GAMMA-RAY-INDUCED POLYMERIZATION OF THE CARBORANES. Klingen, Theodore J. (The University of Mississippi, Department of Chemistry, University, Mississippi 38677). Contract AT-(40-1)-3781.

This research involves the radiation-induced polymerization of organo-substituted derivatives of 1,2-dicarba-closo-dodecaborane(12) in the solid and liquid states. The first aspect of the present work is the effect of the plastic crystalline nature of the solid state of 1-vinyl- and 1-ethyl-o-carborane on the polymerization. The unusual phase transition behavior observed for these compounds is being investigated by examining a series of well-known organic plastic crystalline compounds to determine whether this behavior is common to all plastic crystals or only to the carboranes. This work should also shed light on the role of diffusion control on radiolytic reactions in this condensed state of matter. A second aspect of the polymerization of 1-vinyl-o-carborane, the role of the side chain conjugated double bond, is being investigated by examining the radiolysis of 1-ethyl- and 1-allyl-o-carborane where there is no double bond or the double bond is not conjugated with the cage.

The investigation of other phases of the overall problem will include the study of the copolymerization of 1-vinyl-o-carborane under the influence of radiation with compounds such as styrene. Also the screening of other substituted carboranes, such as bromomethyl-o-carborane, o-carboranediacetic acid, and bis(hydroxyethyl)-o-carborane, for their ability to be polymerized by ionizing radiation will be undertaken. In all of this work, the goal is the determination of the polymer structure and kinetics-mechanism of the radiolytic reactions.

PUBLICATIONS

Wright, J. R., and T. J. Klingen, Investigation of Gamma-Ray Induced Polymer Formation in the Carboranes—I. Separation and Structural Identification of the Polymer Formed from 1-Vinyl-o-Carborane, J. Inorg. Nucl. Chem., 32: 2853 (1970).

Klingen, T. J., and J. R. Wright, Radiolytically Induced Polymer Formation in Alkenyl Carboranes: Phase Effects, Mol. Cryst. Liquid Cryst., 13: 173 (1971).

______, and J. R. Wright, Further Evidence for the Plastic Crystalline Nature of 1-Vinyl-o-Carborane, Mol. Cryst. Liquid Cryst., 16: 283 (1972).

03:146 DETERMINATION OF RANGE OF LOW-ENERGY ELECTRONS IN ORGANIC MATERIALS. Berry, W. B., and Y. C. Chang. (University of Notre Dame, Radiation Laboratory).

Low-energy electrons are injected into thin film organic materials by means of photoemission from a silver cathode to determine the electron range, or average depth of penetration, and thereby to obtain information regarding the associated energy-loss mechanisms. At the energies used, in the vicinity of one electron-volt, electrons interact primarily with intermolecular vibrations or phonons.

The electron penetration is determined by measuring the *change in photocurrent following calibrated increases in the* film thickness. These steps in film thickness are typically 2 or 3 nanometers (nm). Average electron range values vary from 15 nm for materials like neopentane to 3 nm for octane. The photocurrent dependence on film thickness is found to be exponential rather than gaussian. This fact is crucial to the evolution of theories, especially as a boundary condition for the Smoluchowski equation.

In addition to yielding information on electron range, the data indicate a potential barrier between the photocathode and the condensed hydrocarbons. This barrier effects an initial decrease in the photocurrent, and it can be determined by projecting the data back to the zero thickness case.

PUBLICATIONS

Berry, W. B., Low-Energy Electron Transmission Through Ice Films at 77°K, J. Chem. Phys., 54: 1837 (1971).

______, Low-Energy Irradiation of Thin Paraffin Hydrocarbon Films, J. Electrochem. Soc., 118: 597 (1971).

03:147 ELECTRONIC STRUCTURE OF IRRADIATED ORGANIC LIQUIDS AND GLASSES. Funabashi, Koichi. (University of Notre Dame, Radiation Laboratory).

The purpose of this study is to provide a unified physical picture for static (stationary) and dynamic (time-dependent) behavior of electrons in irradiated organic liquids and glasses. These problems are related to current experimental measurements in this laboratory of electron drift velocity, optical absorption spectrum of the trapped electrons, and luminescence. The theoretical aspect of this study involves understanding of the electronic structure of disordered molecular systems for various time scales following a stimulus. For the initial stage, the problem is to clarify the physical meaning of ionization in a condensed phase. As long as the charge separation is finite for the ion pair, the significance of ionization and the relevance of ionization potential are not trivial, in contrast to those in the gas phase. We have had partial success on this problem but will continue to work on a more detailed formulation. For the second stage, the mechanism of electron–phonon coupling in electron trapping and also in controlling the electron mobility is being investigated. The problems are how long does it take for an electron to be trapped or scavenged after ionization and what are the controlling factors (molecular geometry, temperature, etc.).

PUBLICATIONS

Maruyama, Y., and K. Funabashi, Electron Drift Mobility in Solid 3-Methylpentane, J. Chem. Phys., 56: 2342 (1972).

Funabashi, K., and Y. Maruyama, Model for Trapped Electron in 3-Methylpentane Glass—An Electron in a Linear Random Lattice, J. Chem. Phys., 55: 4494 (1971).

______, C. Hebert, and J. L. Magee, Effects of Optical Bleaching on Luminescence Decay and Trapped Electron Concentration in Gamma-Irradiated 3-Methylpentane at 77°K, J. Phys. Chem., 75: 3221 (1971).

03:148 THE RANGE AND ENERGY DEGRADATION SPECTRUM OF SLOW ELECTRONS IN DIELECTRICS. Hamill, W. H., and T. Y. Chai. (University of Notre Dame, Radiation Laboratory).

A thin-film sandwich device has been designed and will be applied to the problem of measuring the range of injected electrons of 0- to 100-eV energy.

The device, from top to bottom, consists of dielectric D_1 (10^2 to 10^3 Å), grid G (~50 Å gold), dielectric D_2 (100 Å), collector C (~10^3 Å gold), substrate. Electrons are supplied from a thermionic emitter. The currents I_G and I_C will be measured at each thickness t_1 of D_1, over a range of incident electron energies eV_i. At each V_i the collector voltage V_c will be swept from the saturation current at $V_c > 0$ to $I_c = 0$ at $V_c < 0$. This establishes *the energy distribution of electrons transmitted by D_1 and G.* Electrons thermalized in D_1 will be collected by G. Methods exist for distinguishing hot electron transmission through pinholes and through metal in discontinuous metal films. In a prototype device using SiO as dielectric and $t_1 = t_2 = 10^2$ Å, slow electrons traverse D_1 and enter D_2 with $\lesssim 2$ eV (the practical limit for V_c at that thickness). If ohmic injection can be achieved, $I_c - N_i$ characteristics will be measured to provide information concerning trap concentrations and depths. Having established procedures with the prototype, such dielectrics as cyclohexane will be used with Hg electrodes.

03:149 CHARACTERISTIC ENERGY LOSSES AND LUMINESCENCE BY SLOW-ELECTRON IMPACT ON THIN FILMS OF MOLECULAR AND IONIC SOLIDS. Hamill, W. H., K. Hiraoka, and T. Matsushige. (University of Notre Dame, Radiation Laboratory).

The purpose of this work is the investigation of electronic states of molecules and ions (e.g., n-hexane and NaCl) which are inaccessible by other conventional techniques. Although these states and their associated luminescence and chemical decomposition must dominate the terminal stages of the effects due to high-energy radiation they have not been observed before. Losses in alkanes at ~2 eV (transient negative ions), ~3 eV (triplets) and 4 to 8 eV (unknown excited states), correlate with chemical decompositions at ~3.5 and ~6 eV in n-hexane.

Nine alkali halides show a common pattern of losses, many previously reported for 10- to 20-eV electrons, but on the average three low-lying states of alkali halides appear below the optical exciton fundamental. These states must be due to spin- and symmetry-forbidden halide ion excitations. In pure KI at 77°K, 300 nm and 375 nm luminescence is excited at ~4.6 eV. In KI : Tl^+, this excitation induces emission from Tl^+ and is probably excitonic.

Detailed measurements of losses and luminescence of KCl, KCl : Tl^+, and related systems at $\lesssim$16°K are planned. Studies on CdS and other semiconductors will correlate with other solid state investigations at Notre Dame.

PUBLICATIONS

Merkel, P. B., and W. H. Hamill, Energy Loss Spectra of Low-Energy Electrons Scattered from Thin Solid Molecular Films, J. Chem. Phys., 55: 1409 (1971).

______, and W. H. Hamill, Luminescence from Thin Solid Films at 77°K Under Low-Energy Electron Impact, J. Chem. Phys., 54: 1695 (1971).

Hiraoka, K., and W. H. Hamill, Energy Losses by Slow Electrons in Alkali Halide Films, J. Chem. Phys., 56: 3185 (1972).

Matsushige, T., and W. H. Hamill, Chemical Effects Due to Low-Energy Electron Impact on Thin Films of Cyclohexane and n-Hexane at 77°K, J. Phys. Chem., 75: 1255 (1972).

03:150 THE FORMATION AND NATURE OF SOLVATED ELECTRONS IN POLAR LIQUIDS AND THEIR ALKANE MIXTURES. Hentz, R. R., and G. Kenney-Wallace. (University of Notre Dame, Radiation Laboratory).

Nanosecond and subnanosecond pulse radiolyses are being used for study of the time and concentration dependence of the optical absorption spectrum of the electron in various polar liquids and their mixtures with alkanes. Such a study should enhance understanding of the mechanism of formation and nature of solvated electrons. Absorption spectra have now been determined for the solvated electron (e_s^-) at 30°C in 22 alcohols and in binary mixtures of a number of alcohols and cyclohexane. In each case, the spectrum was present immediately within a 5-nsec pulse and was unchanged in position and shape at longer times. The preliminary results suggest the following conclusions: (1) binding and transition energies of e_s^- in the alcohols are determined by interaction of the electron with an optimum configuration of OH dipoles in a small solvation domain, perhaps a single shell; (2) the optimum configuration for e_s^- is affected by molecular structure of the alcohol (particularly branching); (3) spectra in the mixtures are characteristic of an equilibrium composition of the solvation domain which is attained within 5 nsec at 30°C in the 0.1M alcohol solutions studied and is determined by mixture composition, relative strength of the attractive interactions of e^- with the mixture components, and strength of the attractive interactions between the mixture components. Studies are being extended to lower alcohol concentrations, alkanes of greater viscosity, lower temperatures, and shorter times (for which purpose a new infrared picosecond pulse-radiolysis system utilizing an injection laser diode has been developed). Work with polar substances other than alcohols is planned, and an attempt will be made to form chelates of the electron with single molecules of certain solutes present at low concentrations in alkane solvents. Compounds chosen for such a purpose will include long-chain polyhydroxy alcohols and macrocyclic compounds whose structure includes a "cavity" of about the same size and character as that believed to be associated with the solvated electron in water and the simple alcohols.

03:151 FORMATION OF EXCITED STATES IN THE RADIOLYSIS OF LIQUIDS. Kira, Akira, and J. K. Thomas. (University of Notre Dame, Radiation Laboratory).

The formation of excited states in the irradiation of organic solutions is studied using the pulse radiolysis method. Comparison of the results with those in the laser photolysis makes it possible to estimate the primary yield of each of singlet and triplet excited states of solutes. In benzonitrile solution, most of the solute excited states are produced as triplet states. In dimethyloxyethane solution, the singlet excited state is predominantly formed at low concentration and the contribution of the triplet state increases with increasing solute concentration. Benzyl alcohol solution gives both triplet and singlet excited states, the triplet state contribution again increasing with increasing solute concentration.

03:152 TRIPLET FORMATION IN ION RECOMBINATION IN SPURS. Magee, J. L., and J. J. Huang. (University of Notre Dame, Radiation Laboratory).

The problem of triplet formation from ion recombination in irradiated systems is considered theoretically. In many systems the recombination occurs within spurs and takes place before spin relaxation. In liquid organic solutions at room temperature relaxation times can be estimated to be ca. 10^{-6} s but recombination time is of the order of 10^{-11} s. Under such conditions of conservation of total spin for a spur, the probability for triplet formation is treated as a combinatorial problem. For this case a simple formula is obtained to express triplet formation probability as a function of the number of ion-pairs in the spur.

The various mechanisms of spin relaxation are under consideration. The most important mechanism involves the presence of triplet molecules excited directly by spin-exchange scattering of sub-excitation electrons. The general combinatorial consideration for various numbers of recombining charge pairs in a spur which has a finite spin arising from triplet excitation by low-energy electrons is similar to the treatment for zero spin. General formulas can be obtained in a straightforward way. The triplet/singlet ratio averaged over spur size distribution is estimated to be $\ll 7$. If an appropriate fraction (~30%) of spin exchange by sub-excitation electrons is assumed, the present theoretical work may furnish an explanation of the fact that in some hydrocarbons ion recombination has produced approximately equal initial yields of triplet and singlet excited states. However, a more significant correlation between theory and experimental data requires further efforts in both areas.

03:153 DIELECTRIC RELAXATION AS APPLIED TO RADIATION CHEMISTRY. Mozumder, A. (University of Notre Dame, Radiation Laboratory).

Picosecond pulse radiolysis experiments with polar liquids have demonstrated that the solvated electron is actually formed in a time scale that is much smaller than the dielectric relaxation time measured in the laboratory in (relatively) weak electric fields. Experiments performed at low temperatures exhibit the formation of solvated electrons in microsecond time scale. Even so this time is orders of magnitude smaller than the laboratory-measured relaxation time.

One possible contributing factor is the relaxation under constant charge condition, which makes it faster than laboratory measurements by a factor equal to the ratio of static to high-frequency dielectric constant. This works pretty well for water, ammonia, and some alcohols but not the higher alcohols. Also, it does not explain the low-temperature results. Clearly, a microscopic model is indicated.

At present we are trying out a model based on charge–dipole interaction. It has been applied to solvated electron formation in dilute solutions of polar molecules in nonpolar solvents. The model predicts very fast attachment followed by coagulation in nanosecond time scale for an ~50mM solution. In this model the spectrum of the solvated electron should be approximately the same as that of the neat polar liquid, which is what is observed. We intend to apply this model to neat polar media, which will need modifications to incorporate self-consistent interaction between the electron and the neighboring dipoles.

03:154 ELECTRIC FIELD EFFECT ON FREE-ION YIELD. Mozumder, A. (University of Notre Dame, Radiation Laboratory).

Following ionization in a dielectric liquid the ejected electron travels a certain distance before coming to rest. This could be either thermalization or trapping. The distance that the electron travels depends, in addition to the electronic range, upon the mechanisms of energy loss of the low-energy electron. Once thermalized, the motion of the electron should be describable by Smoluchowski's diffusion equation. One consequence of this equation is that in the long-time limit there is a small probability that the electron escapes neutralization with its sibling positive ion by virtue of Brownian motion. This gives rise to the so-called free-ion yield, which has been measured by various techniques. Onsager's theory describes the steady-state situation rather well; there also have been attempts to treat the time-dependent situation.

An external electric field increases the escape probability of the electron, which also has been observed. Formally, the Onsager theory should be applicable for the evaluation of the enhancement factor but the analysis is too complicated. Our effort in this direction will be aimed at: (1) making the Onsager treatment tractable, (2) studying the effect of initial distribution, and (3) introducing trapping and detrapping in the Onsager model. Results will be compared with experiments.

03:155 DIFFUSION AND ELECTRON TRANSPORT IN IRRADIATED DIELECTRIC LIQUIDS. Mozumder, A., G. Abell, and J. L. Magee. (University of Notre Dame, Radiation Laboratory).

It has now been established beyond doubt that the electron behaves as a classically diffusing entity in many reactions that it undergoes in irradiated dielectric liquids (hydrocarbons). Most important among the experimental results are those on neutralization and scavenging. Quantitative scavenging experiments are successfully interpreted in terms of Smoluchowski's equation including the electric field between the ions. Properties of the solutions of the equation have been investigated for the case of a single pair of charges. The analytical solution is of practical importance only for very small scavenger concentrations, but numerical solutions are possible. Numerical methods have been developed for the calculation of the neutralization (or scavenging) probability of an electron in the field of an ion. We also have worked out approximate solutions for the multiple ion-pair cases. The fact that in most hydrocarbons the measured electron mobility is independent of the applied field up to rather high field strongly suggests a diffusive mechanism for electron transport in such systems.

There remains a fundamental theoretical problem that can be stated as follows: how does a light particle such as an electron exhibit diffusive behavior whereas it should only follow wave mechanics? We think that the answer lies in the destruction of phase correlations of electron scattering by neighboring molecules of the liquid. It is not the electron itself, but the random positions of the molecules, that generates the diffusive behavior. We shall investigate the proposition that the foregoing statements follow from general principles of quantum statistical mechanics and in so doing the time scale over which diffusion is a good approximation should be obtainable.

PUBLICATIONS

Abell, G. C., A. Mozumder, and J. L. Magee, LaPlace Transform

Method in the Theory of Ion Neutralization. Application to Scavenging Probability in the Gamma Radiolysis of Dielectric Liquids, J. Chem. Phys., 56: 5422 (1972).

______, and A. Mozumder, Application of Diffusion Model for Recombination of Isolated Pairs in Condensed Media, J. Chem. Phys., 56: 4079 (1972).

Mozumder, A., Model for Neutralization and Scavenging of Charges in Irradiated Dielectric Liquids. II. Electron Scavenging Under Gamma Radiolysis, J. Chem. Phys., 55: 3026 (1971).

Magee, John L., and A. B. Tayler, Recombination of Ions in a Coulomb Field in the Presence of a Scavenger, J. Chem. Phys., 56: 3061-3066 (1972).

03:156 ELECTRON SPIN RESONANCE STUDIES OF FREE RADICALS FORMED BY IRRADIATION. Livingston, Ralph, Robert W. Holmberg, and Henry Zeldes. (Oak Ridge National Laboratory, Chemistry Division).

Chemical free radicals that are formed in solids and in liquids are being studied by electron spin resonance. The work on solids is largely with single crystals, usually of known structure, and the radicals are most often formed by gamma irradiation. Studies are underway on Fremy's radical (the nitrosodisulfonate radical anion) as well as other radicals formed by irradiating a host crystal of potassium hydroxylamine trisulfonate. For the first time the spectrum of Fremy's radical is available in a single crystal with sufficient detail to allow a complete determination of the hyperfine parameters. Other studies are being made on $NO_3^{\cdot}$ and $NO_3^{=}$ formed in a variety of nitrates. The work on liquids is concerned with the identification and study of free radicals at steady-state concentration during photolysis with ultraviolet light. Typical radical lifetimes are of the order of a millisecond at room temperature. Presently radicals derived from heterocyclic nitrogen compounds are being studied. A rotating sector is also used to allow measurement of radical lifetimes and a general study of radical kinetics. Zeeman polarization phenomena are sometimes seen, and at this time a study is underway on polarization effects and chemical kinetics of radicals formed during photolysis of aqueous solutions of tartaric acid.

PUBLICATIONS

Dohrmann, J. K., R. Livingston, and H. Zeldes, Paramagnetic Resonance Study of Liquids During Photolysis. XII. Alloxan, Parabanic Acid, and Related Compounds, J. Amer. Chem. Soc., 93: 3343 (1971).

______, and R. Livingston, Paramagnetic Resonance Study of Liquids During Photolysis. XIII. Uracil and Derivatives, J. Amer. Chem. Soc., 93: 5363 (1971).

Holmberg, R. W., ESR Study of Gamma-Irradiated Single Crystals of Potassium Bicarbonate at 77°K, J. Chem. Phys., 55: 1730 (1971).

03:157 RADIATION CHEMISTRY OF HOMOLOGOUS SERIES OF ORGANIC COMPOUNDS. Rudolph, P. S. (Oak Ridge National Laboratory, Chemistry Division.).

The systematic study of the radiolysis of an extensive number of members of a specific homologous series of organic compounds was initiated to determine the effects of homology on the radiolytic products and their abundances. This would give the radiation chemical theorists a fund of data in which the classical organic chemical approach of homology can be joined to modern physical theories of the interaction of radiation with matter.

The normal aliphatic monocarboxylic acids from C_1 through C_{22} have been irradiated, the products analyzed, and a mechanistic scheme outlined (for propionic acid and higher) that accounts for the observed products and the decreasing CO_2 yield with increasing chain length.

A parallel study on amines has been started. Deamination has been observed as a major process, and a chromatographic technique for measuring the ammonia has been demonstrated.

A logical extension of this research is to the homologous series of amino acids. This should provide data of rather direct interest to radiobiology, particularly if we extend the study to aqueous solutions of amino acids.

PUBLICATIONS

Jones, A. R., The Radiolysis of Aliphatic Carboxylic Acids: The Decarboxylation of Normal Acids at 38°, Radiat. Res., 47: 35 (1971).

______, The Radiolysis of Aliphatic Carboxylic Acids: On the Decarboxylation of Normal Acids in the Liquid State, Radiat. Res., 48: 447 (1971).

______, The Radiolysis of Aliphatic Carboxylic Acids: On the Decarboxylation of Normal Acids at 77°K, Radiat. Res., 50: 41 (1972).

03:158 RADIATION CHEMISTRY OF INORGANIC CRYSTALLINE SOLIDS AND THEIR MELTS. Boyd, G. E., J. B. Bates, and L. M. Toth. (Oak Ridge National Laboratory, Director's Division).

The damaging effects of nuclear radiations on molecular ions in inorganic crystals and their melts are being investigated in this program. The identification of molecular fragments produced in the crystal lattice or in the molten salt by energetic ionizing radiations and the development of a chemical mechanism for the subsequent reactions of these fragments are important objectives. During the past three years the techniques of vibrational spectroscopy (i.e., laser Raman scattering and infrared emission and absorption) have been applied. This modern and powerful investigative procedure makes possible the direct determination of the physical structure and chemical composition of the damaged region in a crystal, and gives information on the manner in which the decomposition anneals with post-irradiation treatment. Isotopic substitution in a molecular ion with ^{13}C, ^{15}N, ^{18}O, etc., greatly increases the insight gained from the spectroscopic measurements.

Some of our recent work has been concerned with crystalline and molten alkali metal and alkaline earth fluorides and with identifying the complex ions of uranium, thorium, zirconium, and several fission product elements that may exist in these systems. Increasing attention will be given to Raman and infrared emission spectra of molten carbonates, sulfates, hydroxides, and other molten salts because of their possible importance as high-temperature solvents in various new energy technologies.

PUBLICATIONS

Quist, A. S., J. B. Bates, and G. E. Boyd, Raman Spectra of Molten $NaBF_4$ to 606°C and 8% NaF–92% $NaBF_4$ to 503°C, J. Chem. Phys., 54: 4896 (1971).

______, J. B. Bates, and G. E. Boyd, Raman Spectrum of BeF_4^{2-} in Molten NaF and LiF to 686°C, J. Phys. Chem., 76: 78 (1972).

Bates, J. B., M. H. Brooker, A. S. Quist, and G. E. Boyd, Raman Spectra of Molten Alkali-Metal Carbonates, J. Phys. Chem., 76: 1565 (1972).

03:159 THE RADIATION CHEMISTRY OF HIGH POLYMERS. Parkinson, W. W. (Oak Ridge National Laboratory, Reactor Chemistry Division).

The objective of this program is to delineate the radiation-induced chemical reactions involved in the crosslinking and scission of organic high polymers. This information is important in the prediction of the serviceability of plastics and rubbers in a radiation environment and in the development of radiation processing of these materials. The materials studied are simple base polymers typical of commercial plastics and elastomers.

Precursors of chemical reactants, trapped electrons, were studied in a thesis program in cooperation with the University of Tennessee and Professor T. F. Williams. Currently, the changes induced by radiation in the infrared spectrum of polystyrene are being analyzed to correlate the changes in molecular structure with previously measured yields of hydrogen, benzene, and crosslinks. The dependence of the rate of molecular scission on temperature will be studied to explain the apparent decrease in crosslink yields at elevated temperatures while the hydrogen yields are unchanged or increased.

Since earlier infrared analysis of different isomeric types of polybutadiene showed that unsaturated groups disappeared at a high rate, crosslink yields will be measured to account for the change in unsaturation. The crosslink densities are important since they determine the elasticity of these rubber polymers.

PUBLICATIONS

Parkinson, W. W., and O. Sisman, The Use of Plastics and Elastomers in Nuclear Radiation, Nucl. Eng. Design, 17: 247 (1971).

_____, and R. M. Keyser, Polystyrene and Related Polymers, Chap. 5, in Radiation Chemistry of Macromolecules, Vol. II, pp. 57-96, M. Dole (Ed.), Academic Press, Inc., New York, 1972.

03:160 THE RADIATION CHEMISTRY OF HYDROCARBON LIQUIDS. Parkinson, W. W. (Oak Ridge National Laboratory, Reactor Chemistry Division).

The objective of this investigation is to determine the nature and the yields of the products from the irradiation of solutions of naphthalene in hexane. These compounds were selected as models for the aromatics in coal and the light alkane hydrocarbons of petroleum to explore the utilization of radiation to convert coal into liquid chemicals.

Less than 25% of the total radiation product is sufficiently volatile for analysis by gas chromatography. Over 20 compounds have been identified in this fraction, about half from the recombination of alkyl radicals from hexane and half from the reaction of these radicals with naphthalene.

The nonvolatile portion of the total product could be separated into four fractions by gel permeation chromatography. The general types of isomeric compounds making up each of the four fractions have been indicated by mass spectrometry. Samples of different concentrations have been irradiated for various doses and are now being analyzed. The results will delineate the types of reactions and the yields to be expected from irradiation of aromatics in an environment of alkane hydrocarbons. With the potentialities of using radiation in the processing of coal thus indicated, the program will be complete.

03:161 PULSE RADIOLYSIS STUDIES OF FAST REACTIONS IN MOLECULAR SYSTEMS. Dorfman, Leon M. (The Ohio State University, Department of Chemistry, Columbus, Ohio 43210).

The pulse radiolysis fast reaction technique, with fast optical detection into the infrared to 2300 nm, in the uv, and visible, and in the vacuum uv at 121.6 nm, is being used to investigate the optical properties and chemical behavior of many fundamental transient species. These projects are currently active: (a) the optical properties of the solvated electron, in the infrared, in weakly polar liquids and in binary liquids, are being determined. We intend to establish the extent to which aggregate properties of the liquid are dominant in determining the nature of solvated electrons and the extent to which specific molecular properties are dominant. The data provide more rigorous tests of validity of theoretical models and will furnish much-needed empirical guidance in the current development of these models. (b) Solvent effects in electron transfer and proton transfer reactions of aromatic radical ions are being investigated. The solvent dependence of the kinetics is providing information about the role of ion solvation in electron transfer and the dependence of the rates on the dielectric properties of the solvent, a major parameter in current theories of electron transfer. The proton transfer rate data are providing new information on the profound effects of hydrogen bonding of the solvent in binary liquid systems where kinetic effects ranging over several orders of magnitude are being observed. (c) Nanosecond ion-recombination reactions of aromatic radical anions in weakly polar liquids are under investigation with a view to providing information about the properties of geminate ion-pairs in radiation chemistry.

PUBLICATIONS

Dorfman, Leon M., F. Y. Jou, and R. Wageman, Solvent Dependence of the Optical Absorption Spectrum of the Solvated Electron, Ber. Bunsenges. Phys. Chem., 75: 681 (1971).

Dye, J. L., M. G. DeBacker, J. A. Eyre, and L. M. Dorfman, Pulse Radiolysis Study of the Kinetics of Formation of Na^- in Ethylenediamine by the Reaction of Solvated Electrons with Sodium Ions, J. Phys. Chem., 76: 839 (1972).

Hikida, T., J. A. Eyre, and L. M. Dorfman, Pulse Radiolysis Studies. XX. Kinetics of Some Addition Reactions of Gaseous Hydrogen Atoms by Fast Lyman-Alpha Absorption Spectrophotometry, J. Chem. Phys., 54: 3422 (1971).

Brandon, J. R., and L. M. Dorfman, Pulse Radiolysis Studies. XIX. Solvent Effects in Electron Transfer and Proton Transfer Reactions of Aromatic Molecule Ions, J. Chem. Phys., 53: 3849 (1970).

Willson, R. L., C. L. Greenstock, G. E. Adams, R. Wageman, and L. M. Dorfman, The Standardization of Hydroxyl Radical Rate Data from Radiation Chemistry, Int. J. Radiat. Phys. Chem., 3: 211 (1971).

03:162 HOT-ATOM AND RADIATION CHEMISTRY PROGRAM. Lee, Rupert A. (Puerto Rico Nuclear Center, Nuclear Science Division, College Station, Mayaguez, Puerto Rico 00708).

It is now known that ionic-type polymerization reactions can be influenced by the application of an electric field applied during the polymerization. Radiation produces initially both radical and ionic species, and it therefore seemed interesting to investigate the effect of an applied electric field during polymerization induced by ionizing radiation. A study of the copolymerization of mixtures of methyl acrylate and vinyl acetate with crotonic acid in the absence of an electric field has already been carried out. Another system presently being studied is a mixture of aqueous solutions of methacrylic acid and methacrylamide. The electric field effect will be attempted in 1973.

Our other investigations involve the radiolysis of simple gaseous organic fluorides (methyl fluoride and fluoroform) and some simple liquid aromatic fluorides, (o-, m-, and p-fluorotoluenes). Not much has appeared in the literature concerning organic fluorides whereas the fluorocarbons have been fairly well studied. Our studies so far have shown that these simple compounds produce reactive fluorine-containing intermediates that may be suitable for synthesizing organic fluoro compounds. After the mechanisms for the radiolytic decompositions of the above simple compounds have been established, suitable mixtures containing olefinic-type bonds will be irradiated to achieve radiation-induced syntheses.

PUBLICATIONS

Rodríguez, R., and R. A. Lee, Gamma Ray Induced Copolymerization of Vinyl Acetate and Crotonic Acid, Rev. Latinoamer. Química, 2: 50 (1971).

Lee, R. A., Radiolysis of Methyl Fluoride, Rev. Latinoamer. Química, 2: 159 (1971).

03:163 RESEARCH CONCERNING IONIC AND FREE RADICAL REACTIONS IN RADIATIONCHEMISTRY. Williams, T. Ffrancon. (University of Tennessee, Department of Chemistry, Knoxville, Tennessee 37916).

The focus of this research is on the nature and reactivity of the intermediate chemical species that are generated by high-energy irradiation of molecular liquids and solids. A complete characterization of the role of these species in radiation chemistry requires the determination of their molecular structure, the identification of the primary radiation chemical mechanism of their formation, and the kinetic investigation of their subsequent reactions. The experimental methods that are used in this research are those of electron spin resonance and optical absorption spectroscopy. The systems include both organic and inorganic compounds with particular emphasis on comparatively simple molecules such as acetonitrile, methanol, alkyl halides, sulfuryl chloride, and organophosphorus chlorides. Representative research problems currently under investigation include: (1) structural studies of aliphatic radical anions and radical–anion pairs in γ-irradiated crystalline solids; (2) the mechanism of electron attachment to molecules such as acetonitrile and methyl isocyanide; (3) kinetic studies of hydrogen atom abstraction reactions at low temperatures with particular reference to the contribution of quantum mechanical tunneling as evidenced by temperature and kinetic isotope effects; (4) electron spin resonance studies of γ-irradiated phosphorus compounds in the solid state; (5) spin trapping studies in the radiolysis of organic liquids including alcohols, thiols, amines, and ethers; and (6) pulse radiolysis studies on nitriles.

PUBLICATIONS

Kerr, C. M. L., and F. Williams, Electron Spin Resonance, Optical, and Theoretical Studies of the Radical Anion of Sulfuryl Chloride, J. Amer. Chem. Soc., 94: 5212 (1972).

Wang, J. T., and F. Williams, Hydrogen Atom Abstraction by Methyl Radicals in Gamma-Irradiated Crystalline Methyl Isocyanide at 77–125°K, J. Amer. Chem. Soc., 94: 2930 (1972).

Chung, Y. J., and F. Williams, Reversible Line Broadening in the Electron Spin Resonance Spectra of Tert-Butyl Radicals in Gamma-Irradiated Crystalline Tert-Butyl Isothiocyanate, J. Phys. Chem., 76: 1792 (1972).

Le Roy, R. J., E. D. Sprague, and F. Williams, Quantum Mechanical Tunneling in Hydrogen Atom Abstraction from Solid Acetonitrile at 77–87°K, J. Phys. Chem., 76: 546 (1972).

Sprague, E. D., K. Takeda, and F. Williams, The Dimer Radical Anion of Acetonitrile, Chem. Phys. Lett., 10: 299 (1971).

03:164 RADIOLYSIS STUDIES ON REACTIVE INTERMEDIATES. Kevan, Larry. (Wayne State University, Department of Chemistry, Detroit, Mich. 48202).

The objectives of this research are to delineate the chemical and physical properties of reactive intermediates produced by high-energy radiation with emphasis on ionic intermediates trapped in solid matrices. Current areas of study are as follows: (a) A pulsed-electron spin resonance spectrometer is being built to study spin–lattice relaxation mechanisms of radiation-produced ions and radicals. Preliminary experiments suggest that a new relaxation mechanism may be involved in organic matrices near 77°K. (b) Spin–spin interactions of electrons and radicals trapped in the same matrix and the importance of cross relaxation will be assessed by the new technique of electron–electron double resonance. (c) The quasi-free electron state in glassy matrices is being studied experimentally and theoretically. Models to explain excess electron binding in nonpolar matrices are being explored. (d) The thermal decay kinetics of trapped radical pairs is being examined as a model for inhomogeneous thermal decay kinetics in solids. (e) Double modulation Hall effect apparatus is being improved to measure mobilities in low-impedance photoconductors in which the charge carriers are radiation-produced species. The mobility characteristics indicate the scattering mechanisms for photoexcited electrons in amorphous and glassy matrices.

PUBLICATIONS

Kevan, L., Pulse Radiolysis of Alcohol Glasses at 77°K: Mechanism of Electron Trapping, J. Chem. Phys., 56: 838 (1972).
Eisele, I., and L. Kevan, Double Modulation Method for Hall Effect Measurements on Photoconducting Materials, Rev. Sci. Instrum., 43: 189 (1972).
Lin, D. P., and L. Kevan, Optical Bleaching Effects on the Paramagnetic Relaxation of Trapped Electrons in Methyltetrahydrofuran at 77°K, J. Phys. Chem., 76: 636 (1972).
Huang, T., I. Eisele, D. P. Lin, and L. Kevan, Energy Level Structure of Trapped Electrons in Methyltetrahydrofuran Glass from Photoconductivity and Optical Bleaching Studies, J. Chem. Phys., 56: 4702 (1972).
Fueki, K., D. F. Feng, and L. Kevan, Application of the Semicontinuum Model to the Effect of Dipole Reorientation on Trapped Electron Spectra in Glassy Ethanol, J. Chem. Phys., 56: 5351 (1972).

03:165 APPLICATION OF DIFFERENTIAL THERMAL ANALYSIS AND ELECTRICAL CONDUCTIVITY TO THE STUDY OF TRAPPED REACTION INTERMEDIATES PRODUCED IN ORGANIC GLASSES BY γ RADIATION. Willard, John E. (University of Wisconsin, Department of Chemistry, 1101 University Ave., Madison, Wisconsin 53706).

The electric conductivity of γ-irradiated organic glasses as a function of temperature during warm-up reveals migration and neutralization of different populations of charge carriers at different temperatures. Thermoluminescent glow curves obtained in other laboratories give similar data. The present project is designed to better correlate and interpret these data, and to obtain quantitative information on the heats of reactions between electrons and positive ions, and between other trapped reaction intermediates. These data are expected to be of value in evaluating solvation energies in the organic solids and in identifying migrating populations. Measurements are made with irradiated sample and reference in a copper block that can be cooled to any desired temperature, and warmed at a predetermined rate. Preliminary observations have been made on: (1) the magnitude of the endothermic molecular reorganization peak of the unirradiated hydrocarbon, which appears when the sample is warmed above the glass transition temperature, and on the effect of time of annealing below the glass transition temperature on this peak; (2) exothermic peaks attributed to anion–cation neutralization in hydrocarbon glasses; (3) the exothermic peak produced by photobleaching electrons in γ-irradiated 3MP. Calibrations of the heat output against a known phase transition and against known electrical heating agree well.

03:166 CHEMICAL REACTIONS ON γ-IRRADIATED SILICA GEL AND POROUS VYCOR GLASS. Willard, John E. (University of Wisconsin, Department of Chemistry, 1101 University Ave., Madison, Wisconsin 53706).

An adsorbent capable of utilizing the energy of absorbed γ radiation to activate reactions of sorbed molecules to give useful products that can be desorbed into a gas stream would be valuable. G values of unity or higher for chemical conversions on surfaces (based on energy absorbed in substrates) have been demonstrated by several laboratories. The present project seeks to learn more about the conditions controlling such energy transfer in γ-irradiated silica gel, the types of reactions it can initiate, reactions of sorbed radicals with molecules added after irradiation, and saturation of reaction sites as a function of dose and temperature. We find that alkyl chlorides, ethylene, propylene, and methane are all activated to produce sorbed radicals, observable by ESR at 77°K. Admission of O_2 to the radicals converts them to peroxy radicals. C_2H_4 admitted to sorbed CH_3 produces C_3H_8 by addition followed by abstraction from surface silanol groups. Yields as a function of dose and temperature suggest a preempting of the sensitive energy transfer sites by products at 77°K but not at 300°K. The active sites produced by irradiation appear to initiate polymerization of ethylene added either before or after irradiation. Current work on the decay kinetics of sorbed free radicals on silica is furnishing information on their mobility on the surface.

03:167 PRODUCTION, SPATIAL DISTRIBUTION, AND REACTIONS OF TRAPPED FREE RADICALS IN IRRADIATED ORGANIC SOLIDS. Willard, John E. (University of Wisconsin, Department of Chemistry, 1101 University Ave., Madison, Wisconsin 53706).

The purpose of this project is to study the formation of trapped free radicals produced in organic solids by different types of radiation, the mechanisms by which they decay during and after irradiation, their interaction with electrons during irradiation, the energetics of their reactions, and their use as scavengers for determination of diffusion coefficients of small reactive molecules. Past work on the project has demonstrated: (1) different bond selectivity for C–H bond rupture in glassy hydrocarbons than in liquids and gases; (2) first order decay of radicals produced from alkyl halides by dissociative electron capture or photolysis, indicating geminate recombination at rates determined by geometrical rearrangement of the radicals caused by movements of solvent molecules; (3) much slower (sic) germinate recombination rates in deuterated solvents than in protiated solvents; (4) scavenging of electrons by trapped radicals; and (5) radiation-catalyzed recombination of trapped radicals. Recent work has determined the yields and decay kinetics of radicals produced by photolysis of Cl_2 and of HI in glassy hydrocarbons. Current investigations are focused on the matrix isotope effect on decay rates; effects of matrix annealing on decay rates; the spatial distribution of radicals formed by different processes, as revealed by ESR spin relaxation studies; the ultraviolet absorption spectra of trapped radicals; and photochemical reactions of radicals.

PUBLICATIONS

Quintero, R. Arce, and J. E. Willard, Elementary Processes in the Photochlorination of 3-Methylpentane Glass at 77–97°K, J. Phys. Chem., 76: 1807 (1972).
Roy, C. R., and J. E. Willard, Further Evidence on Free Radical Decay in Gamma-Irradiated Alkyl Halide and Hydrocarbon–Alkyl Halide Glasses, J. Phys. Chem., 76: 1405 (1972).
Fenrick, H. W., N. B. Nazhat, P. J. Ogren, and J. E. Willard, Growth and Decay of Alkyl Radicals in Gamma-Irradiated Alkyl Iodides at 77°K, J. Phys. Chem., 75: 472 (1971).

03:168 PROPERTIES OF TRAPPED ELECTRONS PRODUCED BY γ-IRRADIATION OF ORGANIC GLASSES. Willard, John E. (University of Wisconsin, Department of Chemistry, 1101 University Ave., Madison, Wisconsin 53706).

Some of the electrons produced in organic glasses by ionizing radiation are physically trapped, and observable by their optical and ESR spectra. The goal of this project is to further characterize their properties, to aid in understanding the mechanisms of trapping and of the subsequent reactions of the electrons. Work on the project has indicated that trap depths increase with polarity of the trapping matrix; that trapped electron concentrations increase with dose and then decrease, as a result of scavenging by free radicals and positive charge; that electrons that are detrapped by photobleaching may be captured by radicals from which they may be removed by ultraviolet light and be retrapped; that electron capture by scavengers is predominately by tunneling following trapping rather than by capture before trapping. Current and future work includes studies of: (1) effects of matrix annealing on trapped electron decay rates; (2) the long wavelength thresholds of photobleaching to determine trap depths and bound states; (3) the changes in quantum yields of photobleaching with fraction bleached, which stand as a dilemma in the literature; (4) changes in fluorescence yields of photobleaching with fraction bleached; (5) G values of trapping as a function of the nature of the matrices; and (6) time dependence of trapped electron decay following laser pulse photolysis of TMPD, as a means of further examining the tunneling phenomena.

PUBLICATIONS

Miller, J. R., Scavenging Kinetics of Electrons Produced by Irradiation of Organic Glasses; Experimental Evidence for Long Range Tunneling, J. Chem. Phys., 56: 5173 (1972).
Fujii, S., and J. E. Willard, Reactions of Electrons and Free Radicals in Glassy Ethanol, J. Phys. Chem., 74: 4313 (1970).
Ekstrom, A., R. Suenram, and J. E. Willard, Further Studies on the Properties of Electrons Trapped in Glassy Hydrocarbons, J. Phys. Chem., 74: 1888 (1970).

ALSO SEE Radiation Chemistry: Aqueous: 03:113, 03:115; Radiation Chemistry: Gaseous: 03:130; Photochemistry and Energy Transfer: 03:180, 03:183, 03:185, 03:186, 03:190, 03:191; Kinetics and Mechanisms: 03:225; Theoretical Chemistry: 03:288; Miscellaneous Chemical Studies: 03:455, 03:456, 03:463.

PHOTOCHEMISTRY AND ENERGY TRANSFER

Studies of photoexcitation, photochemistry, and energy transfer.

03:169 RADIATION CHEMISTRY OF AROMATIC COMPOUNDS. Kaplan, L. and Wilzbach, K. E. (Argonne National Laboratory, Chemistry Division).

The purpose of this program is to uncover and elucidate the mechanisms of radiation-induced reactions of simple aromatic and heteroaromatic compounds. The reactions of interest are generally those of electronically excited molecules, and are more readily studied using ultraviolet rather than ionizing radiation. Such studies have already shown that the apparent radiation stability of these compounds is attributable largely to the formation of valence isomers which, under ordinary conditions, revert to starting material. They do, however, undergo facile additions in reactive media. Currently under investigation is the photochemistry of benzene in hydroxylic solvents—water, alcohols, and acetic acid. Ultraviolet irradiation of such systems yields a variety of isomeric bicyclo[3.1.0]hexenyl derivatives, at least some of which appear to have their origin in benzvalene, a primary photoproduct. The present studies, aimed at delineating the mechanisms of the photoadditions, include product identification and determination of product ratios, studies of the dark reactions of benzvalene, examination of the photochemical behavior of the various isolated products, and the use of isotopically labeled benzenes to investigate rearrangements that occur prior to product formation.

The reactions that occur upon ultraviolet excitation of benzene in the presence of oxygen will be investigated. An attempt will be made to elucidate the initial reactions in the photo-oxidations and to relate them to the known photochemistry of benzene.

Identification of the photochemically formed valence isomer of pyridine was facilitated by the finding that in aqueous sodium borohydride it was reduced, and stabilized, before undergoing other reactions. Photoreductions of other heteroaromatics, e.g., quinoline, isoquinoline, and indole, by sodium borohydride are now being investigated to acquire information on the excited species formed.

PUBLICATIONS

Kaplan, L., J. W. Pavlik, and K. E. Wilzbach, Photohydration of Pyridinium Ions, J. Amer. Chem. Soc., 94: 3283 (1972).

______, L. A. Wendling, and K. E. Wilzbach, Photo-oxidation of Aqueous Benzene. I. Identification of the Product as 1,3-Cyclopentadiene-1-Carboxaldehyde, J. Amer. Chem. Soc., 93: 3819 (1971).

______, L. A. Wendling, and K. E. Wilzbach, Photo-Oxidation of Aqueous Benzene. II. Role of Benzvalene in the Formation of Cyclopentadiene-Carboxaldehyde, J. Amer. Chem. Soc., 93: 3821 (1971).

Wilzbach, K. E., and L. Kaplan, Photoaddition of Benzene to Olefins. II. Stereospecific 1,2 and 1,4 Cycloadditions, J. Amer. Chem. Soc., 93: 2073 (1971).

______, and D. J. Rausch, Photochemistry of Nitrogen Heterocycles. Dewar Pyridine and Its Intermediacy in Photoreduction and Photohydration of Pyridine, J. Amer. Chem. Soc., 92: 2178 (1970).

03:170 CHLOROPHYLL AND PHOTOSYNTHESIS. Katz, J. J., Norris, J. R. Jr. and Uphaus, R. A. (Argonne National Laboratory, Chemistry Division).

Spectroscopic investigations on chlorophylls of varied isotopic composition reveal chlorophyll to have unusual and previously unsuspected electron donor–acceptor properties intimately implicated in the way chlorophyll functions in the light-conversion step of photosynthesis. These studies have also defined a variety of chlorophyll species in the laboratory, some of which appear to be very similar to chlorophyll as it occurs in the plant. Using ^2H and ^{13}C nuclear magnetic resonance, we are investigating chlorophyll–chlorophyll interactions, transient chlorophyll oxidation products, and chlorophyll–protein interactions. We have recently made the surprising discovery that bacteriochlorophyll from different species of photosynthetic bacteria have different esterifying alcohols, and we are making a comprehensive spectroscopic comparison between the different bacteriochlorophylls. The free radicals associated with photosynthesis are being characterized by electron spin and electron nuclear double resonance studies in chlorophylls and organisms of unusual isotopic composition, and at least one new photo-ESR signal has been detected. Our objective is to utilize the results of laboratory investigations to prepare synthetic chlorophyll systems that can simulate photosynthesis, i.e., that use the energy of light to carry out chemical reactions.

PUBLICATIONS

Katz, J. J., T. R. Janson, A. G. Kostka, R. A. Uphaus, and G. L. Closs, Chlorophyll–Chlorophyll Interactions. Ring V Keto Carbonyl Donor Properties from ^{13}C Nuclear Magnetic Resonance, J. Amer. Chem. Soc., 94: 2883 (1972).

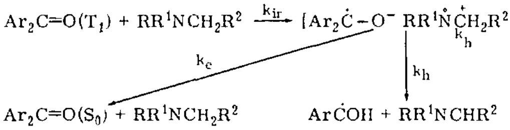
Ballschmiter, K., and J. J. Katz, Chlorophyll–Chlorophyll and Chlorophyll–Water Interactions in the Solid State, Biochim. Biophys. Acta, 256: 307 (1972).

Norris, J. R., R. A. Uphaus, H. L. Crespi, and J. J. Katz, ESR of Chlorophyll and the Origin of Signal I in Photosynthesis, Proc. Nat. Acad. Sci., 68: 625-628 (1971).

03:171 PHOTOREDUCTION BY AMINES VIA CHARGE TRANSFER COMPLEXES. Cohen, Saul G. (Brandeis University, Department of Chemistry, Waltham, Mass. 02154).

The objective of this program is to put on a quantitative basis factors that lead either to quenching or chemical reactions of electronically excited species.

We have proposed, and it is widely accepted, that photoreduction by amines proceeds by formation of a charge-transfer complex, k_{ir}, followed either by charge destruction and quenching, k_e, or by hydrogen transfer and radical formation, k_h. Quenching rates are effectively given by k_{ir}; quantum yields of photoreduction depend on the relative values of k_h and k_e, Scheme A



(a) In photoreaction of fluorenone with p-substituted dimethylanilines, a linear plot of log k_{ir} vs $\sigma\pm$ is obtained showing importance of initial charge transfer. Quantum yields are lower with both strong electron-withdrawing and donating substituents, indicating an optimum in stability of the radical cation. In reaction with N,N-dialkylanilines, ⌬-NRR^1, k_{ir} is unchanged as R,R^1 = CH_3, C_2H_5, i-C_3H_7, while quantum yields rise, R = CH_3, R^1 changed from CH_3 to C_2H_5 to i-C_3H_7. Two large alkyl groups lead to low ϕ. Mono-N-alkylanilines resemble anilines and are not photoreducing agents but quenchers, indicating that reversible N–H transfer may be important.

(b) We have proposed, eq. 1, that interaction of triplet excited carbonyl

$$\log k_{ir} \sim \Delta G_{CT} \sim -{}^3\Delta E_{o,o} - E(A^-/A) + I.P._D + C \qquad (1)$$

compounds with electron donors, k_{ir}, may be described in terms of triplet energy, $^3\Delta E_{o,o}$, and reduction potential of carbonyl compound, $E(A^-/A)$, and ionization potential of donor. For a common acceptor $\log k_{ir} \sim I.P._D$, and this is being explored for varied donors, amines, alcohols, olefins, thio compounds, etc. For a common donor $\log k_{ir} \sim -{}^3\Delta E_{o,o} - E(A^-/A)$, and this is being explored for carbonyl compounds of varying excited state configurations.

PUBLICATIONS

Cohen, S. G., and G. Parsons, Effects of Polar Substituents on Photoreduction and Quenching of Fluorenone by Dimethylanilines, J. Amer. Chem. Soc., 92: 7603 (1970).

______, and G. C. Ramsay, Effects of Quenchers in Photoreduction of p-Benzoylbenzenesulfonic Acid in Aqueous 2-Propanol, J. Amer. Chem. Soc., 93: 1166 (1971).

Guttenplan, J. B., and S. G. Cohen, Triplet Energies, Reduction Potentials and Ionization Potentials in Carbonyl-Donor Charge-Transfer Interactions I, J. Amer. Chem. Soc., 94: 4040 (1972).

______, and S. G. Cohen, Triplet Energies, Reduction Potentials and Ionization Potentials in Carbonyl-Donor Charge-Transfer Interactions II, Tetrahedron Lett., 2163 (1972).

03:172 PHOTOCHEMICAL REACTIONS OF COMPLEX MOLECULES IN CONDENSED PHASE. Linschitz, Henry. (Brandeis University, Department of Chemistry, Waltham, Mass. 02154).

We plan to continue studies on the mechanism of photoredox and isomerization processes, with particular reference to reactions of photobiological relevance. In photoredox systems, we are concerned with both H-atom and electron-transfer processes, and the factors that favor one or the other reaction type. Aromatic ketones are useful test substances for these studies. Using flash photolysis or low-temperature techniques and aprotic solvents, we may isolate the primary step in the ketone–donor reaction and measure its kinetic parameters. Interest centers on kinetic anomalies such as nonlinear Arrhenius plots and concentration-dependent second-order rate constants for the H-atom abstraction reaction. Free-radical processes subsequent to primary redox reactions are being studied by an independent pulsed electrochemical–optical technique, giving data complementary to flash-photolytic experiments. The kinetics of phototransformation of the chromoprotein phytochrome is being studied, as a function of molecular weight, pH, and salt concentration, particularly with respect to the origin of parallel reaction pathways in a homogeneous protein population. Chromophores that may be models for phytochrome are also being investigated.

03:173 ENERGY TRANSFER IN CHEMICAL KINETICS. Weston, R. E. Jr. (Brookhaven National Laboratory, Chemistry Department).

Intermolecular energy transfer is a process of great importance throughout chemical kinetics. In some cases, the rate of energy transfer can be measured by determining the lifetime of a molecule or atom in a fluorescent state as it is changed by the presence of other molecules.

Apparatus has been assembled that will permit the direct measurement of fluorescent lifetimes as short as a few nanoseconds. This uses a single photon technique that measures the time elapsed between the pulse of light that excites the molecule to the fluorescent state and the emission of the first photon by the excited molecule. The lamp is pulsed at a repetition rate of several kilohertz, and signals corresponding to the time elapsed between start and stop signals are collected in a multichannel analyzer. This method will be applied first to studies of electronically excited metal atoms produced with excess translational energy by the photodissociation of metal halides. At present, the quenching of Na (3p) atoms by diatomic and polyatomic molecules is being investigated. The results will be correlated with molecular beam studies and with some recent theoretical work on these systems. It is particularly interesting to extend this method to the quenching of Li (2p) atoms by diatomic molecules, since such systems should be amenable to theoretical treatment, from the standpoint of both potential energy and trajectory calculations.

In the future, we hope to enlarge this program to include fluorescent states of polyatomic molecules in order to determine rates of vibrational energy transfer.

03:174 RADIOACTIVE TRACER STUDIES OF PHOTOCHEMICALLY PRODUCED ATOMS AND RADICALS. Rowland, F. S. (University of California, Department of Chemistry, Irvine, Calif. 92664).

The general purpose of this research is the study of atomic and molecular species formed with extra excitation through photochemical processes. All of the species are radioactively labeled and can be readily studied with radiotracer techniques. The species under current study include hydrogen atoms (tritium), methylene (CHT or $^{14}CH_2$), and methyl (CH_2T or $^{14}CH_3$).

The photolysis of TBr with ultraviolet light dissociates the molecule into the two atoms and any excess energy above that needed to break the T-Br bond (3.81 eV) appears as kinetic energy, with 96% as kinetic energy of the tritium atom. Variation of the wavelength of light leads directly to different initial energies for this photochemically "hot" tritium. Earlier experiments have shown that the photolysis of TBr with Br_2 as scavenger leads to both abstraction and substitution reactions with hydrocarbons (e.g., $DT + CD_3$ or $CD_3T + D$ from $T + CD_4$). As the excess energy is lowered (longer wavelengths), the substitution reaction disappears and its threshold energy can be estimated. Such thresholds are being determined for substitution of T for H, D, or F in alkyl fluorides.

While the TBr photolysis procedure works well for relative yield measurements, absolute yields cannot be determined—the T atoms that do not react while "hot" react with Br_2 to reform TBr, and no trace remains to indicate dissociation had occurred. Considerable progress has been made in the use of tritiated water as a photolytic substrate. In this case, the thermalized T atoms (from HTO) can be scavenged by traces of olefins. Cross-comparisons of TBr and HTO systems are in progress with simple hydrocarbons and halocarbons.

Methylene occurs in two electronic states, singlet and triplet. The singlet state reacts very rapidly with most hydrocarbons while the triplet is quite unreactive. The oxidation of triplet methylene by molecular O_2 has been studied with both CHT and $^{14}CH_2$, and can be used for diagnostic determination of the presence of triplet in other systems. Present studies involve the reactions of methylene with methane, methyl fluoride, propane, ethylene, and 2-butene. The discovery of the isotopic exchange of singlet $^{14}CH_2$ with CO (forming $CH_2 + {}^{14}CO$) was an unexpected bonus arising as a direct consequence of the use of the radioactive tracer method.

The photolysis of $^{14}CH_3I$ with ultraviolet light causes chiefly dissociation into $^{14}CH_3$ plus I, with substantial excess energy on the methyl group. Studies are underway of hot $^{14}CH_3$ reactions with olefins to determine the chemical effects of such excess energy. A minor path, leading to $^{14}CH_2$ formation from $^{14}CH_3I$ photolysis, was discovered through the molecular O_2 diagnostic technique.

PUBLICATIONS

Chou, C. C., and F. S. Rowland, Isotope Effects in the Substitution Reactions of 2.8-eV Tritium Atoms with Methane, J. Phys. Chem., 75: 1283 (1971).

———, P. Angelberger, and F. S. Rowland, Methylene Reactions in Photolytic Systems Involving Methyl Iodide, J. Phys. Chem., 75: 2536 (1971).

Montague, D., and F. S. Rowland, Oxirene Intermediate in the Reaction of Singlet Methylene with Carbon Monoxide, J. Amer. Chem. Soc., 93: 5381 (1971).

———, and F. S. Rowland, The Unimolecular Decomposition of Excited Biradicals Formed by the Addition of Triplet Methylene-^{14}C to cis- or trans-2-Butene, Chem. Commun., 193 (1972).

03:175 INTER- AND INTRA-MOLECULAR ENERGY TRANSFER STUDIES. Nicol, Malcolm F. (University of California, Department of Chemistry, Los Angeles, Calif. 90024).

The continuing objective of this project is to develop a more complete understanding of nonradiative energy transfer in molecules and solids through intensive experimental and theoretical investigations of specific problems in this and closely allied fields. This research is now focused on the following specific studies: dependence of the mechanism and efficiency of intermolecular energy transfer on the separation between donor and acceptor molecules; displacement of absorption and luminescence bands by the molecular environment; bonding and structure of compressed molecular solids; chemistry of the organic solid state at high pressures; radiation damage in organic scintillators; and intramolecular energy transfer, photochromism, and chemiluminescence.

Spectroscopic investigation of the changes of intermolecular energy transfer processes in rigid media brought about by compression of intermolecular distances have an important part in this research. Much effort also is devoted to development of spectromicroanalytical techniques for identification of new molecular species responsible for changes of energy transfer mechanisms. This latter task has recently involved attempts to understand the relationships between structure and spectra of more thoroughly studied inorganic materials under high pressure.

PUBLICATIONS

Fong, M. Y., and M. Nicol, Raman Spectrum of Calcium Carbonate at High Pressures, J. Chem. Phys., 54: 579 (1971).

Nicol, M., W. D. Ellenson, and R. Geffner, Effects of Pressure on the Energies of Low-Energy Singlet and Triplet States of Phenanthrene in Polymethylmethacrylate, in Proceedings of the Second International Conference on Organic Scintillators and Liquid Scintillation Counting, Academic Press, Inc., New York, 1971, pp. 251-263.

Ebisuzaki, Y., and M. Nicol, Raman Spectrum of Hexagonal ZnS at High Pressures, J. Phys. Chem. Solids, 33: 763 (1972).

Hardwick, E. R., and V. Schwartzenbach, Scintillation Efficiency Assessment of Radiation Damage in Plastic Media, in Proceedings of the Third International Conference of Radiation Research, 1971.

03:176 LANTHANIDE IONS AS SENSITIVE PROBES IN INTERMOLECULAR ENERGY TRANSFER AND ORGANIC PHOTOCHEMISTRY. Filipescu, Nicolae. (George Washington University, Department of Chemistry, Washington, D. C. 20006).

This is a multi-faced research program emphasizing the use of various spectroscopic techniques for elucidation of fundamental processes involving electronically excited molecules. Specifically, we use quantitatively uv–visible absorption and emission (fluoresence and phosphorescence), excited state lifetimes, NMR, ESR, and time-lapse spectrometry to detect and identify key intermediates in photochemical reactions of basic significance and to elucidate mechanisms of electronic energy transfer at molecular level. The spectroscopic analysis is correlated theoretically from statistical, quantum mechanical, and kinetic points of view. The work comprises transfer of excitation energy from aromatic ketones to trivalent lanthanide ions both in frozen and in liquid solutions; these form bidentate ligands to chelated rare earth ions, between two nonconjugated organic chromophores incorporated in rigid model compounds in which the interchromophoric separation distance and relative orientation are accurately known, and between separated molecules one of which—either the donor or the acceptor—is in a ground triplet state. In addition, we are combining usual spectroscopic techniques with electron spin resonance to investigate dark transformation following uv irradiation of aromatic ketones, attempting to develop quantum theoretical and statistical models for molecular interactions, and investigating energy transfer and photochemistry involving stable carbonium ions.

PUBLICATIONS

Geiger, F. E., C. L. Trichilo, F. L. Minn, and N. Filipescu, Viologen Radical from Di-4-pyridyl Ketone Methiodides in Hydroxide, J. Org. Chem., 36: 357 (1971).

Filipescu, N., F. E. Geiger, C. L. Trichilo, and F. L. Minn, Electronic and ESR Study of Zinc-Reduced Di(4-pyridyl) Ketone Methiodides, J. Phys. Chem., 74: 4344 (1970).

_____, L. M. Kindley, and F. L. Minn, Effects of 4-Alkyl Substitution on the Photoreduction of Benzophenone, J. Org. Chem., 36: 861 (1971).

_____, F. L. Minn, and J. W. Pavlik, Time-Lapse Spectrometry in Organic Photochemistry, Anal. Chem., 43: 83 (1971).

Pinion, J. P., F. L. Minn, and N. Filipescu, Excimer Emission from Dibenzofuran and Substituted Fluorenes, J. Lumin., 3: 245 (1971).

03:177 PROPERTIES OF EXCITED SPECIES IN THE FROZEN STATE. Moser, Herbert C. (Kansas State University, Department of Chemistry, Manhattan, Kansas 66506).

The objectives of this work are to determine the properties and chemical reactions of excited species in frozen systems. Excitation methods in use are photosensitization and low-energy electron irradiation, and excitation energies from a few eV to above the ionization energy are to be studied. Films of pure compounds or mixtures with mercury are to be irradiated with electrons or uv light. Irradiated films will be examined spectroscopically, and analyses will be made of the reaction products.

Another area of research is the study of the reactions of gas phase atomic species with solid surfaces. Thermal atomization and electrical discharges are in use as methods of generating reactive atomic species. The chemical properties of tritium atoms produced by these methods are to be investigated. The isotope exchange reactions of these energetic atoms are to be used as a means of preparing tritium-labeled compounds that are difficult or impossible to label by other techniques.

PUBLICATIONS

Rathburn, D. W., K. Knarr, and H. C. Moser, Pressure Effects in Hydrogen Atom Reactions with Frozen Propene, Trans. Faraday Soc., 67: 2333 (1971).

Finney, C. D., and H. C. Moser, Low-Energy Electron Radiolysis of Methane, J. Phys. Chem., 75: 2405 (1971).

Vikis, A. C., and H. C. Moser, Quenching of $Hg(6^3Po)$ Atoms by Hydrogen and Hydrocarbons, J. Chem. Phys., 53: 1491 (1970).

_____, and H. C. Moser, Investigation of the Quenching of Excited Mercury Atoms by the Alkanes, J. Chem. Phys., 53: 2333 (1970).

03:178 DIRECT OBSERVATION OF UNSTABLE INTERMEDIATES IN GAS-PHASE CHEMICAL REACTIONS. Johnston, Harold S. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

During the past year we have found that our laboratory research on ozone, oxides of nitrogen, and inorganic free radicals has immediate applications to the problem of stratospheric photochemistry. Ozone in the stratosphere is removed by a direct reaction with an oxygen atom and by catalytic destruction by the oxides of nitrogen (NO and NO_2). To a much lesser extent ozone is removed by transport to the troposphere and by catalytic destruction by free radicals based on water (H, HO, HOO). Other nitrogen-containing compounds (NO_2, N_2O_5, HNO_3) are important in that they may provide additional sources or sinks for ozone, or they may tie up the active forms of nitrogen oxides (NO and NO_2).

We are using our spectroscopic apparatus (infrared, ultraviolet, and mass) to study the photochemistry of the higher oxides of nitrogen and to study the interactions of the NO_x system with the HO_x system. In particular, we are studying wavelength-dependent photolysis of nitric acid vapor (200 to 320 nm), of the NO_3 radical (500 to 700 nm), and of ozone (290 to 340 nm). We plan to study the kinetics of the reaction of ozone and nitrogen dioxide and the kinetics of several reactions of N_2O_5. We are working on two other reactions of great importance to the problem: the formation of nitric acid ($HO + NO_2 + M \rightarrow HNO_3 + M$) and the interaction of peroxyl radicals with nitric oxide ($HOO + NO \rightarrow HO + NO_2$).

PUBLICATIONS

Johnston, H. S., Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysts from Supersonic Transport Exhaust, Science, 173: 517 (1971).

_____, The Effect of Supersonic Transport Planes on the Stratospheric Ozone Shield, Environ. Aff., 1: 735 (1972).

Paukert, T. T., and H. S. Johnston, Spectra and Kinetics of the Hydroperoxyl Free Radical in the Gas Phase, J. Chem. Phys., 56: 2824 (1972).

Wu, C.-H., and H. S. Johnston, Molecular Modulation Mass Spectrometry Kinetic Study of the ClO Free Radical, Bull. Soc. Chim. Belg., 81: 135 (1972).

03:179 STUDIES IN CHEMICAL REACTIVITY. Carr, Robert W., Jr. (University of Minnesota, Department of Chemical Engineering and Materials Science, Minneapolis, Minnesota 55455).

The kinetics of small molecules in both the ground and excited electronic states are being pursued. Four investigations are currently in progress. The kinetics of hydroxyl radical reactions are being studied in a high-velocity discharge-flow apparatus. The equipment is being modified by the addition of a quadrupole mass spectrometer detector to complement the line absorption photometric technique used previously. Attempts will soon be made to investigate the kinetics of the methylene triplet ground state and first excited singlet state by a new apparatus for flash photolysis with time-resolved mass spectrometry, which is just being completed. Work is continuing on radiationless transitions in small molecules. The $S_1 \rightarrow T_1$ intersystem crossing in ketene is being studied by relating singlet and triplet methylene yields to the primary photochemical process in ketene through techniques previously developed in this laboratory. The reactivity of electronically excited sulfur dioxide is being investigated by the techniques of kinetic spectroscopy. Spectroscopic detection of the products of the elementary reactants is being attempted. The kinetics of the transients so produced will be investigated.

PUBLICATIONS

Carr, R. W., Jr., Predictions of the Rates of Hydrogen Abstraction by $CH_2(^3B_1)$ by the Bond-Energy-Bond-Order Method, J. Phys. Chem., 76: 1581 (1972).

Poirier, R. V., and R. W. Carr, Jr., A Tandem Isothermal Calorimetric Probe Technique for Measuring Atomic Flow Rates, Rev. Sci. Instrum., 43: 354 (1972).

_____, and R. W. Carr, Jr., The Use of Tubular Flow Reactors for Kinetic Studies Over Extended Pressure Ranges, J. Phys. Chem., 75: 1593 (1971).

Carr, R. W., Jr., T. W. Eder, and M. G. Topor, Chemical Evidence for a Small $CH_2(^1A_1) - CH_2(^3B_1)$ Electronic Term Difference, J. Chem. Phys., 53: 4716 (1970).

Eder, T. W., and R. W. Carr, Jr., Collision-Induced Singlet → Triplet Intersystem Crossing of Methylene and Methylene-d_2, J. Chem. Phys., 53: 2258 (1970).

03:180 THE CONTRIBUTION OF ELECTRONICALLY EXCITED STATES TO THE RADIATION CHEMISTRY OF ORGANIC SYSTEMS. Lipsky, Sanford. (University of Minnesota, Department of Chemistry, Minneapolis, Minnesota 55455).

Fluorescence spectra and fluorescence quantum yields are being determined for a wide variety of saturated hydrocarbons in the presence and absence of quenchers and as functions of temperature and exciting wavelength (from 1750 to 1250Å). The objective of this work is to characterize the nature of excited states of saturated hydrocarbons and to assess the radiative and nonradiative contributions to the variability of their fluorescence quantum yields with changes in structure and conformation.

Electronic energy transfer from saturated hydrocarbons to aromatic acceptors has been observed under both vacuum ultraviolet and gamma excitation conditions. In addition to sensitization by the fluorescent state of the saturated hydrocarbon, there appears to be another, longer-lived state also capable of sensitizing the acceptor. This state has tentatively been designated as the triplet state and a search for its phosphorescence and characteristic electron impact spectrum is now in progress.

The fluorescence quantum yields of many liquid alkanes decreases with increasing excitation energy until an energy of ca 1 eV below the gas phase ionization potential is achieved. At higher energies the yield has recently been found to increase and to be more efficiently quenched by electron scavengers. It is tentatively suggested that the emission in this excitation energy regime arises, at least in part, from ion + electron recombination and a detailed study is now in progress to confirm this view. If correct, the emission technique may provide a convenient tool for the determination of ionization thresholds in condensed phases. Additionally, by studying the recombination emission in the presence of energy acceptors, it may be possible to determine the extent to which the electron spin relaxes prior to recombination with the positive ion.

With an emission spectrometer capable of measuring quantum yields at the 10^{-6} level, we have just begun to search for fluorescence from highly excited states of aromatic molecules. Once these spectra are located and yields determined, it will be possible to answer such questions as: What are the rates of the nonradiative channels that deplete these states? Are these states utilized as intermediates in cascades from still higher states to the lowest ones? What are the G values for production of these highly excited states under gamma excitation conditions?

PUBLICATIONS

Hirayama, Fumio, and Sanford Lipsky, Saturated Hydrocarbons as Donors in Electronic Energy Transfer Processes, in Organic Scintillators and Liquid Scintillation Counting, Donald L. Horrocks and Chin-Tzu Peng (Eds.), Academic Press, Inc., New York, 1971, p. 205.

______, Craig W. Lawson, and Stanford Lipsky, Fluorescence of p-Dioxane, J. Phys. Chem., 74: 2411 (1970).

______, William Rothman, and Stanford Lipsky, Fluorescence of Saturated Hydrocarbons. II. The Effect of Alkyl Substituents, Chem. Phys. Lett., 5: 296 (1970).

Steelhammer, J. C., and Sanford Lipsky, Electron-Impact Excitation of the He $1'S \rightarrow 2^3S$, $1'S \rightarrow 2^3P$, and $1'S \rightarrow 2'P$ Transitions, J. Chem. Phys., 53: 4112 (1970).

______, and Sanford Lipsky, Angular Dependence of Differential Cross Sections for Electron Excitation of Singlet → Triplet Transitions, J. Chem. Phys., 53: 1445 (1970).

03:181 A MEASUREMENT OF DIFFUSION COEFFICIENTS OF SHORT-LIVED SPECIES IN SOLUTION BY PHOTOCHEMICAL SPACE INTERMITTENCY. Burkhart, Richard D. (University of Nevada, Department of Chemistry, Reno, Nevada 89507).

Spatially inhomogeneous irradiation is being used in combination with photochemical and photophysical processes to study the diffusive behavior of short-lived species in solution. Using photoinitiated chain reactions to monitor steady-state alkyl radical concentrations, it has been possible to evaluate diffusion coefficients of these radical species. The mobilities of these radicals are considerably smaller than those of the parent alkanes. Confirmatory evidence for this unexpected result is being sought using a nonchain photochemical reaction.

Diffusion experiments on electronically excited molecules are also being carried out and, at present, anthracene in solution is the object of study. Anthracene undergoes a triplet annihilation reaction in which one of the collision partners accepts a sufficient amount of energy to cross over to an excited singlet state after which it may emit fluorescence. The rate of this delayed fluorescence may be used to monitor steady-state triplet anthracene concentrations. These studies will be carried out with and without an applied magnetic field and will utilize ruled line intermittency patterns so that any anisotropic effects may be detected. These studies utilize a special optical system to reduce the effective size of the intermittency pattern by two to three times.

PUBLICATION

Burkhart, R. D., R. F. Boynton, and J. C. Merrill, Studies on Diffusion and Diffusion-Controlled Reactions Involving Alkyl Radicals in Solution, J. Amer. Chem. Soc., 93: 5013 (1971).

03:182 TWO-PHOTON LASER PHOTO-IONIZATION OF MOLECULES IN LIQUIDS. Beck, G., and J. K. Thomas. (University of Notre Dame, Radiation Laboratory).

Electrons are produced in several organic liquids by the two-photon laser photolysis of dissolved anthracene and pyrene. The rate constants for reaction of the electrons with biphenyl and O_2 are measured and are in agreement with the known mobilities of the electrons in hexane. With other hydrocarbons, however, the rate constant for reaction of e^- with biphenyl follows the half power of the electron mobility. The mobility of the e_s^- in various hydrocarbon mixtures follows the exponential of the mole fraction of the hydrocarbon with the higher mobility. Complex behavior is observed in alcohol–hydrocarbon mixtures, which may be explained in terms of aggregates of alcohol in these mixtures.

PUBLICATION

Beck, G., and J. K. Thomas, Two Photon Laser Photo-Ionization of Molecules in Liquids, Chem. Phys. Lett., 13: 295 (1972).

03:183 EXCITED STATES IN p-XYLENE. Gangwer, T., and J. K. Thomas. (University of Notre Dame, Radiation Laboratory).

The pulse-radiolysis- and laser-photolysis-induced processes of p-xylene and related aromatics are being investigated. The excited state absorption spectra for the aromatics studied yield three distinct bands in the visible region. From temperature investigations the excimer absorption has been identified as the low-energy band and its decay kinetics found to agree with the corresponding first excited singlet emission. Assignment of the high-energy band to a biradical species seems plausible at this time. The third band occurring on the low-energy side of the biradical peak has been tentatively assigned to the lowest triplet state and its decay kinetics analyzed.

Scavenger experiments have been conducted on the biphotonically excited S_3 state and the excited states produced by pulse radiolysis of p-xylene. It has been found that nitrous oxide efficiently scavenges this S_3 laser-produced state indicating a possible source of error in the use of N_2O for electron-scavenging experiments. Solute transfer studies indicate a total yield of excited states of $G = 4.1$ with approximately equal yields of triplet and singlet states for p-xylene. Kinetic investigations of p-terphenyl in benzene and p-xylene indicate the triplet state of p-xylene has a significantly longer lifetime.

PUBLICATION

Thomas, J. K., The Production of Excited States by Lasers and Ionizing Radiation, Rec. Chem. Progr., 32: 145 (1971).

03:184 ALKANE FLUORESCENCE DECAY TIME STUDIES. Helman, W. P. (University of Notre Dame, Radiation Laboratory).

It was generally believed until very recently that alkanes had no excited states from which fluorescence could be observed. Fluorescence of alkanes has now been established, and the role of these states in radiation chemistry is of great interest. We are currently examining the quenching of alkane fluorescence by added CCl_4 and O_2 using decay times measured by monophoton techniques. By varying the temperature as well as the concentration of quencher we are developing a model for energy migration in the excited alkane system. Our plan is to extend the measurements to a wider temperature range and to use additives that can fluoresce in their own right, thereby further documenting the potential importance of energy transfer and excited states in the radiation chemistry of alkane systems. Mixed solvents will be further investigated, although preliminary experiments have not shown the reduction of quenching efficiency in them expected on the basis of energy migration.

PUBLICATIONS

Helman, W. P., Analysis of Very Fast Luminescence Transients, Int. J. Radiat. Phys. Chem., 3: 283 (1971).

Gregory, T. A., and W. P. Helman, Temperature Dependence of Specific Rates of Benzene Monomer and Excimer Fluorescence, J. Chem. Phys., 56: 377 (1972).

Henry, M. S., and W. P. Helman, Fluorescence Lifetimes of Saturated Hydrocarbons, J. Chem. Phys., 56: 5734 (1972).

03:185 CORRELATION OF RADIATION CHEMISTRY AND PHOTOCHEMISTRY OF 1,4-DIOXANE. Hentz, R. R., L. M. Perkey and J. T. Kiwi. (University of Notre Dame, Radiation Laboratory).

Excited states are among the transient species involved in the radiation chemistry of a system. Therefore, complementary photochemical studies are undertaken, using light within a range of wavelengths from the visible region down to approximately 1100 Å, to provide knowledge of the behavior of specific excited states of a molecule. The photolysis of gaseous 1,4-dioxane at 1849 Å, corresponding to absorption in the first band of the spectrum, is currently being studied. Study of the gas-phase photochemistry at 1470 Å, corresponding to absorption in the third and fourth bands, has been completed. Excitation at 1470 Å results in decomposition with a primary quantum yield of $\phi = 1.0$ and a lifetime of less than 10^{-10} s; quantum yields of products suggest that $C_4H_8O_2^* \rightarrow C_2H_4 + 2CH_2O$ with $\phi = 0.75$ is the major decomposition mode. In future work, photolysis of the liquid at 1849 and 1470 Å will be studied. In addition to their intrinsic interest, results of the photochemical work are expected to elucidate (1) the role of excited states in the previously studied γ radiolysis of liquid 1,4-dioxane and (2) chemical behavior of the recently reported emitting species in liquid 1,4-dioxane excited with 1849 Å light or 12-MeV electrons.

PUBLICATION

Hentz, R. R., and C. F. Parrish, Photolysis of Gaseous 1,4-Dioxane at 1470 Å, J. Phys. Chem., 75: 3899 (1971).

03:186 PHOTOINDUCED LUMINESCENCE AND IONIZATION OF ALKANES IN THE SOLID PHASE AT LOW TEMPERATURE. Hentz, R. R., L. M. Perkey and L. J. Sharp. (University of Notre Dame, Radiation Laboratory).

A study of the photoionization, photochemistry, and photoexcited luminescence of alkanes in the solid phase at low temperatures has been initiated. A long-lived (~5 s) luminescence at ~415 nm and a short-lived (tenths of a nanosecond) fluorescence at ~220 nm are observed from alkane glasses γ-irradiated at 77°K. The fluorescence was first observed in photoexcitation of gaseous and liquid alkanes at room temperature and was shown to be a property of individual molecules. However, the long-lived luminescence has been observed only from γ-irradiated glasses as a consequence of cation–electron neutralization. Thus, it is not known whether such luminescence is a property of individual alkane molecules (e.g., phosphorescence from a triplet state) or a property of some kind of collective excitation characteristic of the alkane glass (e.g., a charge-separated state). Experiments are in progress and are planned in which luminescence from selected alkanes is studied as a function of excitation wavelength in neat glasses and noble gas solutions of the alkanes at temperatures near 77°K and perhaps 4°K. The presence of ionization will be established by spectrophotometric and ESR detection of trapped electrons and will be correlated with luminescence observations. Such a study is expected to provide some insight into the ionization of alkanes and the nature and behavior of excited states of alkanes in condensed media.

03:187 DECAY TIMES OF OPTICALLY EXCITED AROMATIC HYDROCARBONS AT LOW PRESSURE: NAPHTHALENE, BIPHENYL, AND 2-METHYLNAPHTHALENE. Hsieh, J., J. Halpern and P. K. Ludwig. (University of Notre Dame, Radiation Laboratory).

Examination of excited naphthalene by the monophoton technique at a pressure of 0.07 torr, with irradiating light in the range 3080 to 2500 Å shows an irregular increase in decay rate as a function of excitation energy. The effects appear to reveal a relationship between the natural lifetime and the energy of the vibration levels. The oscillation is probably to be attributed to the excitation of sequence bands.

Similar study of biphenyl reveals the existence of two different luminescent systems describable by the relation $I \propto \exp(-t/\tau_1) + \beta\exp(-t/\tau_2)$ in which generally $\tau_1 > \tau_2$, β is always greater than unity and $\tau_1 \approx 10\ \tau_2$. The values of τ_1, τ_2, and β vary with wavelength and reveal the existence of three different regions of excitation and the varying contributions of at least two different vibronic systems in each case.

Work on 2-methylnaphthalene gives results remindful of naphthalene. However, in this current work a study, over a greater range of exciting wavelength, of the relation between bandwidth of the exciting light and decay rate (i.e., $1/\tau$) reveals perplexing relationships, the origins of which are yet to be understood.

PUBLICATIONS

Hsieh, J. C., U. Laor, and P. K. Ludwig, Consideration of the Absorption Characteristics of Organic Vapors in Interpretation of the Decay Properties of Excited Vibronic States: Naphthalene, Chem. Phys. Lett., 10: 412 (1971).

Laor, U., and P. K. Ludwig, Fluorescence Lifetimes of Vibronic States of Naphthalene Vapor in the Region of Excitation from 3080–2150 Å, J. Chem. Phys., 54: 1054 (1971).

03:188 DIFFUSION OF REACTIVE FREE RADICALS. Noyes, Richard M. (University of Oregon, Department of Chemistry, Eugene, Oregon 97403).

Ultraviolet light and ionizing radiation can generate extremely reactive radical species whose reactions are often controlled by the rates of diffusion together. We have shown that the diffusion coefficients of photochemically produced free radicals can be measured by determining the dependence of their concentration on the size of the illuminated area in which they are produced. By means of this technique of photochemical space intermittency, we have measured diffusion coefficients of iodine atoms in various solvents in order to test theories of diffusion-controlled reactions. It would also be of great interest to measure the diffusion of hydrogen atoms in water because these atoms are generated by radiation in aqueous systems and in living organisms and because it is hard to approximate their diffusive behavior with that of stable molecules. We have attempted to measure this coefficient by generating hydrogen atoms through photolysis of a hydrogen-saturated solution of hydrogen peroxide, but the effort was unsuccessful, apparently because oxygen is also produced directly by the photolysis. Other systems more suitable for this study are being sought.

03:189 DEUTERIUM ISOTOPE EFFECTS IN ELECTRONIC RELAXATION OF LARGE POLYATOMIC MOLECULES. Lim, Edward C. (Wayne State University, Department of Chemistry, Detroit, Michigan 48202).

The objective of the project is to study deuterium isotope effect on fluorescence of aromatic and heteroaromatic molecules (as vapor and in solution) to gain better understanding of singlet–triplet intersystem crossing in large polyatomic molecules. This requires determination of quantum yield and lifetime of fluorescence under various experimental conditions. The quantum yield measurements are already underway for several compounds, while the determination of lifetime is awaiting construction of a time-correlated single photon counting apparatus. Our initial efforts will be directed to the study of mechanism of singlet deactivation in "isolated" anthracene and its derivatives. Variation of radiative and nonradiative decay rates with excitation energy, temperature, and deuteration of the molecule will be deduced for these systems.

PUBLICATION

Fischer, S. F., and E. C. Lim, Non-Born–Oppenheimer Vibronic Coupling and Deuterium Isotope Effect on $T_1 \rightarrow S_0$ Radiative Transitions of Aromatic Hydrocarbons, Chem. Phys. Lett., 14: 40 (1972).

03:190 ELECTRON PRODUCTION BY PHOTOIONIZATION OF METAL FILMS AND OF SODIUM DISPERSED IN GLASSY 3-METHYLPENTANE. Willard, John E. (University of Wisconsin, Department of Chemistry, Madison, Wisconsin 53706).

We have reported that ultraviolet irradiation of a matrix formed by deposition of a vapor phase mixture of a metal (Li, K, Na, Mg, Cd) and 3-methylpentane (3MP) at 77°K produces a narrow (0.1-gauss) electron spin resonance singlet with several flanking lines, all of the signals being observable only in the photostationary state. Current investigations show that the same signals are produced when a sodium film in an evacuated tube at 300°K is exposed to ultraviolet radiation in the absence of 3MP. When a matrix containing Na in 3MP is scraped from the cold finger in vacuo and isolated from any metallic film, exposure to the lamp, with a filter to remove visible and ir radiation, produces a trapped electron ESR signal with a width (ca. 1 G) and half-life (tens of minutes) similar to that produced by γ irradiation of pure 3MP at 77°K. Future experiments under consideration include comparison of the spectra, decay times, photobleaching quantum yields, and luminescence spectra of trapped electrons produced by photoionization of the Na in 3MP at different wavelengths with these properties of trapped electrons produced by γ irradiation of 3MP, and by photoionization of tetramethyl-p-phenylenediamine (TMPD) in 3MP. The source of the signals from the metal films is also under investigation.

PUBLICATION

Froben, F. W., and J. E. Willard, Paramagnetic Species Produced by Ultraviolet Irradiation of Lithium, Potassium, Sodium, Magnesium, and Cadmium in 3-Methylpentane at 77°K, J. Phys. Chem., 75: 35 (1971).

03:191 ROLE OF H ATOMS IN THE RADIATION CHEMISTRY AND PHOTOCHEMISTRY OF ORGANIC GLASSES. Willard, John E. (University of Wisconsin, Department of Chemistry, Madison, Wisconsin 53706).

Early work on this project showed that no trapped H atoms are produced by γ irradiation of a variety of organic solids at 4°K or above. However, photolysis of HI present in radiolyzed perdeuterated 3-methylpentane (C_6D_{14}) below 50°K produced trapped H atoms, proving that the matrix is capable of such trapping, and, therefore, that thermal H atoms are not produced in the radiolyses. Photolysis of HI in C_6H_{14}, in contrast to C_6D_{14}, produced no trapped H atoms. In a systematic investigation of the yields of stable products and radicals from the photolyses of HI and DI in C_6H_{14} and C_6D_{14} as a function of temperature we have now shown that the absence of trapped H atoms from photolysis of HI in C_6H_{14} results from the greater ease with which hot H atoms abstract hydrogen from C–H bonds as compared to C–D bonds. This reduces the yield of thermalized H atoms available for trapping to a negligible value. In future work on this project it is planned to investigate H-trapping yields in C_6H_{14} and C_6D_{14} as a function of the initial energy of the H, by varying the photolysis wavelength, and also to investigate further the kinetics of trapped H atom production and decay, which pose significant questions about the nature of the trapping sites.

PUBLICATION

Long, M. A., and J. E. Willard, Properties of Trapped H and D Atoms Produced by the Photolysis of HI in 3MP$-d_{14}$ Glass, J. Phys. Chem., 74: 1207 (1970).

03:192 THE GAS PHASE RADIOLYSIS AND VACUUM ULTRAVIOLET PHOTOLYSIS OF HETEROCYCLIC ORGANIC COMPOUNDS. Scala, Alfred A. (Worcester Polytechnic Institute, Department of Chemistry, Worcester, Mass. 01609).

The long-range objective of this research is the determination of the modes of decomposition of highly electronically excited molecules and ions, produced when relatively complex molecules absorb large amounts of energy, either in radiolysis or in photolysis. At present this type of information is available for only a relatively few simple molecules, primarily the lower-molecular-weight hydrocarbons. Presently under investigation are cyclic ethers, sulfides, and amines.

In order to meet the long-range objective of this work, an orderly progression of investigations through a series of complex molecules is planned. The effects of various atoms and functional groups upon the decomposition modes of complex molecules will be determined.

The results of these studies will be more than just a series of mechanisms for the compounds studied. It is envisioned that the kinetic and thermodynamic considerations that apply to these systems of intermediate complexity will be useful in understanding the interaction of high-energy radiation with still more complex systems.

PUBLICATIONS

Scala, A. A., and D. G. Ballan, The Vacuum Ultraviolet Photolysis of Cyclohexanone, J. Phys. Chem., 76: 615 (1972).

______, and J. P. Colangelo, The Photochemical Type II Reaction of Carbonates and Thiolcarbonates, J. Chem. Soc., D: 1425 (1971).

______, The Photolysis and Radiolysis of 3-methyl-2-butanone, J. Phys. Chem., 74: 2639 (1970).

ALSO SEE Radiation Chemistry: Aqueous: 03:101, 03:105, 03:116, 03:117; Radiation Chemistry: Gaseous: 03:119, 03:122, 03:126, 03:128, 03:129; Radiation Chemistry: Other: 03:136, 03:138, 03:146, 03:156, 03:167, 03:168; Hot Atom Chemistry: 03:206, 03:208; Kinetics and Mechanisms: 03:216, 03:220, 03:221, 03:222; Chemical Spectroscopy: 03:244, 03:248, 03:253, 03:260, 03:261, 03:265; Theoretical Chemistry: 03:282, 03:283, 03:284; Isotope Chemistry: 03:293, 03:296; Thermodynamics: 03:316; Miscellaneous Chemical Studies: 03:447, 03:463.

HOT ATOM CHEMISTRY

Studies of the chemical effects of nuclear transformation.

03:193 HOT ATOM CHEMISTRY OF CARBON AND IODINE. Voigt, A. F.; Warren, J. L.; Elgart, M. F.; and van Ooij, W. J. (Ames Laboratory. Chemistry Division).

Nuclear reactions that produce radioactive atoms also give them excess energy by recoil or excitation. With this energy they behave differently from normal atoms, and their radioactivity makes it possible to observe these differences.

Hot ^{11}C atoms produced in the irradiation of organic compounds with high-energy photons interact with the parent compound after most of their energy has been lost, yielding fragments, addition compounds, and larger molecules. Fragments such as carbon monoxide (from compounds containing oxygen) and acetylene are formed in large yields. The carbon atoms may add to the parent molecules yielding a product with an additional carbon or they may serve to bind two molecules of the parent compound together. These products are observed by radiogas chromatography and their formation can be attributed to interaction of the carbon atoms with the various bonding or nonbonding electrons in the parent molecule.

The beta decay of several tellurium isotopes produces radioactive isotopes of iodine with excess energy of excitation. The behavior of hot iodine atoms, after other methods of production, has been studied intensively, providing a basis for comparison for the beta decay study. Thus, it can be determined whether the particular mode of production has an important effect on the chemical behavior of high-energy iodine atoms.

PUBLICATIONS

Jewett, G. L., and A. F. Voigt, Recoil Reaction Products of ^{11}C in C_5 Hydrocarbons, J. Phys. Chem., 75: 3201 (1971).

Voigt, A. F., G. F. Palino, and R. L. Williams, Reactions of Recoil Carbon Atoms with Oxygen Containing Molecules. II. Structural Dependence of Carbon Monoxide Yields, J. Phys. Chem., 75: 2248 (1971).

Williams, R. L., and A. F. Voigt, Reactions of Recoil Carbon Atoms with Oxygen Containing Molecules. III. Reaction Mechanisms in Methanol, J. Phys. Chem., 75: 2248 (1971).

03:194 CHEMICAL EFFECTS OF NUCLEAR TRANSFORMATION. Hillman, M.; Nagy, A.; Weiss, A. J. (Brookhaven National Laboratory. Department of Applied Science).

This program has two parts: (1) to study the fate of hot tellurium atoms following an Auger cascade, and (2) to study retentions in organometallics following the capture of neutrons by the nucleus of the metal atom.

We have recently completed the study of the decay of ^{121}I and have observed similarities with and differences from the decays of ^{129m}Te and ^{127m}Te. Further study is planned with various Sb isotopes that decay to Te. In the solid state the retention of 1,1′-trimethyleneferrocene was found to be half that of ferrocene. This study will continue with the study of the retentions of 1,1′-trimethylenetitanocene dichloride and the analogs of zirconium and hafnium, and of 1,1′:2,2′-bis(trimethylene)ferrocene and the 1,1′,3,3′-derivative.

PUBLICATIONS

Harbottle, G., and M. Hillman, Szilard–Chalmers Processes for Isotope Production, in Radioisotope Production and Quality Control, Technical Reports Series, No. 128, pp. 617-632, International Atomic Energy Agency, Vienna, 1971 (STI/DOC/10/128).

Hillman, Manny, and Allen J. Weiss, Chemical Effects of the Isomeric Decay of ^{127m}Te and ^{129m}Te in Aqueous Solution, Radiochim. Acta, 15(2): 79-83 (1971).

03:195 INORGANIC HOT ATOM CHEMISTRY. Harbottle, G. (Brookhaven National Laboratory, Chemistry Department).

The study of hot atom chemistry (chemical effects of nuclear transformation) in the solid state allows one to determine (a) the chemical reactions of atoms formed in states of high kinetic or electronic excitation energy in crystals, and/or (b) the slow, thermally induced annealing reactions by which such atoms, at rest in the crystal, can be made to change their chemical forms. Since hot atoms in crystals often give rise to labeled interstitial species or to chemical structures that may be regarded as impurities in the host lattice, hot atom chemistry is the chemical analogue of the study of defects, color centers, etc., in solid state physics.

Another interesting parallel is the thermal spike concept of radiation damage in solid state physics. In the chemical investigations of our program, evidence is sought for chemical reactions taking place in the thermal spike. This evidence is then rationalized by solid state theory. It is desired to broaden these studies to include Mössbauer and/or perturbed angular correlation measurements to provide a better understanding of the chemistry of recoil atoms in situ in crystals.

PUBLICATIONS

Harbottle, G., and M. Hillman, Szilard–Chalmers Processes for Isotope Production, in Radioisotope Production and Quality Control, Technical Reports Series, No. 128, pp. 617-632, International Atomic Energy Agency, Vienna, 1971 (STI/DOC/10/128).

Groening, H., and G. Harbottle, Recoil and Annealing Studies in Neutron-Irradiated Crystalline Molybdenum Hexacarbonyl, Radiochim. Acta, 14: 109 (1970).

03:196 EFFECT OF DEFECTS ON POSITRON ANNIHILATION. Lambrecht, R. M. (Brookhaven National Laboratory, Chemistry Department).

The objectives of the program are to study the interactions of positrons and the hot atom chemistry of positronium in matter. The The annihilation of a positron is predominately accompanied by the emission of two 511-keV photons. The angular correlations and the rates and intensities of the annihilation photons provide a method of nondestructive physical-chemical measurements. The change in photon energy and the angular deviation of the two photons from 180° are related to the momentum distribution of the center-of-mass of the annihilating electron–positron pair. While positron annihilation processes have been studied under many conditions, the role of defects on the annihilation processes is not well understood. Results of several workers suggest that variations in Doppler line width and annihilation rates are due to the electronic environment associated with the defects and to an increased probability of annihilation with conduction electrons relative to annihilation with core electrons. A high-resolution Ge(Li) detector is being used for characterizing the electronic environment sampled by positrons in solid state matrices, such as silver halide, that have been doped with defects by high-energy ion implantations. The Doppler-broadened spectrum is expected to vary with the nature of the defects, the spatial distribution of the ions, the matrix, etc. Positron annihilation rates and the diffusion rates of positrons in doped ionic crystals and metals will be determined when possible.

03:197 HOT ATOM CHEMISTRY AND REACTION MECHANISMS. Wolf, A. P. (Brookhaven National Laboratory, Chemistry Department).

Atoms or molecular fragments having nonequilibrium distributions of translational and internal energy are produced by nuclear transformations, by photon irradiation, and in microwave plasmas. Experimental studies of the reactions of these hot atoms or radicals are of particular interest because a general theoretical treatment of such reactions is lacking. The emphasis is on the study of primary events in fast chemical reactions.

The mechanism of ethylene production in reactions of ^{11}C atoms is being investigated. Work on reactions of ^{11}C with simple halocarbons will be continued and the observations will be correlated with the results of theoretical calculations. Reactions of vinyl radicals are being studied in order to correlate reactions of these radicals with purported intermediates in hot atom reactions. Several cyclotron-produced nuclides will be used in investigations of hot halogen-atom reactions at structurally controlled sites such as asymmetric centers.

Microwave discharge production of tritium atoms is being used to label molecules to high specific activity. Tritium-labeled hormones, peptides, and proteins prepared in this manner have been found to retain their biological activity. This work will focus on the repair mechanism, which permits the production of peptides of specific activity much greater than that of the constituent individual amino acids. The direct observation of atoms (C, Si, Ge, halogens) in excited states, and the determination of their rates of reaction with a variety of substrates, involves vacuum uv spectrophotometry coupled with a microwave discharge generator as the atom generation source. This method is currently being applied to the observation of chlorine atoms in the first excited state and to the study of their reactions with alkenes and other reagents.

PUBLICATIONS

Gaspar, P. O., K. Y. Choo, E. Y. Y. Lam, and A. P. Wolf, A Flow Method for the Study of Silicon and Germanium Atom Reactions by Direct Spectroscopic Observation, Chem. Commun., 1012-1013 (1971).

Lam, E. Y. Y., P. P. Gaspar, and A. P. Wolf, States of Atomic Carbon Produced in Decomposition of Organic Compounds in a Microwave Plasma, J. Phys. Chem., 75: 445 (1970).

Shevlin, P. B., and A. P. Wolf, The Formation of Carbon Atoms in the Decomposition of a Carbene, Tetrahedron Lett., 46: 3987 (1970).

Lambrecht, R., N. Furukawa, and A. P. Wolf, Evidence for ^{11}C Stripping and Abstraction Reactions Leading to Acetylene Formation, J. Phys. Chem., 74: 4605 (1970).

Majerski, Z., S. H. Liggero, P. v. R. Schleyer, and A. P. Wolf, The Degenerate Isomerization of Adamantane, Chem. Commun., 1596 (1970).

03:198 NUCLEAR MEDICINE AND RADIOPHARMACEUTICALS LABELED WITH ISOTOPES OF SHORT HALF-LIFE. Wolf, A. P. (Brookhaven National Laboratory, Chemistry Department).

Five years ago, the Chemistry and Medical Departments began collaborative research in nuclear medicine. This has expanded into a vigorous and diverse program utilizing short-lived, cyclotron-produced isotopes. Research experience in nuclear chemistry, hot atom and radiation chemistry, organic synthesis, and radiochemical assay procedures is brought to bear on the preparation of compounds labeled with these isotopes. Radiopharmaceuticals are used in tumor detection, in the diagnosis of metabolic disorders and organ malfunction, and in therapy.

^{11}C-labeled amino acids, sugars, and other physiologically active compounds are being produced in research quantities. New methods of producing large quantities of carrier-free $H^{11}CN$, an important synthetic intermediate, are being developed. ^{123}I production will be expanded, with emphasis on new intermediates and on the incorporation of this isotope into physiologically active compounds. ^{18}F research will be directed towards the production of $F_2-{}^{18}F$, $H^{18}F$, $CF_3O^{18}F$, and other labeled intermediates to be used in the preparation of compounds such as 5-fluorouracil, 5-fluorocytosine, and steroids. ^{15}O, ^{13}N, other halogen isotopes, and platinum isotopes will be among those used in new research directions.

Pure research applications of short-lived isotopes will also continue, emphasizing more detailed studies of DNA synthesis with the high-specific-activity thymidine-^{11}C successfully prepared at BNL.

PUBLICATIONS

Christman, D., E. J. Crawford, M. Friedkin, and A. P. Wolf, A New Means of Detecting DNA Synthesis in Intact Organisms with Positron-Emitting [Methyl-^{11}C]Thymidine, Proc. Nat. Acad. Sci., 69: 988 (1972).

Wolf, A. P., The Preparation of Organic Radiopharmaceuticals Containing Isotopes of Short Half Life, Radioisotopy, 12: 499 (1971).

Lambrecht, R. M., C. Mantescu, C. Redvanly, and A. P. Wolf, Preparation of High Purity Carrier-Free ^{123}I Monochloride as an Iodination Reagent for the Synthesis of Radiopharmaceuticals. IV, J. Nucl. Med., 13: 266 (1972).

Hoyte, R. M., S. S. Lin, D. R. Christman, H. L. Atkins, W. Hauser, and A. P. Wolf, Organic Radiopharmaceuticals Labeled with Isotopes of Short Half Life. III. ^{18}F-Labeled Phenylalanines, J. Nucl. Med., 12: 280 (1971).

Finn, R., D. R. Christman, H. J. Ache, and A. P. Wolf, The Preparation of Cyanide-^{11}C for Use in the Synthesis of Organic Radiopharmaceuticals. II, Int. J. Appl. Radiat. Isotop., 22: 735 (1971).

03:199 NUCLEAR RECOIL STUDIES IN CHEMICAL DYNAMICS AND RADIATION CHEMISTRY. Root, John W. (University of California, Department of Chemistry, Davis, California 95616).

The broad objectives of this research include the following: (1) to provide new systematics information pertaining to chemical reactions at very high energies; (2) to provide definitive laboratory tests for current theories that relate to high-energy chemistry; (3) to provide new knowledge about the behavior of molecules under conditions of very large internal excitation; (4) to provide new information about molecular properties through high-energy chemistry research; and (5) to elucidate any special effects that may arise in radiation chemistry induced by fast neutrons.

Both recoil ^{18}F and ^{39}Cl are generated for hot atom experiments via cyclotron-produced fast neutrons. In the hot atom work we seek generalized systematics, energetics, and molecular dynamics descriptions for the unique chemical processes that occur at high energies. Through carefully chosen experiment sequences, we hope to be able to determine whether common features exist between the potential energy surfaces for high-energy reactions taking place in different experimental systems. Current results suggest that the respective hot F-for-F and F-for-H atomic substitution, hot F-for-R alkyl replacement, and hot F-to-HF abstraction processes are strongly similar in fluoroethanes. Preliminary evidence has also been obtained for hot Cl-to-HCl abstraction in alkanes, and we are attempting to determine whether the hot Cl-for-H, Cl-for-F, and Cl-for-Cl processes take place at the typically large reaction energies that are characteristic of the analogous F-atom processes. During the coming year classical trajectory and molecular beam methods will be employed to augment the nuclear recoil techniques. A new investigation into the nature of fast-neutron-induced radiolysis has been initiated using cyclotron-produced fast neutrons. The zero degree neutron velocity spectra and thick-target yields have been measured for (d,n) reactions in Li, Be, C, and Al between 15 and 40 MeV. Other efforts in the radiolysis work have been restricted to the development of suitable fast-neutron dosimetry methods for applications in aqueous media.

PUBLICATIONS

McKnight, C. F., N. J. Parks, and J. W. Root, Chemistry of Nuclear Recoil ^{18}F Atoms. III. The Average Energy and Mechanism for F-for-F Substitution in CH_3CF_3, J. Phys. Chem., 74: 217 (1970).

Parks, N. J., K. A. Krohn, and J. W. Root, Chemistry of Nuclear Recoil ^{18}F Atoms. IV. Hot F-to-HF and F-to-F_2 Abstraction in CH_3CF_3, J. Chem. Phys., 55: 2690 (1971).

Krohn, K. A., N. J. Parks, and J. W. Root, Chemistry of Nuclear Recoil ^{18}F Atoms. V. Mechanism and Systematics in CH_3CF_3, J. Chem. Phys., 55: 5771 (1971).

———, N. J. Parks, and J. W. Root, Chemistry of Nuclear Recoil ^{18}F Atoms. VI. Approximate Energetics and Molecular Dynamics in CH_3CF_3, J. Chem. Phys., 55: 5785 (1971).

03:200 CHEMISTRY OF TRITIUM AND HALOGENS FORMED WITH NUCLEAR RECOIL ENERGY. Rowland, F. S. (University of California, Department of Chemistry, Irvine, California 92664).

The basic purpose of this research is the understanding of the chemical reactions initiated by atoms with excess translational energy (hot atoms). We are trying to extend our knowledge of the mechanisms through which chemical changes occur beyond that based on thermal reaction systems, and hot atoms are an especially convenient form of nonthermal reactant. Since the radioactive atoms formed by nuclear reactions are almost invariably highly excited, such nuclear processes are advantageously used in these studies. An inevitable practical by-product of these experiments is that some knowledge is gained of the chemical condition of those radioactive atoms formed in nuclear processes whenever and wherever they occur. Our current experiments rely most heavily on the formation of tritium atoms by the nuclear reactions $^6Li(n,\alpha)T$ and ^3He (n,p)T, and of fluorine atoms from the nuclear reaction, $^{19}F(n,2n)^{18}F$.

We have emphasized precision quantitative measurements of product yields from carefully controlled reactions with simple molecules, usually in the gas phase. These choices have been made because the predictions of different theories concerning the importance of various factors in controlling these reactions often are rather similar and can be distinguished only with good accuracy in relative yield measurements.

Recent experiments with tritium atoms from nuclear recoil have emphasized the importance of chemical factors (bond energy, electron density, electronegativity) in contrast to physical factors (substituent mass, inertia, steric effects) in the control of such reactions. Further confirmation is being sought, especially for H-atom abstraction from substituted ethylenes and from bonds to Si, O, and N. Other experiments are being carried out at −196°C to determine the effects of low temperature and solid phase on the stabilization of excited product molecules.

Much less is known about the reactions of fluorine atoms, thermal or hot, than is known about hydrogen atoms. We are concurrently investigating the reactions of both hot and near-thermal ^{18}F atoms. In 50−50 SF_6-substrate mixtures, hot reactions are readily observed while most ^{18}F atoms react while essentially thermal in energy when SF_6 has a mole fraction >0.95. Current experiments are emphasizing the substitution reactions of ^{18}F-for-halogen in alkyl halides, the abstraction of H by thermal ^{18}F atoms, and the various addition processes with olefins. Simple substrate molecules are being used to reduce the number of unusual ^{18}F-labeled molecules found as products. After a number of simple systems are well understood, later experiments can concentrate on the identity and yields of these unusual species.

PUBLICATIONS

Tang, Y-N, E. K. C. Lee, E. Tachikawa, and F. S. Rowland, A Study of the Roles of Chemical Factors in Controlling the Yields of Substitution Reactions by Energetic Tritium Atoms: Electronegativity, Electron Density and Bond Energy, J. Phys. Chem., 75: 1290 (1970).

Palino, G. F., and F. S. Rowland, Complete Retention of Configuration During the Replacement of Hydrogen by Energetic Tritium in dl- and meso-$(CHFCl)_2$, J. Phys. Chem., 75: 1299 (1971).

Smail, T., R. S. Iyer, and F. S. Rowland, Competitive Addition of Near-Thermal ^{18}F Atoms to Olefins, J. Amer. Chem. Soc., 95: 1041 (1972).

Williams, R. L., and F. S. Rowland, Addition of ^{18}F Atoms to Acetylene, J. Amer. Chem. Soc., 95: 1047 (1972).

Kushner, R., and F. S. Rowland, Temperature Dependence of the Reaction Yields from Recoil Tritium Reactions. II. Tritium Atom Addition to 1-Butens and cis-2-Butene, J. Phys. Chem., 76: 190 (1972).

03:201 STUDIES IN HOT ATOM AND RADIATION CHEMISTRY. Koski, Walter S. (The Johns Hopkins University, Chemistry Department, Charles and 34th Streets, Baltimore, Maryland 21218).

The objective of this study is to investigate certain elementary chemical events that will lead to an understanding of the processes taking place in radiation, and hot atom chemical reactions, and the chemical effects associated with nuclear transformations.

The light emitted by proton (2-MeV)-irradiated water vapor and liquid water is being studied initially in the visible region with the immediate objective of definitely identifying some of the intermediates that play a role in the radiation chemistry of water.

Electrons play an important role in radiation chemical effects; consequently, we are studying the energetics of electron fragmentation. The thresholds, for production of positive, negative, and coincident ion pairs will be measured using a newly completed ion pair mass spectrometer. The electron beam in this instrument has a full width at half maximum of 50 millivolts and the energy can be varied from a few eV to 200 eV. The halogenated methanes will be studied first.

In many nuclear reactions the products initially start out as multiply charged ions. We plan to study the charge states of fast nitrogen ions produced by the $^{12}C(d,n)^{13}N$ reaction. We have previously studied some hot atom chemical reactions involving this nuclear reaction and the present and future study is an attempt to further map out the elementary steps that contribute to the radiation chemistry and hot atom chemistry of the system.

In view of the fact that ions play an important role in radiation and hot atom effects, we have in progress a study of ion−molecule reactions that might be important in post nuclear processes. The reactions of C^+ ions are being studied with a number of target molecules over an energy range of 2 to 200 eV. In view of the large amount of fluorine hot atom work that has been carried out and since ionic fluorine probably plays an important role in these processes, it is planned to study the reactions of F^+ ions with a number of target molecules.

PUBLICATIONS

Wilson, P. S., R. W. Rozett, and W. S. Koski, Reactions of C^+ Ions with Some Methyl Halides, J. Chem. Phys., 53: 3494 (1970).

Koski, W. S., Some Ion Molecule Reactions of the C^+ Ion in the Gas Phase, Rec. Chem. Progr., 31: 155 (1970).

Pipano, A., and Joyce J. Kaufman, Ab-Initio Calculation of Potential Energy Curves for the Ion Molecule Reaction $O^+ + N_2 \rightarrow NO^+ + N$, J. Chem. Phys., 56: 5258 (1972).

03:202 GAS PHASE REACTIONS OF HOT TRITIUM ATOMS WITH CYCLOHEXENES. Markowitz, S. S. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

The purpose of this research is to contribute toward understanding of chemical reactions of fast-moving atoms and ions following a nuclear reaction. The reaction studied mainly is the $^3He(n,p)T$ reaction with hot tritium ions and atoms produced in the Berkeley Campus Nuclear Reactor. Triton addition and unimolecular decompositions in the gas phase are being studied with special techniques developed for gas phase chromatography and proportional counting of the tritium. Cyclohexene and substituted cyclohexenes are being investigated and two papers have been submitted dealing with sulfur dioxide as a radical scavenger in alkene systems and with scavenger effects of H_2S, butadiene-d_6, O_2, and SO_2 in T + cyclohexene gas phase systems. A high-temperature irradiation apparatus is being completed for irradiations in the reactor at temperatures up to approximately 200°C.

Recent work has indicated the possibility of obtaining kinetic data directly from hot atom reactions of tritium to give methyl radical reactions. Work will continue in this field in 1973 and 1974. The above research is due mainly to Ph.D. candidate, Darrell C. Fee.

03:203 HALOGEN ATOMIC REACTIONS ACTIVATED BY RADIATIVE NEUTRON CAPTURE AND ISOMERIC TRANSITION. Rack, Edward P. (The University of Nebraska, Lincoln, Nebraska 68508).

By employing the freeze−thaw technique, radiogas chromatography and other methods for determining organic and product yields induced by the radiative neutron capture (n,γ) and isomeric transition (IT) processes, hot atom reactions of chlorine, bromine and iodine are being studied extensively in various gaseous, liquid, and solid halomethanes and hydrocarbons. The reactions of ^{38}Cl, ^{80}Br, ^{80m}Br, ^{82}Br, ^{128}I, and $^{130}I + {}^{130m}I$, activated by radiative neutron capture and isomeric transition will be investigated in more detail, with special attention given to the effects of density and phase on product yields and the bromine isotope effect. Reactions of ^{128}I, and ^{130}I with various gaseous, liquid, and solid olefins will be studied employing iodine, rare gas moderators or molecular additives in an attempt to learn more about the mechanism of hot and thermal iodine reactions. The (n,γ)-activated reactions of ^{38}Cl will be investigated by radiogas chromatography in the CH_4 and CD_4 systems employing rare gas and molecular additives. The stereochemistry of hot ^{83}Br and ^{132}I reactions will be studied employing the Brookhaven National Laboratory 60″ cyclotron. The general applicability of kinetic theories to heavy halogen gaseous systems will be studied. Of importance will be the calculation of the kinetic energy spectra of hot atoms activated by radiative neutron capture using computer techniques.

PUBLICATIONS

Oates, D. W., R. L. Ayres, R. W. Holton, K. S. Schwartz, and E. P. Rack, Isometric Transition Activated Reactions of ^{82}Br with Gaseous Methyl Bromide, Radiochem. Radioanal. Lett., 4(3): 123 (1970).

Gadeken, O. C., R. L. Ayres, and E. P. Rack, Application of Isotopically Labeled Bromine for the Determination of Trace Unsaturation in Alkanes, Anal. Chem., 42: 1105 (1970).

Ayres, R. L., C. J. Michejda, and E. P. Rack, Reactions of Iodine with Olefins: I. Kinetics and Mechanism of Iodine Addition to Pentene Isomers, J. Amer. Chem. Soc., 93: 1389 (1971).

———, O. C. Gadeken, and E. P. Rack, Reactions of Iodine with Olefins: II. Radiative Neutron Capture Induced Reactions of ^{128}I with Various C_5 Isomers: Evidence for a Mechanism Other Than Autoradiolysis in the Condensed State, J. Phys. Chem., 75: 2880 (1971).

Helton, R. W., M. Yoong, and E. P. Rack, Kinetic Energy Isotope Effects of Bromine Reactions Activated by Radiative Neutron Capture in Gaseous CH_3F and CD_3F, J. Phys. Chem., 75: 2072 (1971).

03:204 POSITRONIUM CHEMISTRY. Tao, S. J. (The New England Institute, P. O. Box 308, Ridgefield, Connecticut 06877).

We are studying the reactions of positronium, the lightest hot atom, in molecular liquids and solids. There were two fundamental properties of positronium not clearly understood—the exact state of positronium in a solvent and the kinetics of positronium reactions. We have found and proved that positronium atoms in various liquid solvents can be treated classically as ordinary atoms or molecules, even in their limited lifetime of about 10^{-9} sec. The behavior of positronium in a solvent can be correlated to the properties of the solvent. We are studying the kinetics of positronium reactions in various solvents with iodine, benzoquinone, and others as solutes. We are also studying the exact state of positronium and the kinetics of positronium reactions in molecular glass solids. At present, we are using polyglycols as the medium system. From this study, we are hoping to understand more about the difference between the hot atom reactions in glass solids, such as the frozen solvated electrons, and the hot atom reactions in liquids. Furthermore, we are studying the positronium reactions with chlorine, bromine, iodine, nitric oxide, and others in various media. We feel that from the work we are doing now we are making a solid foundation for the study of positronium reactions, hence, hot atom reactions. We are planning to continue our study in two directions. First, we shall investigate quantitatively the hot atom reactions that lead to the formation of positronium atoms. Second, we shall study more about the kinetics of positronium reactions with simple atoms and molecules and hot atoms.

PUBLICATIONS

Tao, S. J., Positronium Annihilation in Molecular Substances, J. Chem. Phys., 56: 5499 (1972).

Chuang, S. Y., S. J. Tao, and J. M. Wilkenfeld, Ortho-Positronium Annihilation and the Glass Transition of Nylon 6, J. Appl. Phys., 43: 737 (1972).

———, and S. J. Tao, Study of Various Properties of Silica Gel by Positron Annihilation, J. Chem. Phys., 54: 4902 (1971).

Merrigan, J. A., J. H. Green, and S. J. Tao, Positron Annihilation, in Physical Methods of Chemistry, Vol. I, Part IIID, pp. 501-586, A. Weissberger and B. W. Rossiter (Eds.), John Wiley & Sons, Inc., New York, 1972.

03:205 REACTIONS OF HIGH-ENERGY RADIOACTIVE ATOMS RESULTING FROM NUCLEAR TRANSFORMATION IN THE SYSTEMS OF SILICON-CONTAINING COMPOUNDS. Tang, Yi-Noo. (Texas A&M University. Department of Chemistry. College Station, Texas 77843).

The major objectives of this study are to investigate the hot ^{31}Si and ^{32}P atom reactions in the gas phase and to study chemical reactions involving other hot atoms with silicon-containing compounds. Recoil ^{31}Si atoms are formed from the nuclear transmutation $^{31}P(n,p)^{31}Si$ by fast neutrons either converted from a 20-MeV deuteron beam of a cyclotron or derived from the screening of thermal neutrons of a nuclear reactor. ^{31}Si may undergo abstraction reactions to give $^{31}SiH_2$ or $^{31}SiF_2$, which can be trapped by butadiene to form silacyclopent-3-ene or 1,1-difluorosilacyclopent-3-ene. Reactions of silicon atoms in the presence of other olefins are also under study. Recoil phosphorus atoms are obtained via $^{31}P(n,\gamma)^{32}P$. It is possible to derive the degree of partial and total retention of bonds in PF_5 following the above nuclear transformation. Experiments are also in progress to reveal the controlling factors for ^{32}P abstraction reactions to give $^{32}PH_3$ or $^{32}PF_3$ as the final product. Recoil tritium and recoil halogen reactions with silicon-containing compounds such as silane, the methylsilanes, and the halomethylsilanes have indicated that chemical factors such as bond dissociation energy and inductive effect are operating during these hot atom reactions.

PUBLICATIONS

Tang, Y.-N., G. P. Gennaro, and Y. Y. Su, Direct Evidence for the Reaction of Monomeric Silicon Difluoride with 1,3-Butadiene, J. Amer. Chem. Soc., 94: 4355 (1972).

———, W. S. Smith, J. L. Williams, K. Lowery, and F. S. Rowland, Secondary Unimolecular Reactions Subsequent to Substitution Reactions by High-Energy ^{38}Cl and ^{39}Cl Atoms, J. Phys. Chem., 75: 440 (1971).

Daniel, S. H., G. P. Gennaro, K. M. Ranck, and Y.-N. Tang, Recoil Tritium Reactions with Hexamethyldisilane in the Gas Phase, J. Phys. Chem., 76: 1249 (1972).

———, and Y.-N. Tang, Recoil Tritium Reactions with Trimethylfluorosilane. A Study on Parameters Affecting Hot Atom Substitution Reactions, J. Phys. Chem., 75: 301 (1971).

03:206 GAS PHASE STUDIES OF THE KINETICS AND MECHANISMS OF HIGH-ENERGY SULFUR ATOM REACTIONS AND SOME NOVEL ASPECTS OF HOT HALOGEN REACTION. Spicer, Leonard D. (University of Utah, Department of Chemistry, Salt Lake City, Utah 84112).

Gas phase reactions of translationally excited ^{35}S, ^{38}Cl, and ^{3}H are being studied to characterize molecular dynamics of reactive and nonreactive collisions at energies significantly above thermal thresholds for reaction. The few previous studies of hot sulfur atom reactions have clearly indicated the complexities involved in such polyvalent, reactive systems. This research is presently directed toward identifying basic mechanistic paths for reaction of sulfur atoms in alkane, alkene, O_2, H_2S, SO_2, and H_2 reactant systems. Differences in reactivities between n; γ; and n; p-generated ^{35}S recoil atoms are also being investigated.

Utilizing known primary reactions of nuclear recoil chlorine atoms, a study of secondary reactions of high-energy hydrogen chloride molecules is proposed. This investigation is designed to answer a fundamentally important question regarding the availability of efficient, limited, and discrete reaction paths for high-energy polyatomic reactants. This is to be compared with hot atom chemistry where such channels have been demonstrated but for which fewer degrees of freedom in the projectile are available. Studies of reactive deuterium isotope effects in hot chlorine atom systems are also being expanded in an effort to identify dynamical reasons for observed differences in reaction efficiencies.

A study of energy transfer efficiencies from systems chemically activated by reaction of recoil hydrogen is also proposed. It has been demonstrated by other investigators that molecules formed in such reactions may have much higher internal excitation than was previously anticipated. The dynamics of collisional stabilization from such very-high-energy states is being investigated.

03:207 REACTIONS OF CHARGED AND NEUTRAL RECOIL PARTICLES FOLLOWING NUCLEAR TRANSFORMATIONS. Ache, Hans J. (Virginia Polytechnic Institute and State University, Department of Chemistry, Blacksburg, Va. 24061).

An important but still little understood field of fundamental chemical kinetics in the area that deals with those chemical reactions that occur above the threshold or activation energy. In this program translationally hot species (atoms or ions) are generated following nuclear reactions and their interactions with various substrates are studied in order to assess the reaction efficiencies as a function of the kinetic energies associated with the reactants.

The dependence of the lifetime of the positronium atom (Ps), which is the bound state of a positron and electron, on its environment allows the study of hot and thermal reactions of this species (separately from each other) with various substrates by simple lifetime measurements. This method will be applied mainly to assess the effect of intrinsic and thermodynamic energy barriers on the reaction rates of Ps with solutes in aqueous solutions as a function of the kinetic energy of the Ps.

Nucleogenic Br^{+1} ions will be used to evaluate statistical, geometrical, bond energy, and electronic effects on the cross sections of electrophilic Br^{+} substitution in halogenated aliphatic hydrocarbons and organic molecules in general.

Energetics and mechanisms involved in the reactions of energetic ^{11}C atoms with organic molecules will be studied in view of possible applications of this method to the preparation of ^{11}C-labeled radiopharmaceuticals.

PUBLICATIONS

Bartal, L. J., J. B. Nicholas, and H. J. Ache, The Reactions of Energetic Positronium Atoms in Solutions, J. Phys. Chem., 76: 1124 (1972).
Ache, H. J., Chemistry of the Positron and Positronium, Angew. Chem. Int. Ed. Engl., 11: 179 (1972).
Finn, R. D., D. R. Christman, H. J. Ache, and A. P. Wolf, The Preparation of Cyanide$-^{11}C$ for Use in the Synthesis of Organic Radiopharmaceuticals, Int. J. Appl. Radiat. Isotope., 22: 735 (1971).
Swordsma, H. B., C. S. Tumosa, and H. J. Ache, The Effect of Gamma Radiation on the Oxidation State of Manganese in $KMnO_4$, Radiochim. Acta, 16: 112 (1971).
Tumosa, C. S., J. B. Nicholas, and H. J. Ache, The Interactions of Positrons with Defects in NaCl Crystals, J. Phys. Chem., 75: 2030 (1971).

03:208 REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS. Gaspar, Peter P. (Washington University, Department of Chemistry, Saint Louis, Missouri 63130).

We are studying the reactions of recoiling silicon and germanium atoms in order to understand the interplay between structure and energy as factors that determine what happens in a reactive collision between an atom and a molecule — a fundamental chemical process.

We have carried out experiments of various kinds:

1. Since polyvalent free atoms are difficult to produce for study by other kinetic techniques, the recoil technique has been the method of choice for silicon and germanium. The operative reaction mechanisms and the important reaction intermediates have been identified by determining the effects on product yields of changes in reaction conditions. Silylene (SiH_2) and germylene (GeH_2) are the principal product-forming intermediates in the reactions of silicon and germanium atoms in silane and germane, respectively.

2. It has been our experimental philosophy to complement recoil studies with experiments in which probable intermediates in the recoil reactions are produced in macroscopic amounts to facilitate direct rate measurements. Separate studies of individual reactive species illuminate their roles under the complex conditions of a recoil experiment. Silyl radicals ($\cdot SiH_3$) have been studied by a new flash photolysis–electron spin resonance technique. Free silicon and germanium atoms have been produced in a flow system for kinetic studies and detected by atomic absorption spectroscopy.

3. The reactions of Si^+, SiH^+, SiH_2^+, and SiH_3^+ with silane and methane have been studied by ion cyclotron resonance spectroscopy. Knowledge of these and other secondary ion–molecule reactions have permitted the definite conclusion to be reached that positive ions are involved in the recoil chemistry of silicon.

We are concentrating now on the primary reactions of recoiling silicon and germanium atoms. A complete picture of the reaction sequence which leads from recoiling atoms to chemically stable products is being developed. The next phase of our work is to elucidate the details of the primary steps and to obtain the excitation functions, the reaction cross sections as functions of energy.

PUBLICATIONS

Henis, J. M. S., G. W. Stewart, M. K. Tripodi, and P. P. Gaspar, Ion Molecule Reactions in Silane, J. Chem. Phys., 57: 389 (1972).
Gaspar, Peter P., Peter Markusch, J. Dewey Holten III, and John J. Frost, The Chemistry of Recoiling Silicon Atoms. V. Product-Forming Reactions in $PH_3-Si_nH_{2n+2}$ Mixtures, J. Phys. Chem., 76: 1352 (1972).
———, and B. Jerosch Herold, Silicon, Germanium, and Tin Structural Analogs of Carbenes, Chap. 13 in Carbene Chemistry, 2nd ed., W. Kirmse (Ed.), Academic Press, Inc., New York, 1971.
———, Kwang Yul Choo, Ernest Y. Y. Lam, and Alfred P. Wolf, A Flow Method for the Study of Silicon and Germanium Atom Reactions by Direct Spectroscopic Observation, Chem. Commun., 1012 (1971).
Lam, Ernest Y. Y., Peter P. Gaspar, and Alfred P. Wolf, States of Atomic Carbon Produced in Decomposition of Organic Compounds in a Microwave Discharge, J. Phys. Chem., 75: 445 (1971).

ALSO SEE Nuclear Reactions: 03:53; Photochemistry and Energy Transfer: 03:173, 03:174, 03:177, 03:191; Kinetics and Mechanisms: 03:211, 03:212, 03:220, 03:222, 03:224, 03:226, 03:229; Chemical Spectroscopy: 03:266; Theoretical Chemistry: 03:281, 03:282; High-Temperature and Inorganic Chemistry: 03:339; Analytical Chemistry: 03:398; Engineering Chemistry: 03:439.

KINETICS AND MECHANISMS

Studies of the kinetics and mechanisms of gas phase reactions and reactions in solution, including crossed molecular beam experiments.

03:209 LIGAND SUBSTITUTION AND ISOTOPIC EXCHANGE FOR SOME SQUARE-PLANAR PLATINUM COMPLEXES. Martin, Don S. (Ames Laboratory, Chemistry Division).

The extent to which chloride and bromide ligands of several square-planar platinum complexes are replaced by water is being measured by rapid titrations of the acidic protons of the aquo-ligands with automatic titration equipment. In this way not only will the extent of aquation at equilibrium be evaluated but the rates of replacement of the halide ligands will be determined for the cis-dichlorodiammineplatinum(II) and for the cis- and trans-dibromodiammineplatinum(II). Alternative methods that involve potentiometric titrations with a selective bromide indicator electrode together with the measurement of ionic conductance will be utilized to follow the loss of bromides from dibromo-(o-phenanthroline)platinum(II) in nitromethane solvent.

The rates of replacement of halide ligands by the same halide will be studied with the radioactive tracers ^{36}Cl and ^{82}Br. Attention will be directed to some previously unexpected but recently demonstrated mechanisms in which one complex species, for example $PtBr_4^{2-}$, either catalyzes the exchange of bromide ligands for another complex with free bromide or else trades its bromide ligands with another complex without forming a free bromide intermediate. Although such processes have been found in bromide systems, an examination of chloride systems is just underway.

PUBLICATIONS

Gunther, R. G. and D. S. Martin, Jr., Kinetics of Ammonation of t-Dichlorobis(triethylphosphine)platinum(II) t-Dichloroammine-(triethylphosphine)platinum(II), t-Dichlorodiammine-platinum(II), Inorg. Chim. Acta, 6: 81-87 (1972).
Paxson, J. R., and D. S. Martin, Jr., Aquation Equilibrium and Isotopic Exchange of Chloride and Chloro-(diethylenetriamine)-platinum(II) Chloride, Inorg. Chem., 10: 1551-1552 (1971).
Carturan, G., and D. S. Martin, Jr., Kinetics of Ligand Substitution Reactions for Platinum Complexes. Relative Influence of cis-triethylphosphine and Amine Ligands upon the Isotope Exchange Between Chloride and Bromide Ions and the Halo Ligands, Inorg. Chem., 9: 258-261 (1970).

03:210 APPLICATIONS OF CHEMICAL ACCELERATOR-CROSSED BEAM FACILITY TO STUDY OF ATMOSPHERIC CHEMISTRY. Wexler, S. and E. K. Parks (Argonne National Laboratory, Chemistry Division).

The species of greatest importance in the chemical processes that occur in the atmosphere are the diatomic molecules H_2, O_2, and CO; the triatomic molecules O_3, CO_2, and H_2O; and the free radicals OH, O, HO_2, and H. In addition, several pollutants are of considerable importance — the nitrogen-containing compounds NO, N_2O, NO_2, and NH_3: the sulfur-containing compounds SO_2 and SO_3; metallic atoms such as the alkalis, Mg, and Fe, and particulate matter such as in aerosols. These species, either in their ground states or excited, react and/or are formed in the individual steps in often long chains of consecutive and competitive chemical reactions. Usually, the reactions are exoergic, but frequently they require activation energies, and some consequently are the rate-determining steps in the chains of reactions.

In order to understand, and hopefully control, the bulk chemistry of the atmosphere, quantitative information is required on the microscopic collision processes leading to the products observed macroscopically. The necessary data are the relative and absolute cross sections as functions of the relative kinetic energy and internal energies of the two reactants, and the mechanisms and dynamics of the collision process. Such information may be obtained most effectively by the use of molecular beams.

The Aerodynamic Chemical Accelerator is capable of accelerating several molecules of interest in atmospheric chemistry to well defined kinetic energies in the region from 0.5 to 10 eV, which is the range in which these endoergic reactions or reactions requiring activation energies take place. Alterations in the machine are presently being designed to make possible the determination of excitation functions for the reactions

$$\underline{SO_2} + O_3 \rightarrow SO_3^* + O_2$$

and

$$\underline{NO} + O_3 \rightarrow NO_2^* + O_2$$

where the underline signifies the accelerated collision partner. Chemiluminescence from the reactions (assumed here to be radiation from the excited products denoted by asterisks) will be observed by photon counting through interference filters. As the research program proceeds, a small fast optical spectrograph will be installed to facilitate identification of the products and to allow a more detailed study of the various reaction channels. Reactions of metastable species may also be studied with this accelerator. Examples are

$$NO^* + O_3 \rightarrow \begin{cases} NO^+ + O_3^- \\ NO_2^+ + O_2^- \end{cases}$$

$$SO_2^*(^3B) + CO \rightarrow CO_2^* + SO$$

$$SO_2^*(^3B) + SO_2 \rightarrow SO + SO_3^*$$

Beams of the metastable species will be produced by electron bombardment of the expanded jet.

The Cathode Sputtering Chemical Accelerator will accelerate metallic atoms to well defined kinetic energies in the range from 0.5 to 150 eV. This machine may be employed to study the dynamics and mechanisms of reactions of metallic pollutants in the atmosphere, e.g., Na, Fe, Hg, Cu, Zn, Se, and Mg, with normal atmospheric gases and pollutants, such as O_2, O_3, NO, and CO_2.

03:211 APPLICATIONS OF CHEMICAL ACCELERATOR-CROSSED BEAM FACILITY TO STUDY OF REACTIONS OF ATOMIC AND MOLECULAR HYDROGEN.

Wexler, S. and E. K. Parks (Argonne National Laboratory, Chemistry Division).

Plasma arc jets have been used successfully to produce beams of fast He and Ar atoms with kinetic energies of several electron volts. Attempts will be made to adapt this technique for the production of beams of H and D atoms. The energy range of D atoms may be extended by seeding D_2 in H_2. If stable beams of fast hydrogen and deuterium can be achieved by this method, the source will replace the sputtering source on the Cathode Sputtering Accelerator, and the energetics and dynamics of the reactions of these fast atoms will be studied. Some reactions that lend themselves for observation by this approach are important in atmospheric chemistry.

$$\underline{H} + O_3 \rightarrow \begin{cases} HO_2^* + O \\ OH^* + O_2 \end{cases}$$

$$\underline{H} + O_2 \rightarrow OH^* + O$$

Reactions of importance in hot atom chemistry also appear feasible. These include hydrogen and halogen displacement in hydrocarbons and halogen-containing organic compounds, respectively. The chemiluminescent radiation from the reactions may possibly be detected by a photomultiplier after passing through an interference filter, but the angular distribution of the products should be determined by ionization followed by mass spectrometric analysis.

Fast H_2, D_2, and T_2 molecular beams with well-defined energies in the range from 5 to 100 eV and higher have routinely been produced in the Ion Accelerator. Combination of the acceleration-neutralization section of this accelerator with the detection section of the aerodynamic machine may make possible studies of reactions of these energetic molecules with organic and inorganic molecules, illustrations of which are double bond addition and hydrogen displacement. These reactions can be studied if chemiluminescence from the reactive collisions can be observed and analyzed.

03:212 CROSSED-BEAM STUDIES OF REACTIONS OF ACCELERATED ATOMS AND MOLECULES.

Wexler, S., E. K. Parks, C. E. Young, and R. B. Cohen (Illinois Institute of Technology).

An extensive and diversified program of research in the discipline of colliding fast (0.5- to 150-eV) molecular beams is in progress. By this approach it is possible to elucidate the detailed characteristics of chemical reactions that are endoergic or require activation energies. Such reactions comprise most of chemistry. Characteristics such as the threshold laws, the energy dependences of the cross sections, and the collision dynamics of the various reaction channels give an insight into the fundamental processes occurring in chemical reactions. Three unique chemical accelerator-crossed beam machines have been constructed and are currently in operation. The machines are based on three different and widely applicable methods of acceleration of atoms and molecules into the range of energies where they can react. The three techniques adopted are aerodynamic acceleration in seeded supersonic jets, cathode (surface) sputtering, and ion acceleration followed by neutralization (by near resonance charge exchange). Each accelerator has been designed to facilitate the study of certain broad classes of reactions. In addition, sections of the machines are interchangeable, so as to allow the use of a great number and variety of collision partners.

Using the Aerodynamic Chemical Accelerator, we have recently completed determinations of the threshold energies and the excitation functions (i.e., absolute cross sections as functions of the collision energy) for polar ionization of the thallium halides by collision with Xe(Kr) atoms with well-defined kinetic energies up to 15-eV(10-eV). Measurements were made on both monomer and dimer molecules, and the various reaction channels were identified by time-of-flight mass spectrometry. Near future investigations will be on collision-induced ionization of alkali halides, of uranium oxides, and of some metals.

The Cathode Sputtering Accelerator is currently being employed in the investigation of the dynamics of inelastic collisions of accelerated metallic atoms. The angular distributions of positive ionic products from collisions of fast Li, Pb, Ag, and Al atoms with Br_2, SF_6, O_2, HBr, Cl_2, etc., have been measured as functions of the collision energy, and from these experiments have come details of the dynamics and energetics of the medium energy collision processes. The program will continue with measurements on the angular distributions for the negative species formed in the above collisions and the study of associative ionization of fast metallic atoms with molecular and atomic collidants.

The Ion Accelerator has recently been converted into an instrument for the investigation of chemical sputtering of materials being considered for containment vessels in controlled thermonuclear reactors. Beams of D_2^+ ions of well-defined energy in the range from 10 to 300 eV have been impinged on heated niobium surfaces, and the ejected species analyzed by mass spectrometry. An alternative experiment involves collecting the ejected niobium on a platinum catcher and later measuring the amount deposited spectrochemically. Thus far, no niobium has been observed by either method, and a preliminary sputtering yield of <0.05 has been assigned. The research is continuing in an effort to enhance the sensitivity of the experiment and to extend the range of kinetic energies, target temperatures, and nature of the impinging particle.

PUBLICATIONS

Beatty, J. W., and S. Wexler, Hydrogen Displacement in n-Butane by Fast T_2 and T_2^+ Collisions, J. Phys. Chem., 75: 2417-2425 (1971).

______, L. G. Pobo, and S. Wexler, Reactions of Fast T_2 Molecules with 1-Butene, J. Phys. Chem., 75: 2407-2408 (1971).

Parks, E. K., and S. Wexler, Collisional Dissociative Ionization of TlBr by Accelerated Xe and Kr Atoms, Chem. Phys. Lett., 10(3): 245-250 (1971).

______, C. E. Young and S. Wexler, Electron Bombardment Ionizer for Accelerated Molecular Beams, Rev. Sci. Instrum., 42(10): 1404-1407 (1971).

03:213 RESEARCH WITH MOLECULAR BEAMS OF SHORT-LIVED RADIOACTIVE NUCLIDES.

Grover, J. Robb. (Brookhaven National Laboratory, Chemistry Department).

In crossed beam systems that employ labeling with radioactive nuclides and counting of nuclear disintegrations for detection, the signal-to-noise ratio is a maximum if the half-life is comparable to the travel time of products from the interaction region to the detector. Advantages of using this principle are: (1) high detection efficiency; (2) modest vacuum requirements; (3) good generality, since most elements possess at least one isotope of suitable lifetime (10^{-5} to 10^{-1} sec); (4) accessibility of highly unstable beam species, made possible by tracer intensity; (5) practicability of species-specific surface phenomena for detectors; and (6) multiple deployment of detectors, due to small bulk. This is the only technique offering sufficient generality and sensitivity to comprise a real alternative to the crossed-beam supermachines, which, although extensively developed and in wide use, have limited capability. A prototype apparatus has been constructed to study the reactions $M + HAt \rightleftharpoons HM + At$ using 0.032-sec ^{217}At, M being an atom or molecule. Experimental testing has verified the theoretically expected sensitivity for scattering in crossed molecular beams and has shown that reaction between HAt and Br apparently takes place with high enough cross section to allow detailed study. Experiments for consolidation of the latter result and investigations of other systems are under way. Future plans include construction of apparatus for velocity resolution of scattered products, and development of molecular beams of short-lived nuclides generated on-line using cyclotron beams.

PUBLICATIONS

Grover, J. R., Molecular Flow of Gases of Short Lived Radioactive Nuclides, J. Inorg. Nucl. Chem., 32: 3136 (1970).

______, F. M. Kiely, E. Lebowitz, and E. Baker, Molecular Beams of Short Lived Radioactive Nuclides, Rev. Sci. Instrum., 42: 293 (1971).

______, and H. V. Lilenfeld, Molecular Beams of Short Lived Radioactive Nuclides. *II. Preparation of Beams by Wall Reactions,* Rev. Sci. Instrum., 43: 690 (1972).

03:214 USE OF PERTURBED ANGULAR CORRELATIONS FOR MEASUREMENT OF CHEMICAL REACTION RATES IN FLUID PHASES.

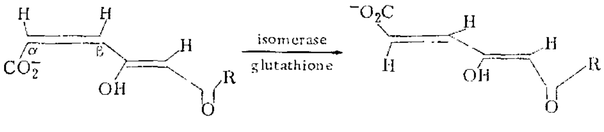
Grover, J. R., and R. A. Holroyd. (Brookhaven National Laboratory, Chemistry Department).

Time-differential measurement of the angular correlation of nuclear two-photon cascades offers a way to study chemical reactions on a time scale comparable to the lifetime of the intermediate state involved in the cascade. The rate of decay of the angular correlation depends on the tumbling rate and structure of the radioactive molecule, and is therefore sensitive to chemical alterations of the molecule that take place during the relaxation. The time scale for observation of the relaxation, instrumentally confined to the range of microseconds to nanoseconds, is highly interesting for chemistry. Extraction of chemical rate information from the compound relaxation rates expected for the angular correlations is theoretically straightforward. At least 12 elements with suitable nuclear decay schemes and intermediate level properties are daughters of conveniently long-lived precursor nuclides. Since on-line accelerator production adds many more, the technique promises considerable generality. Apparatus has been constructed and partially tested for carrying out such measurements. As rapidly as available resources allow, the testing will be completed and the apparatus tried on one or more known reactions. This method should broaden considerably the restricted catalogue of reactions proceeding in this time range now accessible to known techniques.

03:215 ENZYME-CATALYZED cis-trans ISOMERIZATION ABOUT CARBON-CARBON DOUBLE BONDS.

Seltzer, S. (Brookhaven National Laboratory, Chemistry Department).

A few enzymes capable of catalyzing cis $\rightleftharpoons$ trans isomerization about carbon-carbon double bonds in specific molecules are known. Such reactions are important in metabolism and in the process of vision. The mechanisms of these efficient catalysts, however, are still unknown. It is the purpose of this work to understand, on a molecular level, how one of these enzymes, maleylacetone cis-trans isomerase, catalyses the isomerization shown in the equation. Purification of the enzyme has been accomplished.



$R = CH_3$ or $CH_2CO_2^-$

Possible modes of catalysis are being studied by the use of model systems. For example, silver ion is a unique, efficient catalyst for the reaction. From a study of analogs of I, it appears that a π-complex between silver and the isomerizing double bond forms and rearranges to a silver-carbon σ-complex, thereby allowing rotation about the α-β carbon-carbon bond. However, samples of homogeneous isomerase that have been analyzed by neutron activation contain no significant amount of metals, so that this type of mechanism is ruled out.

Another possible mechanism supported by studies on another model system is that of Schiff base formation. The labeled precursor to I ($R = C^{14}H_2CO_2^-$) has been synthesized and experiments designed to trap the radioactive enzyme-substrate Schiff base, if present, are planned.

Studies with inhibitors have also been carried out to determine the chemical functionality at the active site. So far it appears that one to three sulfhydryl groups are important for reaction. The study of other inhibitors that mimic the substrate is planned to obtain information about the binding of the substrate.

PUBLICATIONS

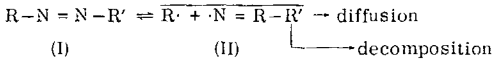
Santiago, C., and S. Seltzer, The Effect of Schiff Base Formation on the Thiocyanate-Catalyzed Isomerization of cis-β-Acetylacrylic Acid. A Study of a Possible Model for the Enzyme-Catalyzed Cis-Trans Isomerization of Maleylacetoacetic Acid, J. Amer. Chem. Soc., 93: 4546 (1971).

Seltzer, S., Cis-Trans Isomerization. The Enzymes, Vol. VI, 3rd ed., P. Boyer (Ed.), Academic Press, Inc., New York, 1972, p. 381.

03:216 INTERNAL RETURN OF CAGED GEMINATE RADICALS FROM OPTICALLY ACTIVE AZO COMPOUNDS.

Seltzer, S. (Brookhaven National Laboratory, Chemistry Department.

Aspects of the decomposition mechanism of azo compounds . (R-N = N-R) are being studied. When the two carbon-nitrogen bonds are broken in stepwise fashion it is thought that a caged pair of radicals (II) exists for a finite time.

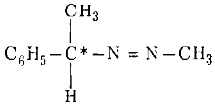


$$\underset{\text{(I)}}{R{-}N=N{-}R'} \rightleftharpoons \underset{\text{(II)}}{\overline{R\cdot + \cdot N=R{-}R'}} \rightarrow \text{diffusion}$$
$$\hookrightarrow \text{decomposition}$$

Depending on the solvent, the pair may diffuse apart or undergo rupture of the second carbon-nitrogen bond. The possibility of return (II → I) also exists and this is presently under study.

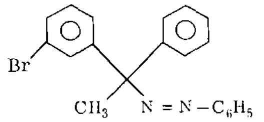
The method of investigation uses an optically active azo compound that undergoes stepwise rupture of its two bonds. The seat of chirality is at the carbon-nitrogen bond undergoing cleavage. Rotation of R· within the cage is anticipated. Therefore, the returned azo compound might be racemic. The process is studied by comparing the rate of nitrogen evolution to the rate of loss of optical activity.

The first such study was carried out on III and the results suggest



$$C_6H_5{-}\underset{H}{\overset{CH_3}{C^*}}{-}N=N{-}CH_3$$

III



IV

a small amount of return. In order to demonstrate return more firmly, optically active IV was synthesized by a newly developed method. The kinetics of the loss of nitrogen and the rate of loss of optical activity are presently being measured. Similar studies are to be carried out on the photodecomposition of IV.

PUBLICATIONS

Tsolis, A., S. G. Mylonakis, M. T. Nieh, and S. Seltzer, On Internal Return of Caged Geminate Radicals Produced from Optically Active Methylazo-α-phenylethane, J. Amer. Chem. Soc., 94: 829 (1972).

Fowler, J. S., A New Synthesis of Unsymmetrical Azo Compounds, J. Org. Chem., 37: 510 (1972).

03:217 KINETIC STUDIES OF BASE-PAIRING AND ELECTRON-TRANSFER REACTIONS INVOLVING BIOCHEMICAL SYSTEMS.

Sutin, N. (Brookhaven National Laboratory, Chemistry Department).

Most models for the melting of double-stranded helices like DNA postulate that the melting or collapse of the secondary structure occurs by the unwinding of the two complementary strands. An objective of this work is to understand the factors controlling this melting process and its reverse. This is pursued by investigating the interactions between free aromatic bases in solution, between coupled bases in dinucleoside phosphates and in single-stranded polynucleotides, and between paired bases in double-stranded polynucleotides. The initial attack will be by way of studies on the kinetics of the aggregation of acridine dyes, the rates of unfolding of ApA (Adenylyl-(3′ : 5′)-adenosine) and ApApA, and the kinetics of the melting of daT (copolymer of deoxyadenylate and deoxythymidylate).

A second objective of this work is to elucidate the mechanisms of electron-transfer reactions involving metalloenzymes by making use of the knowledge gained in recent years on the factors that influence the rate of electron transfer between complex ions in solution. It is known that the rate of electron transfer is affected by the stability of the precursor complex, the magnitude of the reorganization energy, the change of symmetry in going from the initial to the final electron state, and the standard free energy change for the reaction. An attempt is being made to use this knowledge to characterize the electron-transfer pathways in the cytochrome-c system.

The techniques that will be used in this work include conventional and stopped-flow spectrophotometry, and new temperature-jump methods capable of studying reactions with relaxation times down to about 15 nanoseconds.

PUBLICATION

Sutin, N., Some Aspects of Electron Transfer in Chemical and Biochemical Systems, Chem. Brit., 8: 148 (1972).

03:218 STUDY OF CHEMICAL REACTIONS BY MEANS OF MOLECULAR BEAMS AND SHOCK WAVE TECHNIQUES. Greene, Edward F. (Brown University, Chemistry Department, Providence, Rhode Island 02912).

The objective of scattering experiments with molecular beams is to reveal details of what happens in molecular collisions. This can be helpful in the interpretation of more complicated experiments in chemical kinetics. Some molecules are more susceptible to chemical reaction when they are in excited vibrational states. Thus the study of how effectively molecules convert translational to vibrational energy in collisions helps to show how chemical reactions occur. Continuing experiments with beams of diatomic molecules of cesium iodide colliding with atoms of argon give this kind of information.

Other experiments in which atoms of iodine collide with atoms of krypton can be interpreted to show how the potential energy of interaction between the atoms varies with the distance of their separation. A knowledge of this energy is useful in trying to solve a long-standing problem, the variation with temperature of the rates of more complicated reactions such as the recombination of atoms of iodine to form iodine molecules.

Part of the work is directed toward improving detectors that are sensitive to the small numbers of scattered molecules produced in the experiments. Neutral molecules containing halogen atoms can be converted to negative ions and then easily measured as an electric current by letting them hit a hot niobium surface.

PUBLICATIONS

Ross, J., and E. F. Greene, Elastic Scattering of Reactive Systems, in Proceedings of the International School of Physics, Course 44, Molecular Beams and Reaction Kinetics.

Cardillo, M. J., M. S. Chou, E. F. Greene and D. B. Sheen, Differential Cross Sections for the Scattering of CCl_4 by Iso-Octane, J. Chem. Phys., 54: 3054 (1971).

Greene, E. F., R. H. Hammond, J. M. S. Henis, and J. Ross, Kinetic Energies of Ionization Products from Collisions of Ar–Ar, He–He Below 150 eV c.m. Energy, J. Chem. Phys., 55: 3506 (1971).

Westberg, Karl, and E. F. Greene, Dissociation of HBr and Br_2 in Shock Waves, J. Chem. Phys., 58: 2713 (1972).

03:219 THE APPLICATION OF ION CYCLOTRON RESONANCE TO THE STUDY OF ION–MOLECULE INTERACTIONS. Beauchamp, Jesse L. (California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, California).

Applications of ion cyclotron resonance spectroscopy to study the reaction kinetics and properties of ions in the gas phase are being explored in depth. Three ion cyclotron resonance spectrometers, each with unique capabilities, are in operation at the California Institute of Technology. The results of studies with these instruments are greatly extending our knowledge of ionization phenomena in general and our ability to describe and predict the chemical behavior of ions in gases in particular. Ion cyclotron resonance trapped ion techniques are being applied to examine the kinetics of reactions that approach and establish equilibrium. Equilibrium data will in turn be used to determine accurate thermochemical data relating to acidities and basicities (studies of proton transfer reactions) and carbonium ion stabilities (studies of hydride and halide ion transfer reaction). Reference data for these projects will be obtained using photoionization mass spectrometry. Molecular properties such as proton affinities will be correlated and interpreted with the aid of information relating to the electronic structures of the corresponding ions and neutrals determined by photoelectron spectroscopy and in photodetachment experiments. Many of the reactions observed and studied with ICR techniques represent new classes of gas phase ionic processes which are amenable to further study using single and crossed beam techniques. Studies are being initiated with an apparatus comprising a mass and energy selected ion beam, scattering chamber and fixed detector, with the purpose of determining whether reactions proceed through long- or short-lived intermediates (complex formation vs. direct processes).

PUBLICATIONS

Beauchamp, J. L., D. Holtz, S. D. Woodgate, and S. L. Patt, Thermochemical Properties and Ion–Molecule Reactions of the Alkyl Halides in the Gas Phase by Ion Cyclotron Resonance Spectroscopy, J. Amer. Chem. Soc., 94: 2798 (1972).

Caserio, M. C., and J. L. Beauchamp, Ion–Molecule Reactions of 2-Butanol by Ion Cyclotron Resonance Spectroscopy, J. Amer. Chem. Soc., 94: 2638 (1972).

Foster, M. S., and J. L. Beauchamp, Gas Phase Ion Chemistry of Azomethane by Ion Cyclotron Resonance Spectroscopy, J. Amer. Chem. Soc., 94: 2425 (1972).

McMahon, T. B., and J. L. Beauchamp, A Versatile Trapped Ion Cell for Ion Cyclotron Resonance Spectroscopy, Rev. Sci. Instrum., 43: 509 (1972).

Henderson, W. G., D. Holtz, J. L. Beauchamp, and R. W. Taft, Methyl Substituent Effects in Protonated Aliphatic Amines and Their Radical Cations, J. Amer. Chem. Soc., 94: 4728 (1972).

03:220 STUDIES IN CHEMICAL DYNAMICS AND RADIATION CHEMISTRY. II. CHEMICAL DYNAMICS. Kuppermann, Aron (California Institute of Technology, Division of Chemistry, Pasadena, California 91109).

The objective of this part of the program is to provide an understanding of reactive and nonreactive molecular collisions of importance to radiation chemistry, hot atom chemistry, and thermal chemistry. The approach used is a combination of experimental and theoretical studies aimed at separating the effect of different kinds of energy (translational, vibrational, etc.) on the outcome of molecular collisions, reactive and nonreactive. The current experimental work involves: (a) the use of crossed molecular beams to investigate intermolecular forces and to obtain from them information about elastic energy transfer in moderating collisions; (b) the use of photoexcited high vibrational states of molecules, such as HI, to determine the effect of vibrational energy of reagents on reaction cross sections. In the near future we plan to study, with the crossed molecular beam machine, the reactions of hydrogen and other atoms with molecules at energies in the neighborhood of 1 eV. The theoretical work involves investigating such collisions using quantum mechanical, classical and semiclassical methods in an attempt to obtain insight into and generalize the results of these studies. We hope, as a result of such studies, to develop an overall understanding of the details of energy flow in chemical processes.

PUBLICATIONS

Truhlar, D. G., and Aron Kuppermann, Exact and Approximate Quantum Mechanical Reaction Probabilities and Rate Constants for the Collinear H + H_2 Reaction, J. Chem. Phys., 56: 2232 (1972).

Bowman, Joel, and Aron Kuppermann, Classical and Quantum Reaction Probabilities and Thermal Rate Constants for the Collinear H + H_2 Exchange Reaction with Vibrational Excitation, Chem. Phys. Lett., 12: 1 (1971).

Winicur, D. H., A. L. Moursund, W. R. Devereaux, L. R. Martin and Aron Kuppermann, Differential Elastic Scattering of D_2 by N_2 in Crossed Molecular Beams, J. Chem. Phys., 52: 3299 (1970).

03:221 DETERMINATIONS OF ELEMENTARY REACTION RATE CONSTANTS FOR THE REACTION OF HYDROGEN ATOMS WITH VARIOUS SUBSTRATE MOLECULES IN THE GAS PHASE. Michael, Joe V. (Carnegie-Mellon University, Department of Chemistry, Pittsburgh, Pennsylvania 15213).

The purpose of this project has been to develop and use the sensitive technique of Lyman α absorption spectrometry in atomic hydrogen (or deuterium) reaction studies in the gas phase. These reactions are of particular interest in combustion, air pollution, photochemistry, and radiation chemistry. The methods devised have yielded rapid and accurate determinations of apparent rate constants for the hydrogen atom with various substrate reactions.

Most work has been concerned with the effects of variable pressure on the measured rate constants at room temperature. Also the relative effects of the mass of the heat bath molecule have been studied with six different molecules. The reactions investigated are of hydrogen atoms with several alkenes and alkynes, and the diatomics, O_2, NO, and CO. Several deuterated modifications have also been studied in an attempt to gain mechanistic information. These studies are continuing.

New experiments are in progress with variable temperature apparatus that will allow the determination of the energies of activation and preexponential factors for hydrogen atom with substrate reactions. These experiments include shock tube and flash mercury photosensitization techniques. The information gained will be of interest to both experimental and theoretical chemical kineticists.

PUBLICATIONS

Cowfer, J. A., D. G. Keil, J. V. Michael, and C. Yeh, Absolute Rate Constants for the Reactions of Hydrogen Atoms with Olefins, J. Phys. Chem., 75: 1584 (1971).

Michael, J. V., and C. Yeh, Absolute Cross Section for Hg($^3P_1$ + H_2 and the Imprisonment Lifetimes for Hg($^3P_1$) at Low Opacity, J. Chem. Phys., 53: 59 (1970).

Barker, J. R., D. G. Keil, J. V. Michael and D. T. Osborne, Reaction H + C_2H_4: Comparison of Three Experimental Techniques, J. Chem. Phys., 52: 2079 (1970).

03:222 THE DYNAMICS OF CHEMICAL REACTIONS. Lee, Yuan Tseh (The University of Chicago, The James Franck Institute, Chicago, Illinois 60637).

One of the programs being studied at the present time is the transfer of translational energy to rotational energy. One rotational quantum transition in the process of HD(J = 0) + He → HD(J = 1) + He has been measured as a function of scattering angle by the time-of-flight method. HD(J = 1) molecules are identified from their laboratory velocities which differ from those of HD(J = 0). Another project that is also under investigation is the interaction and reactions of metastable rare gas atoms and ground state rare gas atoms. The angular distributions of He* + He and Ar* + Ar as well as He* + Ar are obtained. These angular distributions should provide valuable information on intermolecular potentials (both gerade and ungerade) and opacity functions for ionization processes.

We have just finished product velocity analysis for the reactions of F with D_2 and various unsaturated hydrocarbons. These measurements conclude the most precisely performed crossed molecular beam experiments. Velocities of both reactant beams are selected and both angular and velocity distributions have been measured in these experiments.

In the immediate future, we will study the scattering of rotational-state-selected hydrogen halides and continue projects of collisional dissociations.

PUBLICATIONS

Siska, P. E., J. M. Parson, T. P. Schafer, and Y. T. Lee, Intermolecular Potentials from Crossed Beam Differential Elastic Scattering Measurements III, He + He, and Ne + Ne, J. Chem. Phys., 55: 5762 (1971).

Parson, J. M., and Y. T. Lee, Intermolecular Potentials from Crossed Beam Differential Elastic Scattering Measurements IV. Ar + Ar, J. Chem. Phys., 56: 1511 (1972).

______, and Y. T. Lee, Crossed Molecular Beam Study of F + C_2H_4, C_2D_4, J. Chem. Phys., 56: 4658 (1972).

Lee, Y. T., Reactive Scattering of Atoms and Molecules Crossed Molecular Beam Experiments, in the VIIth International Conference on the Physics of Electronic and Atomic Collisions, Book of Invited Talks and Progress Reports, North Holland Publishing Company, Amsterdam, 1972.

Farrar, J. M., and Y. T. Lee, Intermolecular Potentials from Crossed Beam Differential Elastic Scattering Measurements V. The Attractive Wells of He_2, J. Chem. Phys., 56: 5801 (1972).

03:223 STUDIES OF GAS PHASE COLLISIONS OF NEUTRAL SPECIES. Herm, Ronald R. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

This is an experimental project that is aimed at a fundamental analysis of the dynamics of inelastic and reactive collisions between neutral gas molecules. Molecular beam and spectroscopic techniques are being employed to determine the angular and energy dependences of the collision cross sections. The following collision phenomena are under study.

Studies of the collisions of electronically excited atoms include: (a) measurements of the cross sections for collisional quenching of excited alkali atoms; (b) a chemiluminescence determination of the vibrational distribution in electronically excited HgCl*($B^2\Sigma^+$) formed in the reaction of Hg*(6p $^3P_1$) with Cl_2; and (c) a crossed beam study of the transfer of electronic excitation from Hg*(6p $^3P_{0,2}$) to Tl and Li atoms.

Thermal energy reactions of Mg, Ca, Sr, Ba, Li, and Na atoms with halogen- and oxygen-containing molecules are being studied in crossed molecular beams. These studies, as well as those listed as (a) and (b), are intended to complement the abundant data already available on reactions of K, Rb, and Cs and should extend our understanding of the reactivity of metallic vapors. These studies should also provide lower limits for some of the alkaline earth halide bond energies that are presently uncertain.

Crossed beam studies of reactions of some ionic salt molecules (e.g., BaF_2 + BCl_3) will also be initiated in the near future.

PUBLICATIONS

Earl, Boyd L., Ronald R. Herm, Shen-Maw Lin, and Charles A. Mims, Photodissociation of NaI Vapor and the Energy Dependence of the Quenching of Na*(3p ^2P) by Foreign Gases, J. Chem. Phys., 56: 867 (1972).

Parrish, David D., and Ronald R. Herm, Molecular-Beam Kinetics. II. Magnetic Deflection Analysis of Reactions of Li with NO_2, CH_3NO_2, SF_6, CCl_4, and CH_3I, J. Chem. Phys., 54: 2518 (1971).

______, and Ronald R. Herm, Harmonic Forces Linear Model for Reactions of Cs Atoms with Alkyl Iodes, J. Chem. Phys., 53: 2431 (1970).

Herm, Ronald R., and Dudley R. Herschbach, Molecular Beam Kinetics: Reactions of Alkali Atoms with NO_2 and CH_3NO_2, J. Chem. Phys., 52: 5783 (1970).

03:224 CHEMICAL DYNAMICS STUDIES. Mahan, Bruce H (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

The object of this work is to gain an understanding of the collision processes that gaseous ions and neutrals of moderate kinetic energy undergo. The work centers on ion–molecular beam studies of the elastic, inelastic, and reactive collisions of simple ions with molecules, and their theoretical interpretation. Current experiments involve a study of the dynamics of the collision of D_3^+ with H_2, with the object of elucidating the processes

$$\begin{aligned} D_3^+ + H_2 \rightarrow\ & D_2 + D^+ + H_2 \\ & D_2^+ + D + H_2 \\ & D_2 + DH_2^+ \end{aligned}$$

that are important in devices containing hydrogen plasmas. The energy ranges in which the various processes are important are being mapped out, the product energy distributions determined, and estimates of the cross sections made.

Another reaction currently under study is $O^+(H_2,H)OH^+$, and its isotopic variants. This is an important impurity reaction in hydrogen plasmas and is also very interesting from a fundamental point of view. Besides its electronic ground state, O^+ has a metastable excited state of kinetic importance, whose reactions we can study separately. We expect that this excited state will display dynamic properties that are quite different from those of the ground state ion.

Our future plans are to continue investigations of the reactions of simple ions with small molecules, particularly hydrogen, since these processes combine the possibilities of practical utility and fundamental interpretation. In particular, we shall begin experiments on the reactions of several metal ions that occur in the upper atmosphere or as impurities in plasma devices.

PUBLICATIONS

Chiang, M. H., E. A. Gislason, B. H. Mahan, C. W. Tsao, and A. S. Werner, Dynamics of the Reactions of O_2^+ with H_2 and D_2, J. Phys. Chem., 75: 1426 (1971).

______, E. A. Gislason, B. H. Mahan, C. W. Tsao, and A. S. Werner, Large Angle Elastic Scattering of Ar^+ by He, J. Chem. Phys., 55: 3937 (1971).

Gislason, E. A., B. H. Mahan, C. W. Tsao, and A. S. Werner, Dynamics of the Reaction of N^+ with H_2, J. Chem. Phys., 54: 3897 (1971).

______, Approximate Differential Cross Sections at Large Scattering Angles for Simple Repulsive Potentials, J. Chem. Phys., 55: 3929 (1971).

Mahan, B. H., Molecular Orbital Correlations and Ion–Molecule Reaction Dynamics, J. Chem. Phys., 55: 1436 (1971).

03:225 PROPERTIES OF SOLVATED ELECTRONS AND ASSOCIATED SPECIES IN METAL SOLUTIONS AND KINETICS OF ELECTRON- AND PROTON-TRANSFER REACTIONS. Dye, James L. (Michigan State University, Department of Chemistry, East Lansing, Michigan 48823).

Our discovery that cyclic polyethers greatly enhance the solubility of alkali metals in amines and ethers provides the opportunity to study many properties of solvated electrons for comparison with the results of pulse radiolysis. By controlling relative concentrations, it is possible to prepare solutions in which either

e^{-}_{solv} or the alkali anion, M^-, is the major reducing species. Optical spectra provide the most definitive information, but this will be supplemented with ESR and metal–NMR studies. Concentrated solutions in ethers and amines will be studied for evidence of metallic behavior. Synthesis of large amounts of one of the polyethers (cryptate) is being carried out because it appears that this compound traps the alkali cation in a relatively nonlabile form. This might permit the preparation of new solid compounds that contain the alkali anion and/or the free electron.

We have completed the interface of a scanning stopped-flow system to a PDP8-I computer. Studies of the kinetics of reaction of solvated electrons and alkali anions will be continued. This apparatus is also ideal for the study of the kinetics of reaction of aromatic radical ions. Such studies, which complement similar studies by pulse radiolysis, will be continued.

PUBLICATIONS

Dye, J. L., M. G. DeBacker, J. A. Eyre, and L. M. Dorfman, Pulse Radiolysis Study of the Kinetics of Formation of Na^- in Ethylenediamine by the Reaction of Solvated Electrons with Sodium Ions, J. Phys. Chem., 76: 839 (1972).

_____, M. T. Lok, F. J. Tehan, R. B. Coolen, N. Papadakis, J. M. Ceraso, and M. G. DeBacker, Alkali Metal Solutions—Effect of Two Cyclic Polyethers on Solubility and Spectra, Ber. Bunsenges. Phys. Chem., 75: 659 (1971).

_____, and V. A Nicely, A General Purpose Curvefitting Program for Class and Research Use, J. Chem. Educ., 48: 443 (1971).

_____, M. G. DeBacker, and L. M. Dorfman, Pulse Radiolysis Studies. XVIII. Spectrum of the Solvated Electron in the Systems Ethylenediamine–Water and Ammonia–Water, J. Chem. Phys., 52: 6251 (1970).

DeBacker, M. G., and J. L. Dye, Metal–Ethylenediamine Solutions. Extinction Coefficients and Equilibria, J. Phys. Chem., 75: 3092 (1971).

03:226 MOLECULAR BEAM STUDIES IN PHYSICAL CHEMISTRY. Datz, S. and H. F. Krause. (Oak Ridge National Laboratory, Chemistry Division).

Atom–molecule collisions leading to chemical reactions and intermolecular energy transfer are under study using crossed-molecular-beam techniques. Recently the velocity dependence of electronic to vibronic energy transfer was investigated for the first time. The reaction was $Hg(6^3p_2) + M = Hg(6^3p_1) + M^*$ where $M = H_2$, D_2, N_2, NO, and CH_4. It was followed by the 2537 Å light from the decay of $Hg(6^3p_1)$. For the molecules listed, the cross sections decreased with increasing energy as $E^{-0.5}$ above 0.1 eV in accord with the model predictions by Bykhovskii and Nikitin in which the transition probability above threshold reduces to the Landau–Zener theory. When Cl_2 is used as the reactant, an additional light signal (5400 Å) attributable to the electronically excited B state of HgCl is observed. The velocity dependence of the chemical reaction is being investigated.

With accelerated alkali atom and ion beams, it was found that dissociative collisions of the type $M + X_2 \rightarrow M + X + X$ proceeded via a spectator-stripping process at high energies (i.e., direct interaction with only one atom in the X_2 molecule). This was observed in collisions of Na and K with H_2 and D_2 and of Cs^+ with N_2 at relative energies above 30 eV. Studies of chemi-ionizing collisions of K and Cs with Cl_2, Br_2, and O_2 at 50 to 350 eV indicated a dominance of molecular excitation into dissociative states.

PUBLICATIONS

Dittner, P. F., and S. Datz, Collision Induced Vibrational Excitation and Dissociation of Hydrogen with Alkali Atoms and Ions from 2 to 50 eV, J. Chem. Phys., 54: 4228 (1971).

03:227 EXCHANGE OF ELEMENTARY IODINE WITH ORGANIC IODIDES. Noyes, Richard M. (University of Oregon, Department of Chemistry, Eugene, Oregon 97403).

Most free radicals are so reactive that competing reactions generate very complicated product distributions. Iodine atoms are much less reactive and often react with organic iodides only by a substitution that can be followed by isotopic labeling. Thus we can examine effects of substituents on rates of reactions of radicals including those with aromatic molecules. Our studies have also revealed an unexpected mechanism of exchange involving a transition state that resembles an ion pair even in nonpolar solvents. The iodine portion of the transition state may be either positively or negatively charged, and substitution of benzoyl or benzhydryl iodide affects the rate by a bigger factor than has been observed for any other reaction of neutral molecules. Either isopropyl or tert-butyl iodide will exchange with iodine by this mechanism at a conveniently measurable rate in any aprotic solvent from hexane (dielectric constant less than 2) to propylene carbonate (dielectric constant about 65), and these reactions are excellent for testing theories for effects of solvent properties on rates of reactions involving considerable separation of charge.

PUBLICATIONS

Muizebelt, W. J., and Richard M. Noyes, Polar Exchange of Iodine Molecules with Substituted Benzhydryl Iodides, J. Amer. Chem. Soc., 92: 6012 (1970).

Noyes, Richard M., and Endre Körös, Radical and Polar Mechanisms for Exchange of Iodine with Organic Iodides, Accounts Chem. Res., 4: 233 (1971).

03:228 OSCILLATIONS IN CHEMICAL SYSTEMS. Noyes, Richard M. (University of Oregon, Department of Chemistry, Eugene, Oregon 97403).

In a closed chemical system at constant temperature and pressure, the total free energy remains constant or decreases monotonically. However, concentrations of certain intermediates may oscillate in such a system. We have explained the detailed mechanisms of oscillations of bromide ion and of cerium(IV) during the cerium-catalyzed reaction of bromate ion with malonic acid and can also explain the propagation of oxidizing bands we can generate at will in such a medium. This is probably the most complicated chemical system whose reactions are understood in so much detail. We can also use flow methods to produce chemical oscillations that continue indefinitely and can transmit repetitive signals by traveling bands of chemical action. The behavior of this inorganic system shows striking analogies to biochemical processes like heart beats and nerve impulses. The bromate–malonic acid system is not unique as a chemical oscillator, and we are evolving principles to guide the search for other oscillating systems.

PUBLICATIONS

Noyes, Richard M., Richard J. Field, and Richard C. Thompson, Mechanism of Reaction of Bromine(V) with Weak One-Electron Reducing Agents, J. Amer. Chem. Soc., 93: 7315 (1971).

_____, Richard J. Field, and Endre Körös, Oscillations in Chemical Systems. I. Detailed Mechanism in a System Showing Temporal Oscillations, J. Amer. Chem. Soc., 94: 1394 (1972).

Field, Richard J., A Reaction Periodic in Time and Space. A Lecture Demonstration, J. Chem. Educ., 49: 308 (1972).

_____, and Richard M. Noyes, Mechanism of Propagation of Spatial Bands in the Belousov Reaction, Nature, 237: 390 (1972).

03:229 RESEARCH ON HIGH-ENERGY CHEMICAL REACTIONS. Cross, R. James, Jr., R. L. Wolfgang (Yale University, Department of Chemistry, New Haven, Connecticut 06520).

We are using molecular beam techniques to measure the energy dependence of hot tritium reactions from a few electron volts on up. A beam of T^+ is formed from a plasma source, the ions are accelerated, focused, mass-selected, and then neutralized in a crossed beam of CO_2. The resulting beam of T is at a known and variable energy. The beam passes through a separately pumped chamber into a reaction chamber filled with a mixture of reactant gas and an inert moderator such as He. The T loses energy on collision (mostly with He) and reacts. The products are trapped and separated by gas chromatography, and counted in a proportional counter. Since we know the T-He potential, we can calculate the energy distribution of the reacting tritium atoms. By measuring the amounts of products as a function of initial beam energy, we can obtain the cross section for reaction as a function of energy. This will answer many questions unanswerable from nuclear recoil studies.

ALSO SEE All summaries in the following sections: Radiation Chemistry: Aqueous; Radiation Chemistry: Gaseous; Radiation Chemistry: Other; Photochemistry and Energy Transfer: and Hot Atom Chemistry (Summaries 03:100 through 03:208) and Heavy Element Chemistry: 03:76, 03:78; Chemical Spectroscopy: 03:245, 03:252; Theoretical Chemistry: 03:277, 03:281, 03:282, 03:285; Isotope Chemistry: 03:291, 03:294, 03:295, 03:297, 03:304; Thermodynamics: 03:316; High-Temperature and Inorganic Chemistry: 03:333, 03:348, 03:349, 03:351, 03:352, 03:355; Engineering Chemistry: 03:430, 03:435, 03:436; Miscellaneous Chemical Studies: 03:440, 03:458, 03:460.

CHEMICAL SPECTROSCOPY

Spectroscopic studies including infrared, Raman, visible, ultraviolet, nuclear magnetic resonance, electron spin resonance, photoelectron, electron impact, and Mössbauer spectroscopy.

03:230 MATRIX ISOLATION SPECTROSCOPY. Calder, G. Vincent. (Ames Laboratory, Chemistry Division).

The structure and spectra of reactive molecules and molecules that have appreciable vapor pressure only at extremely high temperatures are difficult to determine because of experimental limitations. Matrix isolation infrared spectroscopy is a generally applicable technique for obtaining such information. For example, one intermediate commonly invoked in the mechanism of a wide range of chemical reactions is the molecule benzyne, . At room temperature in solution or the gas phase this molecule is extremely short-lived; however, it has been recently isolated in argon matrices at cryogenic temperatures where it can be maintained indefinitely. The vibrational and electronic spectra of the molecule are currently being examined. In addition to the spectroscopic study of reactive molecules, matrix isolation can also be used to prepare compounds that are difficult, if not impossible, to synthesize by other, more classical, approaches. For example a new class of metal carbonyl compounds of the form $M(CO)_x$, where M = Nd, Yb, have been prepared successfully by codeposition of metal atoms in CO and CO/Ar matrices. The spectra and stoichiometry of these compounds are presently under study. Similar studies on the thio analogues, $M(CS)_x$, are also under active study by means of matrix-isolation reactions of the vaporized metal atoms with the unstable diatomic CS.

PUBLICATIONS

Pacansky, Jacob, and V. Calder, Matrix-Isolation Spectra of H_2S and D_2S: An Example of the Application of the Uncoupled Oscillator Approximation, J. Chem. Phys., 53: 4519 (1970).

______, and G. Vincent Calder, Anomalous Isotope Shifts in the Vibrational Spectrum of Hydrogen Cyanide in Argon Matrices, J. Phys. Chem., 76: 454 (1972).

Burnham, A. K., G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec, and R. Willis, Identification and Estimation of Neutral Organic Contaminants in Potable Water, Anal. Chem., 44: 139 (1972).

03:231 POLARIZED SINGLE CRYSTAL SPECTRA FOR COORDINATION COMPLEXES OF PLATINUM(II) AND PALLADIUM (II). Martin, Don. S. (Ames Laboratory, Chemistry Division).

An improvement will be sought in the techniques to prepare the exceedingly thin crystals, 1- to 10-μ thick that are needed for measurements of polarized spectra of pure single crystals. The forbidden d–d transitions of the heavy metal atoms can be measured for crystals with this thickness. The spectra of the square planar complexes are especially interesting because frequently the complexes stack one exactly over the next in a linear chain array. Additional evidence will be sought in the crystals for excited ionic states, evidence for which was observed recently in dichloro(ethylenediamine)platinum(II).

Recently, optical interference from repeated reflections in the crystal faces has served to provide both the thicknesses and the refractive indices for crystals. A continuing effort will be made to prepare crystals with faces of optical quality to apply this technique. Also, absorption spectra will be measured at low temperatures down to 4°K (liquid He) because the temperature dependence of the absorption can serve to identify the different types of transitions. Also the low temperatures provide improved resolution of bands and sometimes provide vibrational structure for the bands. This work will require some crystal structure determinations, and a determination for Rb_2PtBr_4 is underway.

PUBLICATIONS

Martin, D. S., Jr., Electronic Crystal Spectra for Coordination Complexes of Platinum(II), Inorg. Chim. Acta Rev, 5: 107-126 (1972).

______, L. D. Hunter, R. Kroening, and R. F. Coley, Polarized Crystal Absorption Spectra for Dichloro(ethylenediamine) platinum(II). Evidence for Ionic Excited States, J. Amer. Chem. Soc., 93: 5433-5440 (1971).

______, Ultraviolet Spectroscopic Qualities of Platinum Group Compounds, Advan. Chem. Ser., 98: 74-97 (1971).

03:232 THE ELECTRONIC ABSORPTION, LUMINESCENCE, AND NONRADIATIVE PROPERTIES OF π-BONDED ORGANIC MOLECULES AND THEIR CRYSTALS. Small, Gerald J. (Ames Laboratory, Chemistry Division).

Polarized optical spectroscopic and lifetime studies on several of the nitrogen heterocycles of azulene (azaazulenes) and α, β-unsaturated enones are in progress. Such experiments on these systems are designed to improve our understanding of (i) the energetics, electronic symmetries, and geometries of $\pi\pi^*$ and $n\pi^*$ excited states; (ii) the radiative and nonradiative (internal conversion, intersystem crossing, etc.) properties of these states; and (iii) electron–phonon coupling processes in mixed molecular crystals.

The vibronic absorption bandwidths of an impurity molecule in a crystal lattice are determined, in part, by the lifetime of the excited state and electron–phonon coupling. In order to extract the lifetime broadening from an experimental bandwidth it is necessary to subtract the electron–phonon coupling contribution. We have developed a new theory of electron–phonon coupling using the method of moments. The theory provides a much better fit to experimental temperature-dependent bandwidth data than the existing two-phonon elastic scattering perturbation approach. The theory will be used with experimental bandwidth data on mixed crystals containing, as impurities, the aforementioned molecules in order to determine appropriate excited state lifetimes.

Azulene's two lowest excited singlet states are $\pi\pi^*$ and lie at 7500 and 3500 Å. Its fluorescence properties are anomalous because it is the only aromatic molecule known to fluoresce from its second excited singlet state. As such it must be considered a very important test case for all theories on nonradiative transitions. Optical studies on the effect of $^1n\pi^*$ states in azaazulenes on the anomalous emission behavior of the parent are underway. Although these studies are far from complete, the preliminary results are exciting and worthy of comment. Nitrogen substitution in the five-membered ring results in large anomalous blue shifts (2000 to 4000 Å) of the lowest singlet and triplet states of the parent. As a result the azaazulene molecules fluoresce and phosphoresce, respectively, from these two states. The large difference in π-bonding between these molecules and the parent remains to be explained. Nitrogen substitution in the seven-membered ring of azulene does not lead to the aforementioned anomalous blue shifts. However, the molecules that have been studied have not been observed to fluoresce from any state.

Polarized absorption, phosphorescence, and lifetime studies on the α,β-unsaturated enone, 1-indanone, in various media have been initiated. In this way it is hoped that, for example, the intersystem crossing rate, the origin of the anomalous dual phosphorescence, and photochemical behavior of this molecule will be determined.

PUBLICATIONS

Small, G. J., Herzberg–Teller Vibronic Coupling and the Duschinsky Effect, J. Chem Phys. 54: 3300 (1971).

Kruse, N. J., and G. J. Small, The Polarized Fluorescence and Absorption Spectra of Tetracene in p-Terphenyl, J. Chem. Phys. 56: 2985 (1972).

Fischer, Gad, and G. J. Small, Jahn-Teller Distortion of s-Triazine in its Lowest Excited Singlet State, J. Chem. Phys. 56: 5934 (1972).

03:233 MASS SPECTROMETER ION SOURCE CHEMISTRY. Svec, H. J. and G. D. Flesch. (Ames Laboratory, Chemistry Division).

The chemical reactions occurring in the ion sources of mass spectrometers have been of interest since the instruments began to be used for studies of complex molecules. Emphasis has concerned the energetics of processes occurring near the ionization threshold or at ionizing energies of 50 to 70 eV. At or near the ionization threshold the principal reactions involve electronic and vibrational excitations. In the energy range between the threshold and ~50 eV most of the chemical reactions occur. A method for discerning these reactions, based upon deconvoluting ionization efficiency data in the energy range 18 eV above the ionization potential, has been developed that obviates the effects of the excitation processes that generally involve small energy differences. The basis of the method is to use electrons with sufficient energy spread to "wash out" excitation effects in molecular and fragment ions but not those due to chemical reactions. The method has been tested extensively with metal compounds such as the chromyl halides, hexacarbonyls of the transition elements, and the metallocenes of Fe, Ni, and Ru. Recently, application of the method to simple hydrocarbons has been attempted. Basically, these differ from all other compounds used to date in that ionization of the parent hydrocarbon molecules concerns a bonding electron instead of a nonbonding electron associated with a metal atom. The method appears to work for hydrocarbons producing data from which detailed mechanisms of chemical fragmentation schemes can be devised. By use of these schemes, ionization efficiency data can be convoluted which agree with the experimental data within ±1.5% over the 18-eV energy range above the molecular ionization potential. Ethane, propane, n-butane, isobutane, n-pentane, and neopentane have been studied. A salutary thing about all of the deconvolution results to date is that they predict neutral fragments that are being observed directly in some double-electron-beam studies which are also a part of the overall project.

PUBLICATIONS

Flesch, G. D., and H. J. Svec, Deconvolution of Ionization Efficiency Data as a Means of Determining Fragmentation Mechanisms in the Mass Spectrometer, J. Chem. Phys., 54: 2681 (1971).

_____, and H. J. Svec, Fragmentation Mechanisms for Metal Hexacarbonyls by Deconvolution–Convolution of Ionization Efficiency Data, J. Chem. Phys., 55: 4310 (1971).

03:234 RAMAN AND INFRARED SPECTRA OF MOLTEN SALTS AND SALT VAPORS. Maroni, V., and P. Cunningham. (Argonne National Laboratory, Chemical Engineering Division).

Raman spectroscopic studies have been made on solid and molten systems to elucidate the structures and interactions important to the understanding of many thermodynamic and transport properties. The molten $SnCl_2-KCl$ system was examined from 250 to 600°C. It was found that a complex equilibrium exists between polynuclear aggregates of $SnCl_2$ molecules and a monomeric species, most probably $SnCl_3^-$.

Raman studies were also made of solid and liquid $NaNH_2$ and $BiCl_3$ vapor. In the case of $NaNH_2$, low-frequency bands (300 to 800 cm^{-1}) were observed in both the solid and liquid phases. These bands were attributed to hindered rotation of the NH_2^- ion. In the case of $BiCl_3$ vapor, intense resonance fluorescence was observed at temperatures above about 450°C. This was attributed to the formation of a subhalide of bismuth (probably BiCl). The addition of a small amount of an oxidizing agent, such as $HgCl_2$, greatly reduced the concentration of the subhalide, as evidenced by the disappearance of the resonance fluorescence. Studies of the subhalides of bismuth and other metals are expected to contribute to our understanding of gas phase transport in metal–metal halide systems.

Infrared spectroscopic studies were made of iodine-containing species, since these are important to reactor fuel reprocessing technology. The studies showed that IO_3^- is the stable product of the reactions of iodine and I_2O_5 with molten nitrates (MNO_3, where M is Li, Na, K, Rb, Cs, Ag, and Tl). Evidence was also obtained that any IO_4^- formed during these reactions is immediately reduced to IO_3^-.

We plan studies of the spectra of high-temperature associated vapor species in two-component mixtures of strongly interacting molecules in order to understand the nature of the physical and chemical bonds that lead to these associations.

PUBLICATIONS

Maroni, V. A., Laser Raman Spectra of PbX_2-KX Melts (X = Cl and Br), J. Chem. Phys., 54: 4126 (1971).

03:235 MOLECULAR SPECTROSCOPY. Ferraro, J. R., and L. J. Basile. (Argonne National Laboratory, Chemistry Division).

The expression of the potential energy of nonlinear polyatomic molecules is not easily derived even when the structural configuration is established. Several model force fields have been proposed and modifications developed in attempts to describe the potential energy. Although determining which model force field best represents the molecule under consideration is difficult, the advent of fast computers has somewhat simplified this evaluation. Several proposals can be tested and the determination made as to which force field best describes the molecule. We have made a systematic study of the suitability of several force fields with AB_6^n octahedral molecules and AB_4^n tetrahedral molecules, where n is the charge. Five force fields were examined for 62 octahedral molecules. These were the Urey–Bradley, modified Urey–Bradley, orbital valence, modified orbital valence, and the general force fields. The modified orbital valence force field gave the better overall agreement with the observed frequencies of octahedral molecules than the other fields. Similar studies are presently underway with 92 tetrahedral-type molecules. Studies with MX_5 and MX_3 molecules are planned in an effort to determine, if possible, which force field is to be preferred for each structure.

Infrared absorption and Raman scattering experiments of various molecules have been in progress. Recently we have examined the alkali metal haloxenates, and made vibrational assignments for the molecule. A normal coordinate treatment (NCT) was made to verify these assignments. Presently, we are in the process of examining the vibrational spectrum of gaseous, anhydrous $Cu(NO_3)_2$. We hope to conduct a matrix isolation study for this molecule in the infrared and Raman regions. Ultimately a NCT will be attempted for the molecule.

PUBLICATIONS

Ferraro, J. R., P. LaBonville, and T. M. Spittler, Vibrational Investigations of Several Alkali Metal Haloxenates, J. Chem. Phys., 55: 631 (1971).

_____, M. C. Wall, S. M. C., P. LaBonville, and L. J. Basile, A Study of Force Fields for Octahedral Hexahalogen Molecules, Coord. Chem. Rev., 7: 257 (1972).

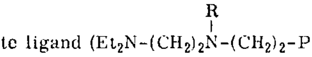
03:236 SPECTROSCOPIC INVESTIGATIONS OF INORGANIC AND COORDINATION COMPOUNDS UNDER VARYING PRESSURES. Ferraro, J. R., and Basile, L. J. (Argonne National Laboratory, Chemistry Division).

Experimental techniques developed at ANL permit studies of the absorption spectra (28,000 to 50 cm^{-1}) and Raman spectra of materials under high external pressures (to 80 kbar). These techniques have been applied to coordination compounds and a number of inorganic systems of both fundamental interest and some practical importance. Five general types of problems have been approached.

(1) Infrared-active phonon modes in ionic and pseudoionic crystals (of the type AB and AB_2) have been observed under high pressures. Such studies are important for developing fundamental concepts of lattice dynamics. The experimentally determined parameter $d\nu/dp$ leads rather directly to an experimental value for the Gruneisen constant (γ). This can then be compared with the γ obtained from equations of state based on certain theoretical models.

(2) Recent pressure studies of ion-pair vibrations in inorganic salt–organic solvent systems have been made. Lattice-like pressure behavior for these vibrations was found (shifts toward higher frequency occurred). These studies are important for developing new concepts involving solution dynamics, an area which has been little explored.

(3) At high pressures, measurement of the visible absorption bands of low-spin 5-coordinate complexes of the type (MLX)Y, MLX_2, (ML_2X) Y, ML_3X_2 (where M = Ni(II), Pt(II), Pd(II), X = halogen or pseudohalogen, L is a tetra-, tri-, bi-, or monodentate ligand, and Y = polyatomic anion) are significant in that they provide an experimental technique for studying the nature and importance of Jahn–Teller effects in these molecules. These studies have also been instrumental in differentiating trigonal bipyramidal and square-pyramidal structures of 5-coordinate systems.

Recently, investigations of the effects of high pressure on high-spin 5-coordinate complexes of the type (MLX_2) where M = Co(d^7), L = tridentate ligand  $(Et_2N\text{-}(CH_2)_2\overset{R}{N}\text{-}(CH_2)_2\text{-}P\phi_2$; R = Me,H), have been made. Systems demonstrating spin state equilibria of the type $NiBr_2 \cdot (\phi_2BzP)_2$ have also been studied and evidence provided that a T_d (high-spin) form in the solid state can be converted to the square planar (low-spin) form. This electron pairing with pressure is possible because of the increased ligand-field effect occurring under high pressures.

A study of the behavior of 4f electrons under high external pressures has also commenced. Although ligand-field effects with pressure on the shielded 4f electrons are less than effects found for d electrons, the absorption of the hypersensitive visible transitions in certain complexes are maintained with pressure. Eventual comparisons with 5f electronic systems are being planned.

(4) Differences in behavior of various modes of vibration under pressure, along with metal isotopic studies, have been observed for coordination compounds, and have led to a better interpretation of their infrared and Raman spectra, with subsequent more definitive information on the structure of the complex and the natural metal–ligand bonding.

(5) Studies of the glassy state under pressure are of direct practical importance. Glass components are widely used in submarines and indeed all-glass vessels are being considered by the Navy for underwater exploration. Preliminary experiments have allowed us some insight into the fundamental factors affecting the nature of structural order and disorder in silicate glasses.

PUBLICATIONS

Ferraro, J. R., D. W. Meek, E. C. Siwiec, and A. Quattrochi, Effect of Pressure on the Ligand-Field Spectra of Some Five-Coordinate Nickel (II) Complexes, J. Amer. Chem. Soc., 93: 3862 (1971).

_____, S. S. Mitra and A. Quattrochi, Pressure Dependence of Infrared Eigenfrequencies of Ki, RbI, and Their Mixed Crystals, J. Appl. Phys., 42: 3677 (1971).

_____, H. Horan, and A. Quattrochi, Pressure Dependence of the Infrared-Active Optical Phonon Modes in Alkaline-Earth Fluorides, J. Chem. Phys., 55: 664 (1971).

———, High Pressure Vibrational Spectroscopy, in Spectroscopy in Inorganic Chemistry, Vol. 2, J. R. Ferraro and C. N. R. Rao (Eds.), Academic Press, Inc., New York, 1971, p. 57.

03:237 EXPERIMENTAL AND THEORETICAL SPECTROSCOPY OF THE FREE ACTINIDES AND LANTHANIDES. Fred, M. and Tomkins, F. S. (Argonne National Laboratory, Chemistry Division).

The experimental work consists of photography of the spectra of all these elements utilizing the Argonne 30-foot spectrograph, in cooperation with a number of other laboratories in the USA and abroad. Present emphasis on term analysis is concentrated on plutonium, which is expected to be essentially completed in 1973. Analyses of neptunium and americium spectra are being resumed now that better facilities are available than existed when the preliminary analyses were attempted some years ago.

The interpretation of the experimental levels by comparison with computer calculations has run into difficulties because the problem is now seen clearly to be too large for existing computers (for the neutral plutonium atom, for example, more than 1000 energy levels are now known). Attempts are under way to transform the present programs. The hyperfine structure of neptunium is being interpreted, to derive the nuclear moments of ^{237}Np and the radial wave functions, and further g-values of the heaviest actinides are being calculated for comparison with atomic beam results.

PUBLICATIONS

Crosswhite, H. M., H. Crosswhite, and M. Fred, Energy-Level Calculations for Truncated-Core $f^N d$ Configurations, J. Opt. Soc. Amer., 61, 1590 (1971).

Goodman, L. S., H. Diamond, H. E. Stanton, and M. S. Fred, g_J Value for the Atomic Ground State of Fermium, Phys. Rev., A, 4: 473 (1971).

03:238 SPECTROSCOPY OF HIGH-TEMPERATURE SYSTEMS. Gruen, D. M. (Argonne National Laboratory, Chemistry Division.

Current work is aimed at the elucidation of the chemical effects of the interaction of energetic particles with surfaces. One of the goals of the research is a better understanding of the mechanism of chemical sputtering. In a very recent study, the uranium oxide molecules UO, UO_2, and UO_3 were produced by sputtering a uranium metal cathode with argon gas containing variable concentrations of oxygen. The chemically sputtered uranium oxide molecules, isolated at 12°K in a matrix of solid argon, were identified by means of their vibrational spectra by use of an isotopic substitution technique. In this way, the frequency of the U–O vibration was established as 820 cm^{-1}.

In future work, matrix isolation spectroscopy will be applied for the first time to the identification of products sputtered from metal and ceramic surfaces bombarded by monoenergetic, mass-selected ions produced in an isotope separator. These experiments are expected to clarify the nature of the molecular products formed during bombardment with reactive gas projectiles and to characterize the surface reactions responsible for their formation.

Studies of sulfur species in fused salts have been conducted using both electrochemical and spectroscopic measurements. Solutions containing known amounts of sulfide ion are prepared electrochemically by use of a specially developed nickel sulfide electrode. Reactions of elemental sulfur with sulfide ion in the molten LiCl–KCl eutectic mixture were followed spectrophotometrically. The brilliant blue reaction product was characterized as the S_3^- ion in laser Raman experiments. These results are relevant to the development of high-energy, high-power-density batteries. Furthermore, they provide strong evidence that the S_3^- species is the color principle of the mineral ultramarine.

PUBLICATIONS

Clifton, J. R., D. M. Gruen, and A. Ron, Fluorescence Spectra of Matrix-Isolated Praseodymium Triiodide Molecules, J. Mol. Spectros., 39(2): 202-216 (1971).

Gruen, D. M., and D. H. W. Carstens, Absorption and Luminescence Spectra of Titanium Atoms Isolated in Noble Gas Matrices, J. Chem. Phys., 54(12): 5206-5214(1971).

———, R. L. McBeth, and A. J. Zielen, Nature of Sulfur Species in Fused Salt Solutions, J. Amer. Chem. Soc., 93: 6691-6693 (1971).

Carstens, D. H. W., and D. M. Gruen, Apparatus for Matrix Isolation Studies of High Temperature Species, Rev. Sci. Instrum., 42(8): 1194-1197 (1971).

Draley, J. E., B. R. T. Frost, D. M. Gruen, M. Kaminsky, and V. A. Maroni, An Assessment of Some Materials Problems for Fusion Reactors, in Intersociety Energy Conversion Engineering Conference Proceedings, Paper 38, pp. 1065-1075 (1971).

03:239 NUCLEAR MAGNETIC RESONANCE IN INORGANIC CHEMISTRY. Hindman, J. C. and Svirmickas, A. (Argonne National Laboratory, Chemistry Division).

This program has been set up with the objective of applying nuclear magnetic resonance techniques to studies on inorganic systems where such studies can provide useful information with respect to molecular structure, electronic configurations, and kinetic behavior. An earlier investigation in this area involved the study of the ^{19}F magnetic resonance of the xenon fluorides with the objective of determining the shielding parameters, structural characteristics, and charge distribution on the fluoride ion. More recently, chemical shift measurements have been made on the fluorine and hydrogen nuclei in gaseous and liquid HOF in order to learn something about the charge distribution and molecular properties of this unstable fluoride.

At present, a detailed study of ^{19}F chemical shifts and relaxation behavior for xenon oxytetrafluoride and xenon hexafluoride and for mixtures of xenon hexafluoride and other xenon fluorides is underway. These studies were undertaken to provide information of general physical interest about the molecular interactions and modes of molecular motion in the condensed states of these highly unusual inorganic fluorides. Of particular interest is the question of whether such measurements will provide information that will aid in deciding what molecular properties of XeF_6 are responsible for its anomalous chemical behavior.

As a logical extension of the present program we are considering the construction of probes that will allow measurements of relaxation times at high temperatures and pressures. The availability of such equipment will make possible the study of other systems of potential importance, e.g., the measurement of transport properties in molten salts.

03:240 STRUCTURE AND MOLECULAR INTERACTIONS IN LIQUID WATER AND IN SOLUTION. Hindman, J. C., and Svirmickas, A. (Argonne National Laboratory, Chemistry Division).

The importance of water, both as a liquid and as a solvent, has resulted in a continued high level of interest in the study of water structure and of water–solute interactions. It has become increasingly apparent that an understanding of the diverse properties of water and aqueous solutions is dependent on the development of experimental methods for the study of structural changes and ionic processes at the molecular level. The primary goal of the present program has been to find experimental approaches that will yield significant information. Both static and dynamic nuclear magnetic resonance techniques have been found useful.

We have found that a very satisfactory interpretation of proton chemical shift data for solutions of 1–1 electrolytes can be given in terms of ion–solvent interactions, hydrogen bond breaking, and structural effects on the solvent. Information available from such studies on pure water were found to be limited by the fact that the chemical shifts are sensitive not only to the breaking but also to the bending and stretching of the hydrogen bonds. Dynamic measurements have proved more useful and our present program is largely devoted to the determination of the relaxation times for the various isotopic species in liquid water and to the development of models for the interpretation of relaxation in terms of structures and lifetimes of states in the pure liquid.

Completion of the present research will allow concentration of effort on the investigation of methods for the determination of both static and dynamic properties of structures induced in water by the dissolution of solutes, either inorganic or organic. The ultimate goal in the study of the simple aqueous systems is to provide a basis for understanding the behavior of water in more complex, e.g., biological systems.

PUBLICATIONS

Hindman, J. C., and J. C. Sullivan, Principles and Methods for the Study of Metal Complex Ion Equilibria, in A. E. Martell (Ed.), American Chemical Society Monograph, No. 168, Van Nostrand Reinhold Company, New York, 1971, Chap. 7.

———, A. J. Zielen, A. Svirmickas, and M. Wood, Relaxation Processes in Water. The Spin-Lattice Relaxation of the Deuteron in D_2O and ^{17}O in H_2O^{17}, J. Chem. Phys., 54: 621 (1971).

03:241 ISOTOPICALLY MODIFIED PROTEINS. Katz, J. J., Crespi, H. L., and Smith, U. (Argonne National Laboratory, Chemistry Division).

Magnetic resonance spectroscopy is a new and important technique for the study of structure and function of proteins and enzymes. The application of high-resolution techniques is greatly facilitated by the use of isotope hybrid proteins containing ^{1}H-amino acid side chains or ^{1}H-prosthetic groups, because chemical shift assignments can then be made unambiguously. Conformational changes in isotope hybrid cytochrome c, ferredoxin, and flavoprotein, proteins important in electron transport, are being studied by proton magnetic and electron spin resonance to learn how energy transduction is affected by the proteins. Electron spin resonance studies with fully deuterated flavins and flavoprotein are being found particularly valuable because the flavin is a natural spin label. These studies make it possible to determine hyperfine interactions otherwise not measurable with the proteins of ordinary isotopic composition. Other physical parameters such as rotational correlation times can also be measured, which makes it possible to ascertain whether the protein is free or found in the (sic) living organism. Electron nuclear double resonance (ENDOR) is a valuable new tool in these studies. We are now applying ENDOR to organized systems such as mitochondria and whole organisms with excellent prospects for new knowledge about protein function in the intact living organisms. Supplementary to these are proton magnetic resonance investigations of chemically modified deuterated proteins, and protein–small molecule interactions as followed by ^{1}H and ^{13}C magnetic resonance. Our long-term goal is to isolate a fully deuterated enzyme containing an ^{1}H-amino acid side chain in its active center and to observe directly the consequences of enzyme–substrate interaction.

PUBLICATIONS

Crespi, H. L., J. R. Norris, and J. J. Katz, Magnetic Resonance of Isotope Hybrid Flavoprotein ^{2}H-Flavoprotein (^{1}H-Flavinmononucleotide), Nature, 263: 178 (1972).

______, J. R. Norris and J. J. Katz, Effect of Isotopic Substitution of the Electron Spin Resonance Spectra of Flavin and Flavoprotein Free Radicals, Biochim. Biophys. Acta, 253: 509 (1971).

03:242 CIRCULAR DICHROISM SPECTROSCOPY. Katzin, L. I. (Argonne National Laboratory, Chemistry Division).

Absorption spectra of colored metal ions reflect in different ways the binding condition of the ion number and types of atoms coordinated, geometric relations, etc. In many common situations though, the ordinary spectra may be quite insensitive to variations in these relations. With optically active ligands, for example, l-amino acids, circular dichroism spectroscopy (CD), differential polarized light absorption may reveal a fine structure within these absorption bands and call attention to otherwise unrecognized interactions. This sensitive added dimension may be vitally important for lanthanide and actinide ions, whose ordinary absorption spectra appear particularly insensitive to environmental influences.

We are continuing to study the absorption and circular dichroism spectra of rare earth and actinide solution systems, using a selection of optically active reagents available to us, to illuminate the following matters: coordination configurations (these ions show a considerable number of different ones) and the types of ligands that influence them; conditions under which certain types of ligands bind, in competition with water and other ligands; absorption spectral characteristics of the states defined with the aid of CD; geometrical relations within mixed-ligand molecules; and the correlations with the spectral states themselves. Analytical implications are obvious.

03:243 MAGNETIC EFFECTS IN METAL VAPOR ABSORPTION SPECTRA. Tomkins, F. S. and W. R. S. Garton. (Argonne National Laboratory, Chemistry Division).

Quadratic Zeeman effect data have been obtained for Ba, Sr, and Ca at magnetic fields varying from 10 to 48 kilogauss, using the Argonne 30-foot spectrograph and the superconducting solenoid magnet.

Two types of magnetic structure are observed in series lines of high principal quantum number and in the ionization continuum: The first, due to mixing of the angular momentum quantum number l between states in which the magnetic energy shift becomes an appreciable fraction of the energy difference between successive series members, is reasonably well understood and the theory worked out to the stage where satisfactory qualitative agreement between calculated and observed structures is being obtained.

The second effect, which appears as regularly spaced absorption resonances in the continuum beyond the ionization limit, is less well understood, and an adequate mechanism is only beginning to come out of the theoretical studies, which are being carried out under the direction of Dr. Allan Edmonds at Imperial College.

The detailed theory for both effects requires accurate photometric data on the two types of magnetic structure, and we have just completed a photoelectric scanning system to be used in conjunction with the large spectrograph that will give data of the quality required. Future plans include complete photometric studies of the alkaline earth elements, as well as both wavelength and photometric data for some alkali metals and thallium.

We are also undertaking cooperative experiments on magnetic effects in He_2 molecular spectra, with Dr. Roger Angel of Columbia University, and on magnetic rotation spectra of alkali metal molecules, with Professor M. M. Hessell of Fordham University.

03:244 MECHANISMS OF METABOLIC AND PHOTOSYNTHETIC REACTIONS. Fajer, J. (Brookhaven National Laboratory, Department of Applied Science).

This work encompasses two broad areas (1) the electronic structure and chemical properties of metalloporphyrins and their radicals and (2) the biological role of porphyrin ions in metabolic and photosynthetic reactions. The goal of the investigations is the use of these compounds in catalytic energy conversion steps.

Cation and anion radicals of porphyrins and related compounds such as chlorins and bacteriochlorins are prepared by chemical and electrochemical techniques and are observed by optical and magnetic resonance techniques:

1) Electron spin densities of radicals are systematically mapped by isotopic labeling with deuterium, ^{13}C, and metal isotopes with nuclear spins other than zero such as ^{57}Fe, ^{67}Zn, ^{25}Mg, and ^{113}Cd. These include ^{2}H- and ^{13}C-substituted chlorophylls.
2) Substituents on the porphyrin molecule are altered and gegenions are varied to determine the factors which control the two ground states we have observed in cation radicals.
3) Homogeneous rates of electron transfer between a porphyrin molecule and its anion or cation radicals will be measured (with and without complexing agents) by ESR (and NMR) line broadening.
4) Nuclear magnetic resonance will be used for measuring rates of electron transfer and for determining the sign and the magnitude of spin density in those radicals which show no resolved ESR spectra. The magnitude of the contact shifts will be used to differentiate between metal and ring oxidations. The NMR technique of Evans will also be used to measure magnetic susceptibilities.
5) Double resonance techniques such as ELDOR (frequency swept electron–electron double resonance) and ENDOR (electron–nuclear double resonance) will be used to help resolve the ESR signals observed for both cation and anion radicals for which definite assignments cannot be made on the basis of our present experimental and theoretical results.

The projected work would thus use four different magnetic resonance methods as well as optical and electrochemical techniques to continue the investigation of structure and counter ion effects on the chemical reactivity of anion and cation radicals of metalloporphyrins, chlorins, and bacteriochlorins as models for biological and energy transfer systems.

PUBLICATIONS

Felton, R. H., G. S. Owen, D. Dolphin, and J. Fajer, Iron (IV) Porphyrins, J. Amer. Chem. Soc., 93: 6332 (1971).

Forman, A., D. C. Borg, R. H. Felton, and J. Fajer, Hyperfine Interaction of Halide Ions with Metalloporphyrin Cation Radicals, J. Amer. Chem. Soc., 93: 2790 (1971).

Dolphin, D., A. Forman, D. C. Borg, J. Fajer, and R. H. Felton Compound I of Catalase and Horse Radish Peroxidase: π-Cation Radicals, Proc. Nat. Acad. Sci., U. S. A., 68: 614 (1971).

Borg, D. C., J Fajer, R. H. Felton, and D. Dolphin, The π-Cation Radical of Chlorophyll a, Proc. Nat. Acad. Sci., U. S. A., 67: 812 (1970).

Fajer, J., D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, π-Cation Radicals and Dications of Metallo-porphyrins, J. Amer. Chem. Soc., 92: 3451 (1970).

03:245 GASEOUS ION CHEMISTRY. Friedman, L. (Brookhaven National Laboratory, Chemistry Department).

Energy-transfer processes and rates of reactions of gaseous ions and neutral molecules are being investigated in both high-pressure ion sources and at lower pressures in the collision chamber of the Brookhaven tandem mass spectrometer. The reaction of ^{40}Ar with C_2Cl_4 was selected as a system of special interest because of the possible role of ion–molecule reactions in the collection of ^{37}Ar produced by the $^{37}Cl(\nu,e^-)^{37}Ar$ reaction in the Brookhaven Solar Neutrino Experiment. A study of the $^{40}Ar-C_2Cl_4$ reaction at pressures between 0.1 and 1.0 torr revealed charge transfer between Ar^+ and C_2Cl_4 to be the dominant process. The rate of charge transfer was found to be at least 300 times as great as the rate of the Ar^+ addition or substitution reactions with C_2Cl_4. This supports the assumption that the Ar^+ is efficiently converted to Ar and collected in the solar neutrino experiment.

Diagnostic studies on the properties of high-pressure cut-off phenomena in high-pressure electron-impact ion sources are being carried out in collaboration with Professor R. Torrey of Tennessee State University. Rates of formation of various ion–molecule reaction products, as well as of ions formed directly by electron impact, are being investigated as a function of source pressure in the vicinity of the high-pressure cutoff to determine why such sources do not produce gaseous ions at pressures above a few torr.

03:246 PHOTOELECTRON STUDIES. Hudis, J., M. L. Perlman. (Brookhaven National Laboratory, Chemistry Department).

Precise measurement of binding energies of inner shell electrons by x-ray photoelectron spectroscopy (ESCA, XPS) provides information about the effective charges of individual atoms in molecules and thus information about the charge distributions and chemical bonding in molecules.

Binding energies of core electrons of both constituents of the Ni–Ir and Au–Sn alloy systems have been measured as a function of binary composition. Also, binding energy measurements of tin and oxygen core electrons in Sn, SnO, and SnO_2 have been made. These data will be combined with available Moessbauer data on the alloys and internal conversion probability results on the tin–oxygen system to provide a detailed picture of the transfer of electrons, both as to number and kind, between the constituent atoms of each species.

Similar measurements on both the metal and ligand atoms in a series of cluster ions of the type $M_6X_{12}Y_6^{2-,3-,4-}$ (M = Nb or Ta; X,Y = halogens) will yield information on how the electrical charge distribution changes with substitution of different halogens at the two unique halogen positions, bridging and terminal. Again, these data will be combined with results of previous work, chemical reactivity, optical properties, and bond lengths, to provide a detailed explanation of the variations in bond type and strength in these compounds.

PUBLICATIONS

Hnatowich, D. J., J. Hudis, M. L. Perlman, and R. C. Ragaini, Determination of Charging Effect in Photoelectron Spectroscopy of Nonconducting Solids, J. Appl. Phys., 42: 4883 (1971).

Watson, R. E., J. Hudis, and M. L. Perlman, Charge Flow and d Compensation in Gold Alloys, Phys. Rev., B, 4: 4139 (1971).

Steinhardt, R. G., J. Hudis, and M. L. Perlman, Attenuation of Low Energy Electrons by Solids: Results from X-ray Photoelectron Spectroscopy, Phys. Rev., B, 5: 1016 (1972).

03:247 "STUDIES IN CHEMICAL DYNAMICS AND RADIATION CHEMISTRY I. ELECTRON SPECTROSCOPY". Kuppermann, Aron. (California Institute of Technology, Division of Chemistry, Pasadena, California 91109).

The objective of this program is to provide an understanding of the electronic states of molecules and ions of importance to radiation chemistry and photochemistry, including spin-forbidden states. The techniques used are those of variable angle electron impact spectroscopy and photoelectron spectroscopy. In the first, a beam of monoenergetic electrons collides with the molecules to be studied and the scattered electrons are energy-analyzed at varying angles. These experiments provide information not only about optically allowed transitions, but also about optically forbidden ones, including those that are spin forbidden. Such states are difficult to detect by other means but are formed in radiation chemical systems. The photoelectron spectroscopy technique is analogous to the electron impact one, with the primary electron beam being replaced by a photon beam capable of ionizing the target molecules. These experiments furnish detailed information about the electronic states of ions, which are also formed in radiation chemical systems. The goal is to use the combination of these two complementary techniques to elucidate the electronic structure of molecules of importance to radiation chemistry.

PUBLICATIONS

Trajmar, S., W. Williams, and Aron Kuppermann, The Angular Dependence of Electron Impact Excitation Cross Sections of O_2, J. Chem. Phys., 56: 3759 (1972).

______, W. Williams, and Aron Kuppermann, Detection and Identification of Triplet States of H_2O by Electron Impact, J. Chem. Phys., 54: 2274 (1971).

______, D. G. Truhlar, J. K. Rice, and A. Kuppermann, Electron Scattering by H_2 With and Without Vibrational Excitation. III. Experimental and Theoretical Study of Inelastic Scattering, J. Chem. Phys., 52: 4516 (1970).

______, James K. Rice and Aron Kuppermann, Electro–Impact Spectrometry, Advance. Chem. Phys., 18: 15 (1970).

Mason, D. C., Aron Kuppermann, and D. M. Mintz, Angular Distribution of Electrons from the Photoionization of Ethylene, in Electron Spectroscopy, D. A. Shirley (Ed.), North-Holland Publishing Company, Amsterdam, 1972, pp. 269-275.

03:248 "VACUUM ULTRAVIOLET SPECTRA AND PHOTOCHEMISTRY OF POLYATOMIC MOLECULES" El-Sayed, M. A. (University of California, Department of Chemistry, Los Angeles, California 90024).

Microwave radiation is shown to have large effects on the phosphorescence intensity of large molecules at 1.6°K. From the observed effects, new information concerning the radiative, nonradiative, magnetic, and structural properties of the lowest triplet state of phosphorescent molecules is obtained. The results of these phosphorescence–microwave double resonance experiments could determine the mechanism of the nonradiative process between the lowest excited singlet state and the lowest triplet state. Furthermore, the geometry of molecules in their triplet state could be conveniently determined from these experiments. It is shown that many symmetric benzene derivatives have a nonhexagon benzene skeleton in their triplet state at 1.6°K. This type of distortion is also found to depend greatly on the crystal field of the solvent. These distortions are manifestations of the electronic nuclear interactions present in these molecules. These studies are important in understanding the complicated field of photochemistry. It is hoped that our understanding of electronic–nuclear interaction would assist in an understanding of the mechanisms of the primary processes of photochemistry.

PUBLICATIONS

El-Sayed, M. A., and C. R. Chen, The Relative Signs of the Zero-Field Parameters from Phosphorescence-Microwave Double Resonance (PMDR) Spectroscopy: 1, 2, 4, 5, Tetrachlorobenzene, Chem. Phys. Lett., 10: 307 (1971).

______, and C. R. Chen, The Intersystem Crossing Process in Symmetric Tetrachlorobenzene, Chem. Phys. Lett., 10: 313 (1971).

______, M. Leung, and C. T. Lin, PMDR Spectroscopy and the Geometry of the Triplet State, Chem. Phys. Lett., 14: 329 (1972).

Tinti, D. S., and M. A. El-Sayed, Multiple Resonance Techniques and the Spectroscopy of the Triplet State, in Organic Scintillators and Liquid Scintillation Counting, Academic Press, Inc., New York, 1971, p. 563.

03:249 SIGNAL ENHANCEMENTS IN ESR SPECTRA. Fessenden, R. W. and Verma, N. C. (Carnegie-Mellon University, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).

The ESR spectra of systems of reacting radicals are generally abnormal in that the lines below the center of the individual spectra are less intense than their high-field mates or are even inverted, implying emission rather than absorption of energy. Studies of this phenomenon can best be made only with experimental systems allowing microsecond time resolution. Pulse radiolytic formation of radicals is being used with a suitably designed ESR spectrometer to enable such studies. Results to date show that the signal enhancements are the result of selective recombination reaction of radicals in the various spin states. A kinetic theory of this effect has been developed that explains the results and quantitatively correlates results from steady-state and pulse experiments. Further work is being carried on to investigate various aspects of this phenomenon as suggested by the theory.

03:250 NUCLEAR AND X-RAY SPECTROSCOPY WITH RADIOACTIVE SOURCES. Fink, R. W., McGeorge, J. C., Schmidt-Ott, W. D., Baker, K. R., Xenoulis, A. (Georgia Institute of Technology, School of Chemistry, Atlanta, Georgia 30332).

Current emphasis is on precision measurement of K, L, and M subshell x-ray fluorescence yields and Coster-Kronig transition probabilities in the lanthanide through the transuranium elements. This is carried out by investigating x-ray and Auger electron emissions, low-energy γ rays, and conversion electron lines from carrier-free radioactive sources, utilizing singles and coincidence spectroscopy with high-resolution Si(Li), Ge(Li), and Ge(intrinsic) x-ray and windowless, gate-valved electron detectors, together with a multiwire, anticoincidence proportional counter. This program requires extensive studies of detection efficiencies in the energy region of 1 to 100 keV.

With publication of the M/L and L/K orbital electron capture results in ^{55}Fe decay, a major question concerning the best agreement of several theoretical approaches for allowed electron capture decay has been answered; best agreement of M/L capture ratios in the decays of ^{37}Ar, ^{55}Fe, and ^{71}Ge, all measured by us, is achieved with the theories based on the Watson–Freeman wave functions and the Vatai exchange correction computed with the same wave functions.

During 1972–73 we expect to devote an increasing effort to the UNISOR project, the joint university isotope separator on-line with the ORIC heavy ion cyclotron at Oak Ridge National Laboratory. Our purpose in this program is two-fold: (1) to carry out on-line studies of new nuclides far from stability, particularly for the Georgia Institute of Technology group, the study of very-high-spin isomers predicted by Gol'danskii to decay by delayed alpha or delayed proton emissions, some of which may have applications in nuclear medicine; and (2) to use the isotope separator off-line for preparation of ultrathin, carrier-free longer-lived radioactive sources for use in our x-ray and Auger studies on campus. In future years, we expect that most of our effort will be devoted to research under the UNISOR program.

PUBLICATIONS

Schmidt-Ott, W. D., J. S. Hansen, and R. W. Fink, Relative X-Ray Transition Probabilities to the K-Shell for Z = 81, 92, 94, and 96, Z. Phys., 250: 191-197 (1972).

McGeorge, J. C., R. W. Fink, L_2 and L_3 Subshell Fluorescence and Coster–Kronig Yields for Z = 96 from the Decay of ^{249}Cf, Z. Phys., 248: 208-219 (1971).

______, and R. W. Fink, The L_1 Subshell Fluorescence and Coster–Kronig Yields for Z = 96, Z. Phys., 250: 293-299 (1972).

______, and R. W. Fink, The Determination by an Independent Method of P_K Electron-capture Probabilities in ^{133g}Ba and ^{139g}Ce Decays, Z. Phys., 249: 286-293 (1972).

Hansen, J. S., J. C. McGeorge, and R. W. Fink, Precision Determination of High-Z K-Shell Fluorescence Yields from ^{195}Au, ^{207}Bi, and ^{235}Np Decays, Z. Phys. 249: 373-385 (1972).

03:251 ION SPUTTERING AND SECONDARY ION EMISSION. McHugh, J. A., Barney, D. M., Boyd, W. T. (Knolls Atomic Power Laboratory, Mass Spectrometry).

This research is directed at understanding the basic mechanics of ion sputtering and secondary ion emission. Such an understanding, for example, is necessary in order to take full advantage of the analytical capability of the ion microprobe mass spectrometer.

One study currently in progress involves an experimental study of the effect and importance of reactive (both electronegative and electropositive) element primary ions and inert gas primary ions on secondary ion yields. The effects of primary ion current density and sample matrix in both conductors and nonconductors are also being considered. A second area of current interest concerns the effect of a sample's crystal lattice orientation on its secondary ion yield production. Results from a large-grain Ni-base alloy show differences in secondary ion yields between grains. Also differences in grain color are observed after $^{16}O^-$ bombardment, which bears a relationship to the secondary ion production efficiency. Studies with oriented Zr single crystals are planned for the near future.

03:252 NUCLEAR MAGNETIC RESONANCE STUDIES OF HYDRATED METAL IONS. Connick, Robert E. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

Nuclear magnetic resonance measurements are being used to determine how long water molecules and other ligands remain attached to metal ions. In favorable cases the coordination number may also be determined, and frequently data on scalar coupling, quadrupole coupling, electronic relaxation times, and tumbling rates may be obtained. Currently the lifetime of water molecules in the second coordination sphere of chromic ion is being investigated; the change produced by complexing of the Cr^{3+} will be studied. The lifetimes of water molecules in the first coordination sphere of nickel ion complexed by one iminodiacetate ion are being measured to find how much the rates of the two kinds of water differ. The method will be extended to other systems to yield kinetic data that can be obtained in no other way. Computer simulation of water exchange on hydrated ions will be attempted in cooperation with Dr. Alder.

PUBLICATIONS

Neely, James, and Robert E. Connick, ^{17}O Nuclear Magnetic Resonance Studies of Aqueous Nickel Ion, J. Amer. Chem. Soc., 94: (1972).

______, and Robert E. Connick, Rate of Water Exchange from Hydrated Magnesium Ion, J. Amer. Chem. Soc., 92: 3476 (1970).

03:253 OPTICALLY DETECTED MAGNETIC RESONANCE (ODMR) IN PHOSPHORESCENT TRIPLET STATES AND IN TRIPLET FRENKEL EXCITONS. Harris, C. B. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

Saturation of the zero-field electron spin transition of a phosphorescent triplet state with microwave radiation causes changes in the intensity and/or polarization of the emission and thus forms the basis for optically detected magnetic resonances (ODMR) in excited triplet states. Because energetic photons are being detected, the sensitivity of the technique is such that it is possible to detect as few as 10^8 molecules in a sample.

If the phosphorescence is monitored from an "isolate" molecule, ODMR can be used to measure many properties associated directly with the electron distribution in the triplet state. These include the electron–electron dipolar interactions, the electron–nuclear hyperfine interactions, and the nuclear quadrupole interactions. In addition, quantitative analysis of the microwave-induced changes in phosphorescence yields a measure of the routes and rates of intermolecular energy transfer processes such as T → S radiative processes and S → T intersystem crossing rates in addition to the radiationless relaxation rates out of the individual spin sublevels of the phosphorescent triplet state under investigation. Analysis of the polarization changes in phosphorescence induced by the microwave field and knowledge of the microwave transition moment allow the unequivocal identification of the orbital symmetry of the emitting state, and in some cases a measure of molecular distortion in these states can even be ascertained.

ODMR also provides a fundamental new technique for studying the dynamics of triplet exciton migration. It can be used to distinguish random walk (diffusion) migration of energy from the case where the exciton dynamics are described by the group velocity of a wave packet (coherent migration). The importance of coherent migration is that it provides an extremely effective means of transporting energy over long distances in times much shorter than those required in the random walk limit. ODMR in fact provides a technique for directly measuring the mean free path (the coherence) of triplet Frenkel excitons in addition to the density of exciton states.

PUBLICATIONS

Harris, C. B., J. Chem. Phys., 54: 972 (1971).

______, and R. J. Hoover, J. Chem. Phys., 56: 2199 (1972).

______, C. B. Harris, and R. M. Panos, J. Amer. Chem. Soc., 94: 3692 (1972).

Francis, A. H., and C. B. Harris, Chem. Phys. Lett., 9: 181, 188 (1971).

Buckley, M. J., and C. B. Harris, J. Chem. Phys., 56: 137 (1972).

03:254 X-RAY PHOTOELECTRON SPECTROSCOPY. Jolly, William L. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

X-ray photoelectron spectroscopy is being used to study molecular structure and bonding. Methods for predicting chemical shifts in core electron binding energies are being devised and evaluated by comparison of theory and experiment.

We are investigating the core binding energies of a series of analogous compounds of silicon, germanium, and tin (for example, the halides, hydrides, and methyl derivatives). We hope that by comparison of these data with the corresponding data for carbon compounds we will be able to estimate the extent and significance of $p\pi - d\pi$ bonding. For example, if this type of bonding is important in SiF_4, one would expect the positive charge on the silicon atom and the negative charges on the fluorine atoms to be exceptionally low. We are devising a simple method for estimating charges of atoms in molecules and will apply this method to a Coulomb potential model for estimating chemical shifts in binding energies. We plan to develop a method for examining vapors at high temperatures; this will vastly expand the scope of gaseous molecules that can be studied.

PUBLICATIONS

Jolly, W. L., The Estimation of Core-Electron Binding-Energy Shifts Using the Concept of the Equivalence of Equally Charged Cores in Electron Spectroscopy, D. A. Shirley (Ed.), North Holland Publishing Company, Amsterdam, 1972, pp. 629-645.

Finn, Patricia, and W. L. Jolly, Chemical Shifts in Boron is Binding Energies of Some Gaseous Compounds, J. Amer. Chem. Soc., 94: 1540 (1972).

Finn, Patricia, and W. L. Jolly, The Nitrogen 1s Binding Energies of Transition Metal Nitrosyls, Inorg. Chem., 11: 893 (1972).

Finn, Patricia, R. K. Pearson, J. M. Hollander, and W. L. Jolly, Chemical Shifts in Core Electron Binding Energies for Some Gaseous Nitrogen Compounds, Inorg. Chem., 10: 378 (1971).

03:255 ELECTRON PARAMAGNETIC RESONANCE AND MICROWAVE SPECTROSCOPY. Myers, Rollie J. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

We have discovered that $Ti(H_2O)_6^{3+}$ has an observable EPR spectrum both in a frozen glass and in solution. The frozen glass has $g_{\parallel} = 1.98$ and $g_{\perp} = 1.91$. These data indicate a fairly large Jahn–Teller distortion for the free hydrated complex. Before the frozen glass melts, its EPR spectrum broadens. This results in a continuous EPR broadening from solid to solution. These data indicate an unusual Orbach process as the principal relaxation mechanism above 200°K both for solid and solution.

We also have been using nuclear magnetic resonance to establish the rate of spin relaxation for Ni^{2+}, Co^{2+}, and similar ions in solution. This involves proton NMR on both the water and on a cation probe in solution. This method is particularly suitable for those ions with very short relaxation times.

Our current work on electron–electron exchange in α-$NiSO_4 \cdot 6H_2O$ has involved a modification of the molecular field model so that it is suitable for spectroscopy. In this regard we have been able to explain the temperature independence of the Ni^{2+} EPR spectrum and the rate of relaxation of substituted Cu^{2+}. Since the molecular field model is an important theoretical tool in interacting solids we will surely do further work on its application to spectroscopy.

PUBLICATIONS

Myers, R. J., and A. Jindo, Electron Exchange for Hydrated Ions in the α-$NiSO_4 \cdot 6H_2O$ Lattice—Electron Paramagnetic Resonance Study of Transition-Metal Ions in $ZnSeO_4 \cdot 6H_2O$, J. Magn. Resonance, 6: 633 (1972).

______, C. A. Arrington, and A. M. Falick, Electron Paramagnetic Resonance Spectrum of O_2 ($^1\Delta_g$)—Its ^{17}O Hyperfine Coupling and Electronic and Rotational g Values. J. Chem. Phys., 55: 909 (1971).

03:256 OPTICAL SPECTROSCOPY. Conway, John G. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

The atomic spectra of an atom reveal the most complete information about the structure of the atom. The most complicated or difficult atoms are those involving f electrons. The elements that contain f electrons are also known as the lanthanide series and the actinide series.

Work is in progress to analyze the spectra of these elements. The information derived from such analyses finds uses in other fields such as metallurgy, physical chemistry, astrophysics, and several other fields of physics and chemistry.

Although there are many years of work ahead on both groups of elements, progress is being made. The actinide group is particularly difficult because of the very limited quantities available and the very toxic nature of the radioactive elements. The experimental part of the work must be done along with the interpretation and theoretical portions to yield the greatest results.

The direction which the work in this field will be taking in the next few years will be to attempt analyses on the spectra of the higher stages of ionization, in particular the stages of +2, +3, and +4, because these are the stages of great interest to solid state chemistry and physics and solution chemistry. These stages are more difficult by factors of 10 than what has been done up to now and will require some very ingenious experimentation, but the information is so important and needed that the workers will not be turned away from the task.

03:257 HYPERFINE INTERACTIONS AND NUCLEAR RADIATIONS. Shirley, David A. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

This project employs the experimental techniques of low-temperature nuclear orientation, Moessbauer spectroscopy, and perturbed angular correlations of γ rays to study hyperfine interactions. The focus of the program is on developments of these techniques and innovative applications to a wide variety of physical problems.

Nuclear orientation studies are carried out at temperatures as low as 0.001°K. Several experiments are in progress. These include the study of anisotropic angular distribution of fission fragments from oriented, spontaneously fissioning transplutonium nuclides. The magnetic moments and spins of high-spin nuclear isomers are studied by magnetic resonance measurements on oriented nuclei. Nuclear relaxation times at very low temperatures are also under investigation.

Perturbed angular correlations are being used to study both static and dynamic hyperfine interactions in solids. Quadrupole coupling constants in solids and magnetic hyperfine fields in metals are of particular interest. Relaxation phenomena in both liquids and gases are also being explored.

Recent work in this laboratory and at Munich has made Moessbauer spectroscopy with ^{181}Ta relatively straightforward. Further experiments are in progress in tantalum alloys and compounds.

03:258 PHOTOELECTRON SPECTROSCOPY IN GASES. Shirley, David A. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

The Berkeley Iron-Free Spectrometer has been adapted to do ESCA (electron spectroscopy for chemical analysis), or x-ray photoemission, studies on gases. It is one of only a few facilities in the world that can be used for this purpose. Measurements are being carried out of the core-level binding-energy shifts in small molecules. Of particular interest are hydrocarbons, fluorine-substituted hydrocarbons, and fluorocarbons all having the same molecular framework of carbon atoms. The measured shifts are interpreted to yield rather direct information about the distributions of electronic charge in these molecules. In fluorobenzene, for example, these shifts have shown that carbons in the ortho positions are negatively charged, in agreement with the chemical properties of this molecule.

The theory of ESCA shifts is also under active study. An intermediate level molecular orbital theory has been used to predict shifts, and it has also been modified to account for electronic relaxation during photoemission. Further development of this theory is in progress.

The ESCA method is also being applied to studies of the valence electrons, by observation of peaks corresponding to direct photoemission from molecular orbitals. In this case molecular orbital theory is used to predict the relative intensities as well as the positions of peaks. Comparison of theory with experiment establishes the hybrid composition of the molecular orbitals in terms of their constituent atomic orbitals.

03:259 PHOTOELECTRON SPECTROSCOPY IN SOLIDS. Shirley, David A. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

ESCA (electron spectroscopy for chemical analysis), or x-ray photoemission spectroscopy, is being applied to a wide range of metals and semiconductors. This work is focused on the valence bands. The first major project is the determination of valence-band densities of states in as many elements as possible. At this writing survey experiments have been carried out on twenty-four elements.

Valence-band density-of-states studies are of utmost importance in understanding the structure and properties of materials because the position of the valence bands is closely related to the stability (i.e., to the cohesive energy) of a material. In addition, the valence bands—together with the unoccupied conduction bands—account for nearly all of a material's observed properties. Unfortunately, although a tremendous effort has been expended on characterizing valence bands over the last two decades, most experimental methods are either indirect or ambiguous. X-ray photoemission appears to be an important, long-awaited method for establishing valence band positions definitively.

Work currently in progress with a monochromatized x-ray source has yielded definitive spectra for gold valence bands. The 5s and 5p bands in the elements Cd, In, Sn, Sb, and Te have been observed for the first time, and a definitive spectrum has been obtained from silicon.

03:260 ORGANIC THIN FILMS—PHOTOEXCITED PROPERTIES AND ELECTRON ENERGY LOSS. Jarnagin, R. C. (University of North Carolina, Department of Chemistry, Chapel Hill, North Carolina 27514).

A low-energy electron spectrometer has been successfully designed and constructed. The spectrometer analyzes electrons photoejected from surfaces, and having energies in the range 0 to 2 V. The apparent resolution is less than 30 mV from 0.1 to 2 V energy and less than 0.1 V between 0 and 0.3 V energy. Photoemissive substrates examined have consisted of silver, gold, and aluminum. The objective of the surface examination has not been to seek the energy band structure of the metal but rather to examine the effect of overlay materials deposited on the surface of the metal and to examine other surface films and "dirts". Such surface films and compounds are the result of both chemical and physical adsorption and oxidation processes. Such surfaces also behave catalytically in other kinds of chemical processes. To date we have been able to locate two states on the surface of oxidized silver. One state has its parentage primarily from the metal, and the emission efficiency is temperature-insensitive. The other state has its parentage primarily in the oxide compound at the surface and its emission intensity is temperature-dependent. Silanization of such an oxidized silver surface with trialkylchlorosilane results in a monolayer or less than monolayer coverage of $Si(alkyl)_3$ groups. Electron penetration of surfaces is selectively attenuated in energy. The general features result in the suppression of all electrons emitted from the unsilanized surface with less than 0.5 V energy. The highest-energy electrons are more severely attenuated by tri-N-propylsilane than by trimethylsilane. The degree of attenuation is currently being examined and analyzed for scattering lengths and scattering mechanisms. In the future it is intended to continue such attenuation studies and to examine the effects of chemisorbed species upon the surface, particularly those species that may be of importance in surface heterogeneous catalysis.

PUBLICATIONS

Jarnagin, R. C., Photoionization Processes in Organic Solids and Fluids, Accounts Chem. Res., 4: 420-427 (1971).

03:261 SPECTROPHOTOMETRIC STUDIES OF SOLUTIONS WITH ALPHA-ACTIVE MATERIALS. Bell, J. T., I. L. Thomas. (Oak Ridge National Laboratory, Chemical Technology Division).

The major objective of this research program is to develop and exploit optical techniques for studying the chemical properties of aqueous solutions, especially of the lanthanide, actinide, and other transition group elements, over wide ranges of experimental conditions. Experimental techniques include absorption and emission spectrometry with ancillary density measurement, use of intense light sources for absorption and photochemistry, and computer techniques for the manipulation and analysis of data. The facilities include a high-temperature-pressure spectrophotometer and a high-temperature-pressure dilatometer, both designed for containment of alpha-active materials. This program also includes theoretical studies of protonic wave functions and spectra of the protonic–electronic structures of light- and heavy-metal hydrides, and related electronic structures.

Current work on the photochemical reduction of uranyl ion may be extended to higher actinides. Uranyl spectra in different aqueous media are being measured and resolved; spectra of UO_2^+ may also be obtained. Equilibria and kinetics in the disproportionation, reproportionation, and polymerization of Pu(IV) have been determined. Studies of uranium(IV) chloride complexes between 25 and 90°C are to be extended to higher temperatures to determine the thermodynamic quantities of formation. Protonic and electronic structures of some light hydrides are being calculated, to be extended to structures of heavy-metal hydrides.

PUBLICATIONS

Bell, J. T., New Absorption Bands for the Uranyl Ion, J. Mol. Spectrosc., 41: 409 (1972).

———, R. D. Baybarz, and D. M. Helton, The Thermodynamics for the Reaction of Americium(III) with Iminodiacetic Acid, J. Inorg. Nucl. Chem., 33: 3077 (1971).

———, and N. A. Krohn, The Near-Infrared Spectra of Water and Heavy Water at Temperatures Between 25 and 390°, J. Phys. Chem., 74: 4006 (1970)

Thomas, I. L., Photoprotonic Effect in Hydrides, Phys. Rev., A 5: 1104 (1972).

———, Angular Dependence of the Vibrational and Rotational Excitations Seen in Photoelectron Spectroscopy, Phys. Rev., A 4: 457 (1971).

03:262 ELECTRON SPECTROSCOPY. Carlson, Thomas A. (Oak Ridge National Laboratory, Chemistry and Physics Division).

Electron spectroscopy has become one of the most important physical tools to be developed during the last decade for application to chemical problems. The work at Oak Ridge played a pioneering role in the United States towards that development in the field of x-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, and Auger electron spectroscopy. A continuing program examines how the potential of electron spectroscopy may be expanded through improvements in technology and in the exploitation of new areas. As an example of the former, a position-sensitive detector is being built for use in electron spectroscopy which ought eventually to increase the data-collecting capacity 100-fold.

As to examples of new areas of research, we have been making systematic investigations of elements throughout the periodic table, examining the nature of the inner-shell chemical shifts and the splitting of photoelectron lines. We have also expanded our studies on molecular orbitals of the outer shells using angular distribution measurements. In the applied field we have demonstrated the use of electron spectroscopy for a wide variety of environmental problems, including the study of chemicals adsorbed on the surface of smoke and other particulate matter, and the behavior of toxic metals on compounds of biological interest.

PUBLICATIONS

Carlson, T. A., Electron Spectroscopy for Chemical Analysis, Phys. Today, 25: 30-39 (1972).

———, and A. E. Jonas, Angular Distribution of the Photoelectron Spectra for Ar, Kr, Xe, H_2, N_2, and CO, J. Chem. Phys., 55: 4913-4924 (1971).

Moddeman, W. E., Thomas A. Carlson, Manfred O. Krause, B. P. Pullen, W. E. Bull, and G. K. Schweitzer, Determination of the K-LL Auger Spectra of N_2, O_2, CO, NO, H_2O, and CO_2, J. Chem. Phys., 55: 2317-2336 (1971).

Hulett, L. D., T. A. Carlson, B. R. Fish, and J. L. Durham, Studies of Sulfur Compounds Adsorbed on Smoke Particles and Other Solids by Photoelectron Spectroscopy, in Determination of Air Quality (Proceedings of Symposium, Los Angeles, Calif., April 1971), J. Mamantov and W. P. Shults (Ed.), Plenum Publishing Corporation, New York, 1971, pp. 187-195.

03:263 SPECTROSCOPY OF FLUORIDE MEDIA. Toth, L. M., and Gilpatrick, L. O. (Oak Ridge National Laboratory, Reactor Chemistry Division).

This program is an experimental study of molten fluoride salts and mixtures using visible and ultraviolet absorption spectroscopy. By absorption measurements, through diamond-windowed cells, the coordination numbers and geometries of transition metal cations can be characterized in dilute solution in molten fluorides. These studies are to: (1) identify the coordination behavior of these metal ions in solution; (2) determine how the chemical reactivity of the coordinated species is affected by the solvent environment; and (3) determine chemical equilibria involving these species by direct measurement.

In such studies of dilute solutions of UF_3 and UF_4 in molten $2LiF \cdot BeF_2$, it was observed that rapid equilibration among the dissolved uranium species, graphite, and insoluble uranium carbides occurred at temperatures below 1000°C. Since accurate thermodynamic data are available for UF_3 and UF_4 in this solvent, measurement of the concentration of these species at equilibrium yields thermodynamic data for the pure carbide phases. Studies in progress will attempt to show that these data are independent of the molten salt solvent system.

Similar studies with fluorides of the potentially useful structural materials niobium and molybdenum, whose redox chemistry is still poorly understood, are being initiated; these studies will occupy much of the immediate future.

PUBLICATIONS

Toth, L. M., Coordination Effects on the Spectrum of U(IV) in Molten Fluorides, J. Phys. Chem., 75: 631 (1971).

03:264 PHOTOELECTRON SPECTROSCOPY. Thomas, T. Darrah. (Oregon State University, Department of Chemistry and Radiation Center, Corvallis, OR 97331).

The major objective of this research is the application of x-ray photoelectron spectroscopy to solving problems of chemical interest. The work divides into three parts: (1) development of equipment suitable for the intended research; (2) understanding of the strengths and limitations of the technique; and (3) use of photoelectron spectroscopy for investigation of specific chemical problems.

In the first of these areas, we have designed and built an electrostatic spectrometer suitable for x-ray photoelectron spectroscopy of both solids and gases. Further work is being aimed at improving the resolution and intensity, at developing new photon sources, and at improved data-taking and analysis facilities.

Of great concern in the second area is the problem of reference level and charging in insulators. We have recently completed an investigation of alkali halides that begins to shed some light on this problem. Further work is in progress.

We have been especially interested in the relation between measured core electron binding energies and the distribution of charge in molecules. Work on fluorinated benzenes and on alkali halides shows that these energies can be related in a simple way to charges on the atoms of the molecules. In addition, we have been concerned with chemical effects on line shapes and line widths and on use of photoelectron spectroscopy as a broad-range analytical tool.

PUBLICATIONS

Shaw, R. W., Jr., and T. D. Thomas, Search for Core Electron Satellites in Carbon Monoxide, Chem. Phys. Lett., 14: 121-123 (1972).

Citrin, P. H., R. W. Shaw, Jr., and T. D. Thomas, Cylindrical Electrostatic Analyzer for Photoelectron Spectroscopy, in Electron Spectroscopy, D. A. Shirley, (Ed.), North Holland Publishing Company, Amsterdam, 1972, pp 105-120.

———, R. W. Shaw, Jr., A. Packer, and T. D. Thomas, X-Ray Photoelectron Spectroscopy of Alkali Halides, in Electron Spectroscopy, D. A. Shirley (Ed.), North-Holland Publishing Company, Amsterdam, 1972, pp 691-706.

Davis, D. W., D. A. Shirley, and T. D. Thomas, K-Electron Binding Energy Shifts in Fluorinated Methanes and Benzenes: Comparison of a CNDO Potential Model with Experiment, J. Chem. Phys., 56: 671-673 (1972).

Thomas, T. Darrah, X-Ray Photoelectron Spectroscopy of Carbon Monoxide, J. Chem. Phys. 53: 1744-1749 (1970).

03:265 MICROWAVE–OPTICAL DOUBLE RESONANCE SPECTROSCOPY. Pratt, David W. (University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15213).

The technique of microwave–optical double resonance (MODR) spectroscopy is being used to study the static and dynamic properties of electronically excited triplet states of organic molecules in low-temperature solids. Particular emphasis is being placed on problems of significant theoretical interest, such as the determination of the signs of zero-field parameters in n,π* triplet states and the measurement of hyperfine tensors of interacting nuclei. A large part of our work in the near future will be devoted to aromatic molecules containing the carbonyl group for which little information has been obtained to date.

In addition, use is being made of the adamantane matrix technique for the measurement of EPR and optical spectra of free radicals. A large number of β-carbonyl radicals containing six-membered rings have been prepared and are being studied over a wide temperature range in order to determine kinetic and thermodynamic properties for the ring interconversion process. Highly resolved optical absorption and emission spectra of free radicals have also been obtained at room temperature by this method, and we are presently exploring the possibility that radical fluorescence can be used to detect EPR spectra of electronically excited states of free radicals.

PUBLICATIONS

Pratt, D. W., J. J. Dillon, R. V. Lloyd, and D. E. Wood, Electron Paramagnetic Resonance Spectra of Pyrrolidino and Pyrrolino Free Radicals. The Structure of Dialkylamino Radicals, J. Phys. Chem., 75: 3486 (1971).

03:266 STUDIES IN NUCLEAR AND RADIOCHEMISTRY. Herber, Rolfe H. (Rutgers University, School of Chemistry, New Brunswick, N. J. 08903).

The major emphasis in this project has been the exploitation of recoilless emission and absorption of nuclear gamma radiation (Moessbauer Effect) in the study of a wide variety of chemical problems including those of structure and bonding in organometallic compounds of iron and tin, chemical effects of nuclear transformation, intra- and intermolecular bonding forces and structural integrity of molecules undergoing phase changes, inter alia. A detailed study of the model compound $[(C_6H_5)_2SnCl_2]$, both as a neat solid as well as in frozen solutions of basic and nonbasic solvents, has been carried out and has clarified the role of crystalline stacking forces in influencing the anomalous bond angles and bond distances which are deduced from an x-ray diffraction study of this material. The temperature dependence of the recoil-free fraction has been determined over the temperature range $78 \leq T \leq 180°K$ to elucidate the role of intra- and intermolecular bonding forces in the neat solid. A detailed and extensive study has been carried out on the structure and bonding of other organometallic compounds including (a) tin(IV) diethyldithiocarbamates; (b) tin(IV) sulfates and thioglycollates; (c) (πC_5H_5)–iron compounds with a variety of phosphorus-containing ligands; (d) hydrazine derivatives of Fe(II), Ni(II, and Sn(IV); and (e) dialkylformamide complexes of Sn(IV). Related studies on solid state properties, hot atom chemistry and chemical effects of isomeric transitions and internal conversion are currently underway.

PUBLICATIONS

Stapfer, C. H., and R. H. Herber, Monoalkyltin Ortho Sulfates, J. Organometal. Chem. (Amsterdam), 35: 111 (1972).

———, R. W. D'Andrea, and R. H. Herber, Complexes of Iron(III), Nickel(II) and Tin(IV) Chlorides with Hydrazine Derivatives, Inorg. Chem., 11: 204 (1972).

Barbieri, R., R. Cefalu, S. C. Chandra, and R. H. Herber, Studies on Adducts of Organotin(IV Halides with a Tetradentate Base, J. Organometal. Chem. (Amsterdam), 32: 97 (1971).

Herber, R. H., Molecular Moessbauer Spectroscopy, Sci. Amer. (October 1971).

———, Moessbauer Spectroscopy of Organometallics: Lattice Dynamics and Structure of Butyl Tin(IV) Compounds, J. Chem. Phys., 54: 3755(1971).

03:267 GASEOUS ION CHEMISTRY: ANALYTICAL APPLICATIONS. Torrey, Rubye P. (Tennessee State University at Nashville, Department of Chemistry, Nashville, Tennessee 37203).

The purpose of this study is to evaluate the performance characteristics of a high-pressure electron-impact ion source. The ionization efficiency of the source is being evaluated in terms of the positive ion current of argon as a function of pressure in the pressure range from 0.15 to 3.0 torr, the pressure above which Ar^+ and Ar^{2+} have disappeared. The electrons are obtained from a heated thoriated iridium filament and energized to 100 eV. From the data it appears that an increase in argon pressure of approximately 0.4 torr causes a reduction in the ionization efficiency by approximately 50% for Ar^+ and approximately 75% for Ar^{2+}.

Experiments are being carried out using 50-eV electrons with argon, helium, and argon–helium mixtures to determine whether pressure affects the energy of the ionizing electrons so that the mechanism by which the ions disappear can be attributed to a reduction of electron energy in the region from which the ions are made.

Future work will include a study of the heteronuclear associative ionization of the argon–ammonia system. It appears that the molecule ion, $ArNH_3^+$, can be formed by this mechanism from the energetics. The mode of formation in terms of the electronic structure of ammonia will be a point of interest.

ALSO SEE Nuclear Spectroscopy: 03:1, 03:7; Heavy Element Chemistry: 03:65, 03:69, 03:71, 03:75, 03:80, 03:86, 03:92, 03:94, 03:98; Radiation Chemistry: Aqueous; 03:105, 03:106, 03:107, 03:108; Radiation Chemistry: Gaseous; 03:120, 03:122, 03:123, 03:126, 03:127, 03:128, 03:131; Radiation Chemistry: Other; 03:132, 03:144, 03:149, 03:151, 03:156, 03:158, 03:161, 03:163; Photochemistry and Energy Transfer: 03:170, 03:175, 03:176, 03:178, 03:179, 03:180, 03:183, 03:189, 03:190; Hot Atom Chemistry: 03:208; Kinetics and Mechanisms: 03:219, 03:221, 03:223, 03:225; Theoretical Chemistry: 03:283, 03:284; Isotope Chemistry: 03:289, 03:296, 03:297, 03:299, 03:302; Thermodynamics: 03:310, 03:311, 03:313; High-Temperature and Inorganic Chemistry: 03:327, 03:331, 03:334, 03:335, 03:338, 03:341, 03:345, 03:351, 03:354, 03:361; Structural Chemistry: 03:370, 03:377; Analytical Chemistry: 03:387, 03:388, 03:399, 03:404; Miscellaneous Chemical Studies: 03:440, 03:453.

THEORETICAL CHEMISTRY

Theoretical studies of structure and reactivity.

03:268 IRREVERSIBLE PROCESSES IN POLYATOMIC GASES. Hoffman, David K. (Ames Laboratory, Chemistry Division).

In recent years there has been increased interest in the theory of transport and relaxation processes in polyatomic gases. This has been encouraged by the discovery of certain transport phenomena that critically depend on internal molecular structure and by simultaneous advances in the kinetic theory of polyatomic gases and in computational methods. Study of these phenomena is important since they shed light on macroscopic processes of basic interest to physicists and chemists and, at the same time, provide a possible means for studying molecular properties such as interaction potentials. Efforts in this laboratory are being directed toward investigation of the theory of certain transport phenomena which are sensitive to rotational degrees of freedom, and to the development of molecular models which can provide a semi-quantitative test of the theory. To the present, model calculations have been limited to rigid molecular models (which give only a crude representation of valence repulsion forces and ignore attractive interactions). Calculations have been performed for both linear and nonlinear molecules. Future studies in this program will be directed toward broadening the range of phenomena under investigation and toward developing more realistic molecular models. In the latter regard, recent advances made in this laboratory and elsewhere show much promise.

PUBLICATIONS

Cooper, E. R., and D. K. Hoffman, A Cartesian Tensor Perturbation Scheme for the Senftleben Effect, J. Chem. Phys., 54: 223 (1971).

———, and D. K. Hoffman, Model Calculations of Transport Coefficients for Diatomic Gases in an External Magnetic Field. II. The Cartesian Perturbation Expansion Scheme, J. Chem. Phys., 55: 1016 (1971).

———, and D. K. Hoffman, Model Calculations of Transport Coefficients for Diatomic Gases in an External Magnetic Field, J. Chem. Phys., 53: 1100 (1970).

Dahler, John S., and David K. Hoffman, in Theory of Transport and Relaxation Processes in Polyatomic Fluids, Chap. 1, Transfer and Storage of Energy in Molecule. Vol. 3, Rotational Energy, G. M. Burnett and A. M. North (Eds.), Wiley–Interscience, 1970.

03:269 EFFECTIVE EXPANSIONS OF ATOMIC AND MOLECULAR ELECTRONIC WAVEFUNCTIONS. Ruedenberg, Klaus. (Ames Laboratory, Chemistry Division).

Because of the development of high-speed computers in the past two decades, quantum mechanical principles have become applicable to molecular problems. Quantum chemical calculations are infusing theoretical predictions of steadily increasing impact into experimental chemistry, a science that for more than a century had to rely on empiricism. Such predictions derive from the electronic wave functions. The calculation of these key quantities is the pivotal and hardest problem. Fundamental contributions to its solution have come from the theoretical chemistry group at the Ames Laboratory.

Expansion in terms of configurations of antisymmetrized spin orbital products is the most effective current wave function construction procedure. In this context, two difficult problems have been solved recently. Simple, efficient expressions for the energy contributions from general configurations that are also spin eigenfunctions with arbitrary couplings have been derived and implemented, using a group theoretical analysis of the permutational symmetry. Furthermore a rapidly convergent optimization procedure for the one-electron molecular orbitals occurring in multiconfigurational expansions has been developed and implemented using the generalized Brillouin theorem and natural orbitals. These novel advances promise considerably easier access to approximations of practical accuracy by means of computer programs currently under construction.

PUBLICATIONS

Ruedenberg, K., Expectation Values of Many-Fermion Spin Eigenstates, Phys. Rev. Lett., 27: 1105 (1971).

———, and R. D. Poshusta, Matrix Elements and Density Matrices for Many-Electron Spin-Eigenstates Built from Orthonormal Orbitals, Advan. Quant. Chem., 6: 267 (1972).

03:270 EVEN-TEMPERED ATOMIC ORBITALS FOR ATOMIC AND MOLECULAR CALCULATIONS. Ruedenberg, Klaus. (Ames Laboratory, Chemistry Division).

The elementary quantitative wave function building blocks are atomic orbitals, one-electron one-center functions that are most economically expressed as spherical harmonics multiplied by exponentials of the type exp $(-\zeta_j r)$ or exp $(-\zeta_k r^2)$. The optimal choice of large sets of parameters ζ_j, ζ_k is a crucial factor and yet, because of the nonlinear dependence, an extremely time- and money-consuming task in atomic and molecular work. Substantial progress has been achieved through our discovery that without loss of accuracy these parameters can be expressed simply in terms of a much smaller number, namely, in the form of geometric series. This reduction increases economy and effectiveness by orders of magnitude wherever many atomic-orbital basis functions are required. In radon, for example, the number of nonlinear parameters is reduced from about forty to four groups of two. In many cases the reduction makes the difference between feasibility and nonfeasibility. Even-tempered atomic orbitals of this type have been determined for a large number of atoms, many of them heavy (e.g., Gd, Xe, Ru), for which no analytical wave functions had been available so far. For certain atoms additional detailed features of these basis sets are being refined to yield optimal usefulness in molecular calculations. Such calculations were made predicting the stabilities, dissociation energies, and geometrical shapes of the, as yet unknown, trialkali ions Li_3^+, Na_3^+, Na_2Li^+, $NaLi_2^+$, Na_2H^+, Li_2H^+, NaH_2^+, and LiH_2^+. In current work optimal even-tempered atomic orbitals are determined in typical molecular environments for such common atoms as carbon, nitrogen, and oxygen, for general use.

PUBLICATIONS

Bardo, R. D., and K. Ruedenberg, Numerical Analysis and Evaluation of Normalized Repeated Integrals of the Error Functions and Related Functions, J. Comput. Phys., 8: 167 (1971).

Hoffman, D. K., R. C. Raffenetti, and K. Ruedenberg, Generalization of Euler Angles to N-Dimensional Orthogonal Matrices, J. Math. Phys., 13: 528 (1972).

03:271 PREDICTIVE INTERPRETATIONS OF ATOMIC WAVE FUNCTIONS. Ruedenberg, Klaus. (Ames Laboratory, Chemistry Division).

Molecular wave functions capable of predicting useful values for observable physicochemical properties are so complicated that it is usually difficult to discern the theoretical origin of interesting quantitative variations of such properties under molecular deformations or between related molecules. It becomes a separate task to devise mathematical procedures in order to extract the essential quantitative factors and form corresponding conceptual interpretations. By analyzing the homopolar and heteropolar one-electron bond, the roles of the kinetic and potential energies, as well as charge rearrangements, were elucidated and past misinterpretations resolved. The partitioning of molecules into electronic subsystems that can be quantitatively recognized in different molecules, and are therefore transferable, has been successfully accomplished by the extraction of localized molecular orbitals for numerous diatomic and polyatomic molecules. The aim is to establish quantitative formulations for concepts of electronic structure, such as lone pairs, bonds, etc., which will allow approximate conceptual syntheses of rigorous theoretical results and, thereby, offer experimental chemists reliable guidelines for intuitive anticipation of structure and properties of new compounds.

PUBLICATIONS

Feinberg, M. J., and K. Ruedenberg, Paradoxical Role of Kinetic Energy Operator in the Formation of the Covalent Bond, J. Chem. Phys., 54: 1495 (1971).

———, and K. Ruedenberg, Heteropolar One-Electron Bond, J. Chem. Phys., 55: 5804 (1971).

England, W., and K. Ruedenberg, Localized pi-Orbitals, Pauling Bond Orders and the Origin of Aromatic Stability, Theor. Chim. Acta, 22: 196 (1971).

———, L. S. Salmon, and K. Ruedenberg, Localized Molecular Orbitals. A Bridge Between Chemical Intuition and Molecular Quantum Mechanics, Fortschr. Chem. Forsch., 23: 31 (1971).

———, Continuous Degeneracy and Energy Localization of Molecular Orbitals, Int. J. Quant. Chem., 5: 683 (1971).

03:272 THEORETICAL STUDIES OF LIQUIDS AND SOLUTIONS. Feder, H., H. Schnyders. (Argonne National Laboratory, Chemical Engineering Division).

A model is being developed that will allow the prediction of thermodynamic properties of gases dissolved in molten alkali metals. Recent improvements in the model were achieved by introducing a more specific and accurate representation of the repulsive forces between solute and solvent atoms and by minimizing the chemical potential of the solute with respect to dilatation. The extended theory thus becomes a method of calculating (for dilute alloys) not only the excess free energy and enthalpy of formation but also the excess volume of formation.

Sophisticated quantum-mechanical calculations of short-range repulsive forces between two argon atoms were performed. From these, a complete nonempirical pair-potential curve was synthesized. Standard tests of this pair potential were performed. Over a wide range of temperatures (100 to 1600°K), second virial coefficients and viscosities of gaseous argon were calculated; agreement with experimental data is one percent or better. Work has begun on the calculation of the equation of state of liquid and solid argon, because agreement with experiment would provide the most sensitive possible test of the accuracy of our representation of the short-range forces and the first thorough test of the ability of a nonempirical pair potential to predict a wide range of thermodynamic behavior.

Application of the results of these various studies can be anticipated in areas such as sodium coolant chemistry for LMFBR's, coolants and blankets for controlled thermonuclear reactors, new methods for the recovery and purification of nuclear fuels, nuclear safety and energy conversion.

PUBLICATION

Veleckis, E., S. K. Dahr, F. A. Cafasso, and H. M. Feder, Solubility of Helium and Argon in Liquid Sodium, J. Phys. Chem., 75: 2832 (1971).

03:273 FOUNDATIONAL PROBLEMS IN PHYSICS. Benioff, P. (Argonne National Laboratory, Chemistry Division).

One important goal of this research is to construct physical theories that are essentially quantum mechanical in nature and maximally self-referential. That is, they refer to as much of their own metaphysics (this term is used here in the same sense as "metamathematics" is used in mathematics) as is possible. The importance of this goal is that the requirement that a theory be maximally self-referential is equivalent to the requirement that a theory be maximally objective.

To this end, work is progressing on modifying a definition proposed earlier of validity or agreement between experiment and a physical theory. The aim of the modifications is to bring the definition from the metaphysical world into the domain of the physical theory under consideration and at the same time make it quantum mechanical.

It is expected that, among other things, this work will make use of the description developed for general procedures in quantum mechanics by means of probability operator measures.

PUBLICATIONS

Benioff, P. A., Some Aspects of the Relationship Between Mathematical Logic and Physics. I., J. Math. Phys., 11: 2553 (1970).

———, Some Aspects of the Relationship Between Mathematical Logic and Physics. II., J. Math. Phys., 12: 360 (1971).

———, Operator Valued Measures in Quantum Mechanics: Finite and Infinite Processes, J. Math. Phys., 13: 231 (1972).

03:274 RELATIVISTIC CALCULATIONS OF ATOMIC PROPERTIES. Benioff, P. (Argonne National Laboratory, Chemistry Division).

The goal of this work is to calculate inner shell electron binding energies in heavy atoms with more accuracy than has yet been reported. In particular, it is hoped to calculate the corrections due to all the fourth order Feynman diagrams to add to the existing second order calculations.

This program has been initiated very recently, and the first phase of the work is to obtain, for the energies contributed by the various diagrams, theoretical expressions suitable for computation. For those fourth order diagrams without any self-energy parts the work is going well and, barring any unforeseen problems, should be completed in the next year.

03:275 DEVELOPMENT OF THEORY, TECHNIQUES, AND COMPUTER PROGRAMS FOR THE COMPUTATION OF CHEMICAL PHENOMENA. Wahl, A. C., G. Das and P. Benioff. (Argonne National Laboratory, Chemistry Division).

Theoretical chemistry has been traditionally both a unifying conceptual language for the chemist as well as a tool for interpreting and (to a more limited extent) predicting chemical behavior. During the past ten years, largely because of the advent of more and more powerful computing machines and methods, the predictive accuracy of modern theoretical techniques has been vastly improved. As a result of this development of new quantitative theoretical capability, more and more constructive interaction is taking place between theoretical and experimental chemists. Some of the most useful results obtainable from modern computations are the binding energies, the interaction potentials and surfaces (including Van der Waals), ionization potentials, electron affinities, excitation energies, dipole and higher moments, and the geometry of simple chemical systems.

When these fundamental atomic and molecular characteristics are computed accurately and coupled with statistical mechanics and dynamics, predictions are being made concerning bulk properties of matter such as its thermodynamics, transport, and kinetic behavior.

One of the most important aspects of this capability for computing the electronic structure of atoms and molecules is the central position that the results of such calculations occupy throughout the full range of chemistry. Namely, the characteristics of individual atoms and molecules and the forces between them form the fundamental information needed as partial input to all phenomenological theory. The theoretical capability we are developing at Argonne can often provide some basic information in a general way as a complement or as an alternative to experiment. The fundamental nature of the information that this facility generates also provides an extremely flexible capability that can yield specific information which we know we will need on a continuing basis regardless of shifts in applied problems.

The results of these quantum mechanical calculations are currently providing necessary fundamental input to a wide variety of areas. Prominent among these are: (1) scattering theory; (2) molecular dynamics; (3) chemical kinetics; (4) spectroscopy; and (5) thermodynamics. In addition to being an alternative and complementary source of reliable information in these major areas of chemistry, some recent computations have played an important role in settling an experimental controversy and, as predictions, in providing a conceptual framework for the experimentalist. It is the flexible utility of the fundamental nature of the results of quantum mechanical calculations that must be stressed.

Our group has been continuously developing, over the past seven years, methods for approximately solving the Schroedinger equation for nontrivial molecules accurately enough to use the resulting energies and wave functions to predict a wide variety of atomic and molecular properties and behavior.

We are extending these techniques to larger systems and developing better methods for including relativistic effects essential to understanding energy levels in heavy elements.

PUBLICATIONS

Wahl, A. C., and G. Das, The Method of Optimized Valence Configurations: A Reasonable Application of the Multiconfiguration Self-Consistent Field Technique to the Quantitative Description of Chemical Bonding, in Advances in Quantum Chemistry, P. O. Lowdin (Ed.), Academic Press, Inc., New York, 1970, pp. 261-296.

———, Chemistry by Computer, Sci. Amer., 222(4): 54-58 (1970).

Das, G., and A. C. Wahl, New Techniques for the Computation of Multiconfiguration Self-Consistent Field (MCSCF) Wave functions, J. Chem. Phys., 56(4): 1769-1775 (1972).

O'Hare, P. A. G., and A. C. Wahl, Quantum-Chemical Study of Some Pnicogen Monofluorides, J. Chem. Phys., 54(11): 4563-4577 (1971).

03:276 THE ELECTRON STRUCTURE, SPECTRA, AND PROPERTIES OF DIATOMIC MOLECULES. Wahl, A. C., G. Das, W. Stevens and M. Attermeyer. (Argonne National Laboratory, Chemistry Division).

Modern a priori theoretical techniques are being applied to a wide variety of diatomic systems in order to predict their energy levels, binding energies, vibrational frequencies, transition probabilities, and electron properties such as dipole and higher moments and polarizabilities.

The rationale for the selection of a given diatomic system or series usually comes from a direct experimental or programmatic interest. Currently, we are studying alkali dimers whose properties are of interest in fusion technology, a series of fluorides in collaboration with the Chemical Engineering Division, atmospheric diatoms related to aeronomic modeling, and metal chlorides that are being concurrently studied experimentally in the Physics Division.

These studies have successfully predicted binding energies, electron affinities, and ionization potentials and, in some cases, aided in settling an experimental controversy. They also, through their direct relation to an ongoing experiment, have provided a framework for interpreting results as they occur.

We intend to continue these collaborative studies. Among the systems scheduled for study in the near future are heavy-metal hydrides whose properties are of possible importance in containment problems connected with the CTR program, other diatomic systems of energetic importance in the earth's atmosphere, and interstellar species.

PUBLICATIONS

Bertoncini, P. J., G. Das, and A. C. Wahl, A Theoretical Study of the 1_{Σ^+}, 3_{Σ^+}, 3_{π}, 1_{π} States of NaLi and the 2_{Σ^+} State of LaLi$^+$, J. Chem. Phys., 52: 5112-5130 (1970).

O'Hare, P. A. G., and A. C. Wahl, Hartree–Fock Wavefunctions and Computer Properties for the Ground ($^2\Pi$) States of SF and SeF and Their Positive and Negative Ions. A Comparison of the Theoretical Results with Experiment, J. Chem. Phys., 53(7), 2834-2846 (1970).

Julienne, P. S., M. Krauss, and A. C. Wahl, Hartree–Fock Energy Curves for $X^2\Pi$ and $^2E^+$ States of HF$^+$, Chem. Phys. Lett., 11(1): 16-20 (1971).

Das, G., and A. C. Wahl, New Techniques for the Computation of Multiconfiguration Self-Consistent Field (MCSCF) Wavefunctions, Chem. Phys., 56(4): 1769-1775 (1972).

03:277 ENERGY SURFACES, COLLISION THEORY, AND MOLECULAR DYNAMICS. Wahl, A. C., A. Karo, A Wagner and C. W. Wilson. (Argonne National Laboratory, Chemistry Division).

In principle, if one has the details of the forces acting between atoms and molecules and a complete knowledge of their low-lying electronic states, predictions can be made of their scattering behavior and, if reactive, of their reactivity.

Because of the relatively recent ability of modern computational theory to yield reliable energy quantities, it is possible to predict collisional phenomenon and, alternately, reaction rates with some confidence.

This is usually done by solving Hamilton's classical equations of motion for the interacting particles over the quantum mechanical energy surface for a statistically selected set of initial particle states. We are currently studying the chemical reactions $Li + H_2 \rightleftharpoons LiH + H$ (collaboratively with LLL), $H + Li_2 \rightleftharpoons LiH + Li$, and a variety of systems being concurrently studied by the Chemistry Division's Molecular Beam Group. These studies yield detailed knowledge and models of reaction mechanisms, charge, and energy transfer processes.

We intend to continue studies of interest to the molecular beam group and to apply similar techniques to selected energy-transfer processes arising in radiation and photochemistry. When our interaction potentials are completed for the heavy-metal hydrides, a prediction of scattering cross reactions will be made. Molecular dynamics calculations will also be made in connection with our program on molecules of atmospheric interest.

An effort will continue to carry these calculations all the way to the first principal prediction of reaction rates.

03:278 THEORETICAL EVALUATION OF VAN DER WAALS FORCES. Wahl, A. C., W. Stevens and G. Das (Argonne National Laboratory, Chemistry Division).

Van der Waals forces dominate the low-energy collision and interaction between atoms and molecules and much of their transport behavior. It is only recently that reliable techniques have been developed for computing these small interaction energies on a first principle basis. Our research group is engaged in the development of a sound theoretical model for the calculation of these forces, which are very difficult to obtain from experimental sources alone. Accurate predictions of the shape of the interaction potential have been made for He_2, HeH, and LiHe. These predictions were subsequently confirmed experimentally. We are currently performing similar calculations on Ne_2, Ar_2, NaLi, and Na_2. We intend to do long-range calculations on heavy-metal hydrides of possible interest to CTR technology.

PUBLICATIONS

Bertoncini, P., and A. C. Wahl, Ab Initio Calculation of the Helium–Helium $1\Sigma_g$ Potential at Intermediate and Large Separations, Phys. Rev. Lett., 25(15): 991-994 (1970).

as, G., and A. C. Wahl, Theoretical Study of the Van der Waals Forces in Alkali–Noble Gas Systems, Phys. Rev., A4(3): 825-833 (1971).

———, and A. C. Wahl, New Techniques for the Computation of Multiconfiguration Self-Consistent Field (MCSCF) Wavefunctions, J. Chem. Phys., 56(4): 1769-1775 (1972).

03:279 THEORETICAL STUDIES OF ATMOSPHERIC TRIATOMIC AND DIATOMIC SPECIES. Wahl, A. C., C. W. Wilson and R. Hosteny. (Argonne National Laboratory, Chemistry Division).

The spectra (both electronic and infrared) and kinetic behavior of small atmospheric triatomic molecules under stressful atmospheric conditions are not well understood. The understanding of these phenomena, which is fundamental to aeronomic modeling, requires a knowledge of the energy surfaces governing the collision and recombination of the triatomic constituents and their subsequent relaxation as well as the prediction of how these surfaces underlie other physical behavior.

Our current work on atmospheric systems consists of two parts. First, a preliminary, critical review of the literature is being undertaken to obtain all the available experimental and theoretical information that would assist the construction of energy curves for H_2O, CO_2, O_3, NO_2, N_2O, and their ions. This critical review is using as a reference a theoretical description of the electronic structure of these molecules drawn from molecular orbital theory and correlation rules as well as existing calculations. Energy points in the neighborhood of the equilibrium geometry and at dissociation limits can be fixed from experiment.

In a few instances, notably H_2O, energy surfaces can already be constructed from existing theory and experiment. This initial review is not sufficient for a detailed construction of energy curves but will be used to establish a list of calculations of varying complexity and priority that can determine the energy surfaces to pre-specified levels of accuracy. It is expected that priority will be given to the determination of all energy surfaces arising from ground and lowest excited state fragments and to the dominant absorption features at the equilibrium geometry.

Second, a planned set of ab initio calculations is being undertaken on the top priority surfaces. At the equilibrium geometry of the ground state accurate multiconfiguration self-consistent field (MC-SCF) and configuration interaction (CI) calculations will be undertaken to fix the vertical excitation energies of the surface to the order of several tenths of an eV. At large internuclear separations a combination of perturbation and MC-SCF calculations will be performed to determine the medium-range behavior of all energy surfaces arising from low-lying energy asymptotes.

Equilibrium positions of excited states and more extensive surveys of energy surfaces between equilibrium and asymptote will then be calculated by the fastest, most reliable techniques that can be used. The resulting energy surface will then be employed in scattering and dynamics studies to yield spectra and the kinetic behavior of these species.

03:280 STATISTICS IN STRUCTURE AND REACTIVITY THEORY. Ehrenson, S. (Brookhaven National Laboratory, Chemistry Department).

The objectives of the work described in this summary are to explore the predictive and correlative abilities of various statistical methods as applied to the theory of molecular structure and reactivity. Three main paths of investigation may be delineated.

Sophisticated Monte Carlo sampling techniques are being used for the numerical integration, by the local energy method, of correlated wave functions for small molecules. Upon determination of efficient weighting functions for the sampling, attempts will be made to extend the flexibility of wave functions limited by analytical integration problems. The James–Coolidge–Kolos functions for H_2 are presently under investigation.

The effects of radial weighting on the expansion of various exponential-type orbital functions in terms of Gaussian-type orbitals are being scrutinized, using full nonlinear least squares fitting procedures. Important weighting effects have been noted for a number of expectation values, including energy, in the STO expansions and SCF expansions for first-row atoms. Of continuing concern is the modification of these effects when molecular orbitals are constructed from the atomic orbital expansions.

The properties of large molecules are being investigated by concurrent application of statistical methods to experimental data in the form of linear free energy equations and to the results of semiempirical MO theory for corresponding typical systems. Valid separations of inductive and resonance effects of substituents on reactivities and physical properties of aromatics are obtained from the dual-substituent linear free energy equation. Future interest lies in wider application of the correlation equations and in the potential utility of charge and bond index measures obtainable from the CNDO/2 method for correlation of these separated effects.

PUBLICATIONS

Ehrenson, S., R. T. C. Brownlee, and R. W. Taft, A Generalized Treatment of Substituent Effects in the Benzene Series. A Statistical Analysis by the Dual Substituent Parameter Equation, in Progress in Physical Organic Chemistry, Interscience Publishers, New York, Vol. 10, 1972.

———, and S. Seltzer, On CNDO Bond Indices and Relations to Molecular Energies, Theor. Chim. Acta (Berl.), 20: 17 (1971).

———, Weighted Small Gaussian Expansions of Slater-Type Atomic Orbitals, Chem. Phys. Lett., 9: 521 (1971).

03:281 QUANTUM CHEMISTRY. Ehrenson, S., J. Muckerman, M. Newton (Brookhaven National Laboratory, Chemistry Department).

This research is concerned with developing orbital theories of quantum chemistry (valence bond, molecular orbital, and configuration interaction), and applying them to problems of molecular structure, energetics, and reactivity, both at the ab initio and the semiempirical level. Current ab initio structural studies involve the nature of solvation complexes (e.g., solvated protons and electrons), the bonding in highly strained hydrocarbons, and biologically important conformational effects (e.g., the stereochemistry of phosphate esters). For the solvation studies, the usual Schroedinger equation formalism has been extended to include the potential energy from a polarized dielectric continuum.

The potential energy surfaces for several reactive systems have also been investigated. For the $F + H_2 \rightarrow FH + H$ reaction, a semiempirical (LEPS) surface has been generated and used in extensive dynamical studies, leading to a detailed microscopic analysis of the kinetics in good agreement with available experimental data. More general semiempirical valence bond methods are being developed for more complex systems such as $CH_4 + H$. Various abstraction and exchange modes for the latter reaction have also been studied by molecular orbital calculations. Ab initio configuration interaction calculations have been initiated to elucidate the mechanisms of reactions of hot ^{11}C atoms in different electronic states (^3P, ^1D, ^1S) with alkane substrates and their halogen derivatives.

PUBLICATIONS

Newton, M. D., and S. Ehrenson, Ab Initio Studies on the Structures and Energetics of Inner and Outer Shell Hydrates of H^+ and OH^-, J. Amer. Chem. Soc., 93: 4971 (1971).

———, and J. M. Schulman, Theoretical Studies of Strained-Ring Systems. Bicyclobutane, J. Amer. Chem. Soc., 94: 967 (1972).

———, and J. M. Schulman, Theoretical Studies of Tricyclo-[1.1.1.$0^{1,3}$]pentane and bicyclo[1.1.1]pentane, J. Amer. Chem. Soc., 94: 773 (1972).

Ehrenson, S., and M. D. Newton, Ab Initio Studies of Hydrogen Exchange and Abstraction in the $H + CH_4$ System, Chem. Phys. Lett., 13: 24 (1972).

Weston, R. E., and S. Ehrenson, Hydrogen Exchange and Abstraction in the $H + CH_4$ System as Calculated by the CNDO/2 Method, Chem. Phys. Lett., 9: 351 (1971).

03:282 THEORETICAL STUDIES OF MOLECULAR COLLISION DYNAMICS. Muckerman, James T. (Brookhaven National Laboratory, Chemistry Department).

This work is directed towards the prediction of single-collision phenomena in the gas phase, with energy transfer and chemical reaction receiving the major emphasis. In the category of energy transfer the research is concerned with the calculation of cross sections and isotope effects in inelastic collisions, especially those related to atomic recombination, fluorescence quenching, collisional dissociation, and photodissociation. The research on chemically reactive systems is directed towards the calculation of reaction cross sections and rate constants, isotope effects, and the deposition of the energy of reaction in reaction products. A further aim of this project is to aid in the interpretation of results of experimental dynamical studies carried out in this department and elsewhere.

Current work, e.g., hydrogen recombination kinetics and thermal and hot atom studies of reactions of fluorine atoms (^{18}F in the hot atom studies) with isotopes of hydrogen, employs both classical and semiclassical interpretations of the exact numerical solutions to Hamilton's equations of motion for a system of atoms interacting according to an appropriate semiempirical potential energy function. To convey the results of these calculations in the most useful form, computer graphics and animation of numerical data are also an integral part of this program.

PUBLICATIONS

Muckerman, J. T., Classical Dynamics of the Reaction of Fluorine Atoms with Hydrogen Molecules. II. Dependence on the Potential Energy Surface, J. Chem. Phys., 56: 2997 (1972).

Truhlar, D. G., J. T. Muckerman, and M. D. Newton, Comment on "Multiple Potential Energy Surfaces for Reactions of Species in Degenerate Electronic States," J. Chem. Phys., 56: 3191 (1972).

03:283 BASIC STUDIES OF ATOMIC DYNAMICS. Fano, U. (University of Chicago, Department of Physics, Chicago, Illinois 60637).

This project investigates the theoretical mechanisms of electron reactions with molecules and atoms, that is, of the detachment, attachment, and energy-exchange processes of low-energy electrons in matter.

One approach, which has been fruitfully emphasized here in recent years, consists of separating a long-range (dissociation) zone, where an electron experiences a simple Coulomb or other attraction, from a short-range (close-coupling) zone where exchange and other many-body forces are essential. Up to this year, we have analyzed various phenomena in the dissociation zone, using boundary values of the electron's wave function at the edge of the close-coupling zone as empirical parameters. The publications listed below are mainly examples of this work.

The next major objective is to develop analytic and numerical methods for studying the close-coupling zone by itself and thus producing ab initio values of the boundary parameters to replace the empirical values.

Much attention is directed now to the connection between inner shell photoabsorption spectra of atoms and molecules and analogous, but still unexplained, structures in spectra of ionic and metallic crystals. In molecules, electronegative atoms present a barrier to electron escape. Analogous barriers do occur in crystals but only when the electrons emerge from a localized hole. The entire project's orientation may thus be veering from gaseous to condensed phase.

PUBLICATIONS

Dehmer, J. L., A. F. Starace, and U. Fano with J. Sugar and J. W. Cooper, Raising of Discrete Levels into the Far Continuum, Phys. Rev. Lett., 26: 1521 (1971).

______, Evidence of Effective Potential Barriers in the X-Ray Absorption Spectra of Molecules, J. Chem. Phys., 56: 4496 (1972).

Rau, A. R. P., and U. Fano, Theory of Photodetachment near Fine-Structure Thresholds, Phys. Rev., A, 4: 1751 (1971).

Starace, A. F., Potential-Barrier Effects in Photoabsorption. I. General Theory, Phys. Rev., B, 5: 1773 (1972).

Dill, Dan, Angular Distribution of Photoelectrons from H_2 in the Range of Rotational Autoionization, in Electron Spectroscopy, D. A. Shirley (Ed.), North Holland Publishing Company, Amsterdam, 1972, p. 277.

03:284 THEORETICAL STUDY OF FINE AND HYPERFINE STRUCTURES AND THEIR EFFECT ON RADIATIVE INTERACTION AND ENERGY-TRANSFER PROCESSES. Chow Chiu, Lue-yung (Howard University, Department of Chemistry, Washington, D. C. 20001).

Rotational and vibrational effects on the fine and hyperfine structure of a diatomic and a triatomic molecule have been studied. Results on the fine structure splittings of a rovibronic level of a linear triatomic molecule have been reported. Spin-spin interaction was found to give rise to additional, new splittings. Hyperfine splittings, which are due to nuclear magnetic dipole and nuclear electric quadrupole interactions, are presently under investigation. As for the diatomic molecules, the stretching vibrational dependence on the coupling constants will be calculated.

We are also studying the energy and coherence transfer process due to collision of the second kind. The coherence transfer process was studied by calculating the polarization of sensitized fluorescence, and coherence was found somewhat transferred in many cases. This suggests that the collisional process does not randomize the phases of the excited states completely. We are now studying the relative cross section of the sensitized fluorescence when different pairs of fine structure levels of the excited states are involved in the excitation transfer. The cross sections obtained this way can be compared directly with the known experimental results. The fine structure dependence of the energy-transfer process gives direct dependence of energy transfer versus angular momentum transfer.

PUBLICATIONS

Chow Chiu, Lue-yung, Fine Structure of the Rovibronic Levels of a Linear Triatomic Molecule, 25th Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1970, p. 37.

______, Spin-Spin Interaction and the Energy Splitting of the Rovibronic Levels of a Linear Triatomic Molecule, J. Chem. Phys., 54: 4100 (1971).

______, Collisional Transfer of Coherence: Polarization of Sensitized Fluorescence, Phys. Rev., A, 5: 2053 (1972).

03:285 THEORY OF LOW-ENERGY ATOMIC AND MOLECULAR COLLISIONS. Miller, William H. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

The overall goal of our research program is a detailed understanding of atomic and molecular collision dynamics in the low-energy region of primary chemical interest (i.e., collision energies from thermal energy up to several electron volts). Current work is involved with developing a general semiclassical theory of molecular dynamics. Much progress has already been achieved in this direction, and effort is now concentrated in extending these methods to the description of classically forbidden (i.e., tunneling) processes for which the usual classical trajectory methods are completely inapplicable. Two examples of such tunneling processes that are extremely important at thermal energy are vibrational energy transfer in simple diatomic molecules and reactive collisions for which there is a significant activation barrier. Initial results for the linear H + H_2 reaction show that the semiclassical theory accurately describes the tunneling region below the classical threshold, which is the dominant factor in the thermal energy rate constant. Another application in progress is a full three-dimensional calculation of vibrational energy transfer in collisions of H_2 and He; this work employs an accurate potential energy surface and should thus give physically meaningful results to compare with recent shock tube measurements of the vibrational relaxation time. Three-dimensional calculations of the H + H_2 reaction are also planned.

PUBLICATIONS

Rankin, C. C., and W. H. Miller, Classical S-Matrix for Linear Reactive Collisions of H + Cl_2, J. Chem. Phys., 55: 3150 (1971).

Miller, W. H., The Classical S-Matrix for Rotational Excitation; Quenching of Quantum Effects in Molecular Collisions, J. Chem. Phys., 54: 5386 (1971).

______, Additional WKB Inversion Relations for Bound-State and Scattering Problems, J. Chem. Phys., 54: 4174 (1971).

______, The Semiclassical Nature of Atomic and Molecular Collisions, Accounts Chem. Res., 4: 161 (1971).

03:286 PHYSICAL CHEMISTRY WITH EMPHASIS ON THERMODYNAMIC PROPERTIES. Pitzer, Kenneth S. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

Aqueous solutions of several solutes, usually electrolytes, are of enormous practical importance in situations all the way from the separation processes for spent nuclear fuel to the biological processes in the human body. While very dilute solutions of single solutes were investigated intensively and, in most cases, successfully several decades ago, the theoretical basis for concentrated solutions, for mixed solutes, and for solutions containing multiply charged ions of each sign is far from satisfactory. Several closely related investigations will attack these problems with the objective of making possible predictions of the properties of mixed electrolytes of realistically high concentration from a minimum of experimentally determined parameters.

Statistical theories are being developed that are applicable to mixtures of ions of different sizes as well as different electrical charges. Separately, but with guidance from theory, we are testing various schemes for empirical representation of the properties of mixed electrolytes. Sufficient progress has been made in both areas to give confidence of a successful outcome of this program. X-ray-scattering studies are planned for a few solutes with very heavy ions where ion scattering will dominate that from the solvent in order to check the radial distribution predicted theoretically.

PUBLICATION

Pitzer, K. S., Thermodynamic Properties of Aqueous Solutions of Bivalent Sulfates, J. Chem. Soc., Faraday Trans., II, 68: 101 (1972).

03:287 STRUCTURES AND BINDING ENERGIES OF SOME MOLECULAR IONS. Huang, J. J. and M. E. Schwartz (University of Notre Dame, Radiation Laboratory).

The geometries and binding energies of univalent molecular ions are investigated by various quantum mechanical methods. This work was initiated as a first step toward theoretical studies *of ion–molecule and ion-clustering reactions. A simplified diatomics-in-molecules* (DIM) energy expression was derived to make possible easy calculations of approximate potential energy functions for M_3^+ ions. Detailed application has been made for H_3^+. With partition of the total binding energy into appropriate diatomic bond energies, the DIM scheme is useful in increasing our understanding of the nature of chemical bonding in these molecular ions. Self-consistent field molecular orbital (SCF-MO) calculations are also carried out for H_3^+ and H_5^+ systems. H_5^+ is found to have a most stable geometry corresponding to an $H_3^+ \ldots H_2$ complex of overall C_{2v} symmetry, in which the H_2 sits about 3 au from the H_3^+ apex and perpendicular to the H_3^+ plane. This ab initio prediction provides a direct indication that H_3^+ is the clustering center. The calculated binding energy of 4.25 kcal/mole leads to $\Delta H =$ 6.35 kcal/mole for $H_3^+ + H_2 \rightarrow H_5^+$, in good agreement with experimental data from ion–molecule kinetics.

Pseudopotential calculations for the systems of Li_3^+, Li_2H^+, LiH_2^+, Na_3^+, Na_2Li^+, $NaLi_2^+$, Na_2H^+, and NaH_2^+ are in progress.

PUBLICATIONS

Huang, J. J., Simple Diatomics-in-Molecules Energy Expression for M_3^+ and Its Application to H_3^+, J. Chem. Phys., 55: 5136 (1971).

———, Analytical Self-Consistent-Field Energy Expression for Ground-State H_3^+ Ion, J. Chem. Phys., 56: 3176 (1972).

———, M. E. Schwartz, and G. V. Pfeiffer, Theoretical Studies of the Binding Energy and Geometry of the H_5^+ Molecular Ion, J. Chem. Phys., 56: 755 (1972).

03:288 THEORETICAL STUDIES OF THE HYDRATED ELECTRON BY USE OF A MOLECULAR CLUSTER MODEL. Naleway, Conrad A., Maurice E. Schwartz and Koichi Funabashi (University of Notre Dame, Radiation Laboratory).

*High quality ab initio SCF-MO studies have been made on sys*tems of one and two water molecules plus an extra electron for numerous different geometries. The energetics of these systems are such that a natural trap for an electron happens to correspond to the well-known Bjerrum faults used to describe properties of ice.

An extension of these ab initio studies on the dimer model of H_2O plus an excess electron is being directed along two alternate routes.

The first approach involves essentially a modified version of the Hückel (tight binding) approximation where all interaction energies are based on the more detailed dimer study. Both single as well as multiband approximations are being investigated.

The second approach attempts to describe the excess electron within a one-electron pseudopotential model. Here all molecular sites are represented as pseudopotential sites. The excess electron wave function will be determined (variationally) within this pseudopotential field. Later extension of the work will embed the molecular cluster plus electron in a dielectric continuum.

Both approaches should lead to a more detailed understanding of the electronic absorption spectrum and of the actual trapping site for the hydrated electron.

ALSO SEE Heavy Element Chemistry: 03:86; Radiation Chemistry: Other; 03:137, 03:147, 03:152, 03:153, 03:154, 03:155; Kinetics and Mechanisms: 03:220; Chemical Spectroscopy: 03:235, 03:237, 03:258, 03:261; Isotope Chemistry: 03:291, 03:293, 03:301, 03:303, 03:304; Thermodynamics: 03:307, 03:309; High-Temperature and Inorganic Chemistry: 03:339; Structural Chemistry: 03:383.

ISOTOPE CHEMISTRY

Studies of equilibrium and kinetic isotope effects and isotope separations.

03:289 MATERIALS AND METHODS FOR THE STUDY OF ISOTOPE EFFECTS IN BIOLOGICALLY IMPORTANT SYSTEMS. Katz, J. J.; Crespi, H. L.; DaBoll, H.; Kostka, A.; Smith, U.; Uphaus, R. A.; and Norris, J. R. Jr. (Argonne National Laboratory, Chemistry Division).

Our research involves the application of stable isotopes (^2H, ^{13}C, ^{15}N, ^{17}O, ^{18}O) to chemical, biological, and biophysical problems. Our current activities fall into three categories: (1) cultivation of living organisms of highly unnatural isotopic composition and the extraction of compounds of biological significance therefrom; (2) structure and function of proteins and enzymes; and (3) the role of chlorophyll in the light conversion act in photosynthesis. In these studies, proteins and photosynthetic pigments of unnatural isotopic composition are key elements in the research.

We are growing various algae, bacteria, etc., on the 160-l (50-gal.) scale in pure heavy water (99.8% ^2H_2O) for the production of deuterated organisms and compounds. The cultivation of organisms of unusual composition has been extended to ^{13}C-algae fed $^{13}CO_2$. These organisms then serve as the source of deuterated (or ^{13}C-) proteins, carbohydrates, lipids, photosynthetic pigments, and the like. Of particular importance is the development of isotope hybrid compounds that are essentially fully deuterated except for ordinary ^1H introduced by biosynthesis into specified positions of the molecule. Thus, isotope hybrid proteins are obtained by growing organisms in ^2H_2O on ^1H-amino acids, which results in proteins that are fully deuterated except for the particular ^1H-amino acid(s) introduced by biosynthesis into side-chain positions. We plan to put another tank into operation, and to extend our operations to cultivate organisms that are depleted in ^{13}C (by using $^{12}CO_2$ from which the ^{13}C has been stripped) to serve as a source of ^{13}C-free compounds.

Because organisms and compounds of unusual isotopic composition find important uses in magnetic resonance spectroscopy, we have an active instrumentation program to develop new and better ways for making effective use of these substances. We have interfaced our nuclear magnetic and electron spin resonance spectrometers to a central Sigma V computer. We are now in the process of interfacing our superconducting 220-MHz spectrometer to the central computer and are well advanced in the direction of using the computer not only for data acquisition and processing, but also for controlling the actual operation of the spectrometer. The great increase in the productivity of these expensive instruments already realized has made it possible to carry out ^1H magnetic resonance at unnatural abundance (^1H in small amounts embedded in a deuterated compound) with remarkable simplification of the spectra. We are actively planning to interface our ENDOR spectrometer to the Sigma V computer, and to develop stochastic excitation of spectra for ^{13}C magnetic resonance.

PUBLICATIONS

Katz, J. J., and H. L. Crespi, Isotope Effects in Biological Systems, in Isotope Effects in Chemical Reactions, C. J. Collins and N. S. Bowman (Eds.), American Chemical Society Monograph, No. 167, Van Nostrand Reinhold Company, New York, 1970, Chap. V, pp. 286-363.

———, G. N. McDonald, and A. L. Harkness, ^1H NMR at Unnatural Abundance. First-order Spectra from Aliphatic and Alicyclic Hydrocarbons by Pulse Fourier Transform Spectroscopy, J. Chem. Soc., D, 542 (1972).

Crespi, H. L., U. Smith, L. Gajda, T. Tisue, and R. M. Ammerall, Extraction and Purification of ^1H, ^2H, and Isotope Hybrid Algal Cytochrome, Ferredoxin, and Flavoprotein, Biochim. Biophys. Acta, 256: 611 (1972).

Taecker, R. G., H. L. Crespi, H. F. DaBoll, and J. J. Katz, Deep-Tank Culture of Blue-Green Algae in H_2O and D_2O, Biotechnol. Bioeng., 13: 779 (1971).

Flaumenhaft, E., R. A. Uphaus, and J. J. Katz, Isotope Biology of ^{13}C. Extensive Incorporation of Highly Enriched ^{13}C in the Alga Chlorella Vulgaris, Biochim. Biophys. Acta, 215: 421 (1970).

03:290 TRITIUM FRACTIONATION BETWEEN WATER AND PROTEINS OR POLYPEPTIDES. R. E. Weston, Jr. (Brookhaven National Laboratory, Chemistry Department).

It is estimated that by the end of the century the rate of production of tritium by ternary fission in nuclear power reactors will equal the natural rate of production by cosmic rays. Therefore, there is some concern about the uptake of tritium by biological systems and by molecules of biological significance. An isotope exchange equilibrium of the form

$$AH + BT \rightleftharpoons AT + BH$$

will, in general, have an equilibrium constant different from unity. This isotopic fractionation is being investigated in the exchange of tritium between water and polypeptides or proteins, using a freeze-drying method to separate the two components. The results obtained for random-chain polyalanine indicate that the fractionation of tritium is quite small in this system. These studies will be extended to polyamino acids with an alpha-helical structure and to proteins.

There is also interest in enlarging this program to include measurements of the rate of exchange of tritium between biologically active molecules and water. In particular, it has been suggested that the exchange from an enzyme inhibitor or cofactor will be influenced by the presence of the enzyme. This should provide a method for investigation of the active site of the enzyme.

03:291 PHENOMENOLOGICAL EFFECTS OF QUANTUM MECHANICAL TUNNELING. R. E. Weston, Jr., M. J. Stern (Department of Chemistry, Yeshiva University). Brookhaven National Laboratory, Chemistry Department.

The rate constant for a chemical reaction involving the motion of hydrogen atoms or ions may be affected by quantum mechanical tunneling through the barrier separating reactants from products. Kinetic isotope effects have often been cited as evidence for this quantum phenomenon.

We are investigating this area, by means of computer experiments in which model reactants and activated complexes are used to calculate vibrational frequencies and rate constant ratios. The specific effects we are searching for are: (i) abnormal differences between isotope effects caused by deuterium and tritium substitution and (ii) abnormal temperature dependence of the deuterium isotope effect, as indicated by large curvatures in the Arrhenius plot, or by abnormal intercepts in such a plot.

Results obtained so far indicate that (i) is not a useful criterion for tunneling whereas (ii) has some merit as a criterion.

PUBLICATIONS

Stern, M. J., and P. C. Vogel, Relative Tritium–Deuterium Isotope Effects in the Absence of Large Tunneling Factors, J. Am. Amer. Chem. Soc., 93: 4664 (1971).

Schneider, M. E., and M. J. Stern, Arrhenium Pre-Exponential Factors for Primary Hydrogen Kinetic Isotope Effects, J. Amer. Chem. Soc., 94: 1517 (1972).

03:292 STUDIES OF CARBON ISOTOPE FRACTIONATION. Takanobu Ishida. Brooklyn College of The City University of New York, Chemistry Department, Bedford Ave and Avenue H, Brooklyn, New York 11210.

The primary purpose of this investigation is to find chemical and physical means for effectively fractionating ^{13}C from its natural abundance. To achieve this objective, experiments are being conducted to obtain data necessary for engineering evaluation of such processes, and theoretical studies are being carried out to interpret such data in light of the isotope effect theory.

Currently, low-temperature distillation of fluorinated hydrocarbons, in particular, chlorotrifluoromethane, tetrafluoromethane, dichlorofluoromethane, chlorodifluoromethane, and fluoroform, is being studied. Systems for chemical purification, two distillation columns covering temperatures from −195 to 0°C, and a catalytic system for the decomposition of the fluorinated methanes to carbon dioxide have been assembled. The unit stage separation factor for the fractionation of ^{13}C will be obtained from the transient behavior of the distillation process.

The shift in zero-point energy on condensation of fluorinated hydrocarbons, due to London dispersion force and various other intermolecular interactions in the liquid phase, is being evaluated. A preliminary result shows that the isotopic inverse vapor pressure effect is most likely to occur in $CClF_3$ and CF_4 at temperatures −80°C and with CCl_2F_2 at temperatures near 0°C. Effects of molecular forces on the isotope effect on thermodynamic properties are under investigation in the light of orthogonal expansion of the reduced partition function.

PUBLICATIONS

Bigeleisen, J., T. Ishida, and W. Spindel, Correlation of Isotope Effects with Molecular Forces. II. Triatomic Molecules. J. Chem. Phys., 55: 5021 (1971).

03:293 THEORETICAL STUDIES ON ISOTOPIC MASS EFFECTS IN CHEMISTRY. Max Wolfsberg. University of California, Department of Chemistry, Irvine, California 92664.

Theoretical studies are being carried out on isotopic mass effects on physical and chemical properties of molecules.

The role of vibrational anharmonicity on isotope effects, in particular isotope effects on equilibria, is being further investigated. Anharmonicity computer programs will be extended to handle more complicated molecules. The evaluation of accurate isotopic partition function ratios (including the effect of anharmonicity) for a variety of molecules will be continued.

Most thinking about isotope effects has been carried out with use of the Born–Oppenheimer approximation, within the framework of which the potential energy surface for nuclear motion is independent of isotopic substitution. Calculations have been almost completed of the effect of corrections to the Born–Oppenheimer approximation on isotopic exchange equilibria involving a number of diatomic hydrides and deuterides. The corrections are significant. The calculations will be extended.

Average values of mean amplitudes and mean square amplitudes of molecular vibrations will be calculated to elucidate isotope effects on some molecular properties.

Classical equations of motion have been integrated exactly to study energy transfer between translations, rotations, and vibrations in nonreactive collisions between molecular systems. Future work in this area will concentrate on collisions between triatomic molecules and atoms.

PUBLICATIONS

Wolfsberg, M., A. A. Massa, and J. W. Pyper, Effect of Vibrational Anharmonicity on the Isotopic Self-Exchange Equilibria $H_2X + D_2X = 2\ HDX$, J. Chem. Phys., 53: 3138-3146 (1970).

Kelley, J. D., and M. Wolfsberg, Exact Classical Calculations on Collisional Energy Transfer to Diatomic Molecules with a Rotational and a Vibrational Degree of Freedom, J. Chem. Phys., 53: 2967-2977 (1970).

03:294 SEPARATION OF ISOTOPES. T. I. Taylor. Columbia University Chemistry Department, New York City, N. Y. 10027.

Chemical exchange between carbon dioxide (CO_2) and amine carbamates ($R_2NCO_2^{\mp}HNR_2$) results in a concentration of ^{18}O in the gas and ^{13}C in the solution phase. A solvent carrier system with thermal reflux for stripping the carbon dioxide from the carbamate is used to test the effectiveness of different amines and solvents. Di-n-butylamine (DNBA) in triethylamine (TEA) as solvent was shown to be practical for the concentration of ^{13}C. A six-section cascade for the preparation of 90% ^{13}C is being operated to study some of the characteristics of the system.

Measurements of single stage separation factors (α) for different amine carbamate systems by batch and by multistage techniques are being continued. Correlations are being made between the effectiveness of amines for separation of ^{13}C and their structure, reaction rates, and thermodynamic properties as well as the physical characteristics of their solutions.

Although nitrogen with more than 99.9% and less than 0.0002% ^{15}N has been prepared by the exchange of NO with HNO_3, studies on the kinetics of the reaction are not yet completed. Further studies include the low-temperature gas chromatographic separation of nitrogen and oxygen isotopes using complexes of nitric oxide.

PUBLICATIONS

Agrawal, J. P., Enrichment of ^{13}C by Chemical Exchange of Carbon Dioxide with Amine Carbamates in Nonaqueous Solvents, Separ. Sci., 6(6): 831 (1971).

———, Fractionation of ^{18}O and ^{13}C Isotopes by Chemical Exchange of Carbon Dioxide with Amine Carbamates, Separ. Sci., 6(6): 819 (1971).

Mathur, B. P., Effect of Chemical Exchange Between D_2 and HBr on the Thermal Diffusion Separation of D and H in a Trennschaukel, J. Chem. Phys., 55: 3966 (1971).

03:295 TUNNELING IN PROTON-TRANSFER REACTIONS IN SOLUTION. Saligrama C. SubbaRao. Lincoln University, Pennsylvania 19352.

There are now a number of investigations of proton-transfer reactions in solution which substantiate the importance of tunnel corrections. From the existing experimental evidence it is possible to make some tentative generalizations about the factors that favor tunneling. The suppositions that seem plausible are that tunneling is favored (a) by a high contribution to the activation energy from repulsion, (b) by a symmetrical energy barrier, and (c) in aqueous solutions.

The data obtained so far tend to be fragmentary and refer to substrates that have little in common with one another. Much more experimental work is needed especially on related series of reactions and on solvent effects to understand the significance of tunneling in proton-transfer reactions. Investigations of this nature, apart from confirming the importance of tunneling corrections, will enlarge our knowledge of the shapes and dimensions of the energy barriers and improve our picture of transiton states.

Rates of base-catalyzed H^+, D^+, and T^+ transfer from several acetylpyridines, acetylfurans, and acetylthiophene will be measured in aqueous medium with the following primary objectives: (a) to see whether the variation in rate as a function of modification to the structure of the substrate could be quantitatively explained; (b) to obtain values of the kinetic hydrogen isotope effects and to see whether the changes could be qualitatively and quantitatively explained, (In this respect accurate work over a wide temperature range should assist in a more complete explanation of the problem.); (c) to see whether curved Arrhenius plots could be obtained and, if so, whether curvature arose from quantum mechanical leakage of protons through the energy barrier. (If tunneling is confirmed then the dimensions (height and width) of the energy barriers will be calculated.); (d) to see whether deviations from Brønsted's relation could be observed when tunneling is significant in reactions where steric hindrance is not important. (It is interesting to see whether it will be possible to observe different values of β from isotopic studies when tunneling is important.); and (e) to test the validity of Swain's relation systematically. (Since the Swain relationship has had few empirical tests and its general validity has been questioned on theoretical grounds, such a study seems necessary.)

03:296 PHOTOCHEMISTRY OF ISOTOPIC MOLECULES. G. M. Begun. (Oak Ridge National Laboratory, Chemistry Division.)

The recent commercial development of a tuneable laser in the far infrared makes possible a promising area of research—photochemistry in the electronic ground state. With such a laser it appears feasible to excite C–H, C=O, C≡N, C=C, and C≡C bond vibrations selectively to the third or fourth overtone by a single photon process. With sufficiently nearly monochromatic beams, isotopically specific activation could be performed with the possibility of isotopic separation upon reaction. This would have an advantage over the electronic excitation in conventional photochemistry in that the subsequent reaction would not so likely proceed via a free radical chain mechanism and thus destroy the specificity. However, the potential for economic isotope separations depends on numerous factors which we intend to explore. To implement this objective, a quadrupole spectrometer has been designed and constructed in such a manner that photochemical reactions may be conducted in the ion source region for continuous monitoring and analysis. Initially, studies will be made of the isotopic reactions of Cl_2 with CO, CH_2F_2, C_4H_8, and C_2H_4 at low pressures. Later, we expect to examine reactions of activated CO, COS, SCl_2, SO_2, and $SOCl_2$ with various substrates with the aim of fractionating carbon and/or sulfur isotopes.

03:297 ORGANIC CHEMISTRY. C. J. Collins, B. M. Benjamin, and V. F. Raaen. (Oak Ridge National Laboratory, Chemistry Division).

The general theme of this work is the application of isotopic methods, together with such techniques as NMR, ir, gas chromatography, and high-speed computing to problems of organic chemistry, both pure and applied. A continuing major interest is the identification of reactive intermediates in a wide variety of reactions that proceed through carbonium ions. In connection with air pollution, we are studying reactions of ^{14}CO with reactants that we hope will give carbonium ions in the gas phase to see whether these cations can trap CO.

The complications in some of our research presented by many alternative reaction pathways have been made tractable by a computer program that can search out all such pathways and tabulate them systematically. This has explained an apparently anomalous product appearing in low yield in a reaction of a deuterated compound, and discovered by a neutron diffraction study of the product. Kinetic isotope effects of ^{14}C and deuterium are being investigated to gain more information about reaction mechanisms, since isotope effect criteria now exist that should tell us whether solvolytic reactions proceed through intermediates or transition states.

PUBLICATIONS

Collins, Clair J., and Charles E. Harding, Molecular Rearrangements. XXVII. The Relative Rates of 6,2- and 3,2-Hydride Shift in Norbornyl Cations, Ann. Chem., 745: 124 (1971).

———, Reactions of Primary Aliphatic Amines with Nitrous Acid, Accounts Chem. Res., 4: 315 (1971).

———, I. T. Glover, M. D. Eckart, V. F. Raaen, B. M. Benjamin, and B. S. Benjaminov, Molecular Rearrangements. XXVIII. Nitrous Acid Deamination of 3-exo-Phenyl-3-hydroxy- and 3-endo-Phenyl-3-hydroxy-2-endo-norbornylamines, J. Amer. Chem. Soc., 94: 899 (1972).

———, and N. S. Bowman (Eds.), Isotope Effects in Chemical Reactions, American Chemical Society, Monograph No. 167, Van Nostrand Reinhold Company, New York, (1971).

Raaen, Vernon F., Ben M. Benjamin, and Clair J. Collins, A Deuterium Tracer Study of 6,1,2-Hydride Shift in Substituted Norbornyl Cations, Tetrahedron Lett., 28: 2613 (1971).

03:298 ISOTOPE CHEMISTRY. J. S. Drury, G. M. Begun, L. L. Brown, L. Landau, D. A. Lee. (Oak Ridge National Laboratory, Chemistry Division).

Chemical reactions that may serve for fractionating isotopes, or for performing other difficult separations, are being examined systematically. Since the chemical exchange technique is most effective for low-mass nuclides, most of our studies are concerned with elements of the first three rows of the periodic chart, but because of the great economic importance of uranium isotopes, that element is also being examined. In general, our investigations are designed to measure the equilibrium constants and kinetics of the exchange reactions, to establish the feasibility of refluxing each isotopic species, to determine pertinent physical and chemical properties of the molecules concerned, and to assess the economic feasibility of the proposed separation process.

Currently, the chemistry of sulfur is being examined with the view of developing a gas–liquid, countercurrent exchange process that can be thermally refluxed. Single-stage fractionation factors in the range 1.01 to 1.02 for $^{34}S/^{32}S$ separations have been measured for reactions involving methyl sulfide and its molecular addition compounds. The prospects for developing a useful system appear attractive.

Measurements are also being made of the isotopic fractionations attainable by ion exchange. Separation factors are being measured for the isotopes of cobalt, calcium, and uranium on sulfonated styrene–divinylbenzene copolymers, polystyrene–divinylbenzene–quaternary amine copolymers, zirconium oxysalts, carboxylic acid resins, and chelating resins.

New, ultraprecise measurements of the isotopic equilibrium constants in exchange reactions involving gaseous and liquid uranium species are being made to establish definitively what contribution, if any, the chemical exchange technique can make to the economics of uranium isotope separation.

PUBLICATIONS

Lee, D. A., Extraction of Osmium Tetroxide and Evidence for Anionic OS(VIII) Species, J. Inorg. Nucl. Chem., 34: 375 (1972).

Brown, L. L., Chemical Exchange Method of Concentrating Carbon Isotopes, U. S. Patent No. 3,607,010, Sept. 21, 1971.

Palko, A. A., L. Landau, and J. S. Drury, Chemical Fractionation of Carbon Isotopes—The Carbon Monoxide System, Ind. Eng. Chem. Process Design Develop., 10: 79 (1971).

03:299 ROTATIONAL ORDERING IN THE SOLID MOLECULAR HYDROGENS. David White. (University of Pennsylvania, Department of Chemistry, Philadelphia, Pennsylvania 19104).

The nature of the intermolecular interactions in the solid and liquid state of the isotopic hydrogens, both radial- and angular-dependent (anisotropic), are being investigated by pulsed nuclear magnetic resonance and calorimetric techniques. In the liquid state the temperature dependence of the spin-lattice relaxation in deuterium is being used to examine the mechanism of molecular diffusion as well as the magnitude of the electric quadrupolar anisotropic intermolecular interactions in both the ground rotational state (J=0, I=2) and first excited state (J=1, I=1). In the solid state, the mechanism of the cooperative ordering of the molecular orientations in the cubic phase of deuterium is being investigated by spin-lattice relaxation measurements employing a spin-echo technique, and from specific heat measurements. Here again the studies focus mainly on the electric quadrupolar anisotropic interactions, which give rise to the librational excitation spectrum in solids consisting of mixtures of ortho and para nuclear spin species. Currently under development is a $^{3}He-^{4}He$ dilution refrigerator for extension of the above studies down to 25 millidegrees, while at the same time permitting measurements at higher pressures where the influence of the valence overlap on the intermolecular interactions in the ordered solid, as well as any effects due to crystal anisotropy, may be seen.

PUBLICATIONS

Wang, Richard, and David White, Deuterium Ortho-Para Analysis by Nuclear Spin-Lattice Relaxation Measurements, Rev. Sci. Instrum., 42: 899 (1971).

———, Malcolm Smith, and David White, Nuclear Spin-Lattice Relaxation in Ortho-Para Mixtures of Solid and Liquid Deuterium, J. Chem. Phys., 55: 2661 (1971).

Meckstroth, Wilma, and David White, Vapor Pressures of Liquid Ortho-Para Solutions of Deuterium: Excess Thermodynamic Functions and Intermolecular Force Constants, J. Chem. Phys., 54: 3723 (1971).

03:300 LOW-TEMPERATURE ELECTROLYTIC ENRICHMENT OF TRITIUM IN WATER. Robert L. Wolke. University of Pittsburgh, Wherrett Laboratory of Nuclear Chemistry, Department of Chemistry, Pittsburgh, Pennsylvania 15213.

The objective of this work is to develop a novel and highly efficient isotopic enrichment method for tritium in water. The method involves electrolysis of the water as a solute in liquid sulfur dioxide at −77°C. This project is currently in a preliminary stage in which the chemical and electrolytic reactions that take place are being characterized under various conditions. Plans are to develop the method on a small scale but not to scale it up for large sample enrichment or to apply it to studies of environmental or geologic processes.

03:301 FUNDAMENTAL STUDIES IN ISOTOPE CHEMISTRY. Jacob Bigeleisen. (University of Rochester, Department of Chemistry, River Campus, Rochester, New York 14627).

Experimental and theoretical studies are directed toward the establishment and understanding of the relationship between isotope effects and molecular and intermolecular forces. Theory and experiment show that effects arising from isotopic substitution are associated almost exclusively with the molecular and intermolecular forces acting at the site of substitution. Thus, isotope effect studies are force probes at the atomic scale. The current experimental program utilizes this property of isotope effects to study liquid structure in simple atomic and molecular fluids. Measurements of vapor pressure isotope effects on simple solids (Ar, Kr, CO_2) is yielding information on the lattice energy and hindered rotation in the solid. Studies of the approach of the isotope fractionation factor for liquid and gaseous argon to the critical temperature have established a critical exponent for $\langle\nabla^2 U\rangle_l - \langle\nabla^2 U\rangle_g$, not too different from the density index β.

PUBLICATIONS

Lee, M. W., D. M. Eshelman, and J. Bigeleisen, Vapor Pressures of Isotopic Krypton Mixtures. Intermolecular Forces in Solid and Liquid Krypton, J. Chem. Phys., 56: 4584 (1972).

———, S. Fuks, and J. Bigeleisen, Vapor Pressures of ^{36}Ar and ^{40}Ar. Intermolecular Forces in Solid and Liquid Argon, J. Chem. Phys., 53: 4066 (1970).

Bigeleisen, J., T. Ishida, and W. Spindel, Correlation of Isotope Effects with Molecular Forces II. Triatomic Molecules, J. Chem. Phys., 55: 5021 (1971).

———, T. Ishida, and W. Spindel, Correlation of Isotope Effects with Molecular Forces I. The Diatomic Molecule, Proc. Nat. Acad. Sci., 67: 113 (1970).

Phillips, J. T., C. U. Linderstromg-Lang, and J. Bigeleisen, Liquid–Vapor Argon Isotope Fractionation from the Triple Point to the Critical Point Mean Laplacian of the Intermolecular Potential in Liquid Argon, J. Chem. Phys., 56: 5053 (1972).

03:302 A NUCLEAR MAGNETIC RESONANCE STUDY OF THE GAS–LIQUID CRITICAL POINT IN HYDROGEN AND ITS ISOTOPIC MODIFICATIONS. Max Lipsicas. (Yeshiva University, Belfer Graduate School of Science, 2495 Amsterdam Ave., New York, N. Y. 10033).

This work represents a detailed nmr study of the gas–liquid critical region in H_2 and its isotopic modifications, HD and D_2. The nmr measurements encompass spin lattice relaxation times, T_1, relative density, ρ, (proportional to the amplitude of the nmr signal) and self-diffusion coefficient, D, (by spin labeling). All measurements are made for both the gas and liquid phases.

The first part of this study is directed at the H_2 system itself. H_2 is in reality a quantum mechanical two-component mixture of ortho-hydrogen (I=1, J=1) and para-hydrogen (I=0, J=0). (Only the lowest rotational states need to be considered at the temperature of the experiments). The aim of our work is to obtain information on:

(1) The dependence of T_c and P_c on the ortho-H_2/para-H_2 ratio. We examine the coexistence curve both by measuring gas and liquid relative densities, ρ_g and ρ_l, and by measuring T_1 for the gas and liquid phases. The coexistence curve for a quantum system is of great interest, as well as the dependence of the coexistence curve, and of T_c and P_c, on the ortho-H_2/para-H_2 ratio.

(2) The proton spin–lattice relaxation time T_1. T_1 for an ortho-H_2/para-H_2 mixture depends on both two-body and three-body molecular correlations. By examining T_1 as a function of the ortho-H_2/para-H_2 ratio, it is possible to separate out the integrated three-body molecular correlation in the critical fluid, and hence obtain information on critical fluctuations.

(3) The behavior of the self-diffusion coefficient in the critical region. Information is still lacking on the behavior of transport properties in the critical region, and especially in quantum mechanical systems.

In later stages of this study we will examine D_2 and HD in a similar way. In HD there are no nuclear symmetry considerations and thus only D_2 exists in ortho and para forms. HD is, however, still a quantum mechanical fluid and will be studied both by proton magnetic resonance and deuteron magnetic resonance. In addition to acquiring information on the critical behavior of D_2 and HD, it will be possible to compare the behavior of H_2, D_2, and HD and thus examine the way in which quantum mechanical considerations affect the critical regime.

A specially constructed cryostat is being used for this work. The cryogenic fluid is liquid para-hydrogen and a combination of helium exchange gas and a heat rod are being used to establish a very constant, and thermal gradient-free, temperature over the sample. The system is designed to allow running times under constant conditions for many hours to ensure that all measurements are made at thermal equilibrium. The required ortho–para mixture is made in a catalysis chamber located in the working space of the cryostat. After catalysis to the required mixture ratio, the mixture is allowed to enter the sample cell via a special cold valve, which is then closed off.

Preliminary measurements of T_1 and ρ have been made and we are now in the process of obtaining final data on normal hydrogen (75% ortho). The measurements will then be extended to samples of lower ortho-H_2 concentration.

03:303 STABLE ISOTOPE STUDIES. William Spindel. (Yeshiva University, Department of Chemistry, Belfer Graduate School of Science, 2495 Amsterdam Avenue, New York, New York 10033).

The primary objective of this research program is to gain a better understanding of the magnitudes and bases of isotope exchange equilibria involving the light elements, such as carbon, nitrogen, and oxygen, and to apply this knowledge toward the development of more efficient and economical processes for concentrating the rarer isotopes of these elements.

Our studies involve both theoretical and experimental aspects of isotope effect studies. Recent theoretical studies have been concerned with an examination of the relationships between reduced partition function ratios of isotopic molecules and molecular force constants in diatomic and triatomic molecules. These relationships were elucidated by developing the partition functions in terms of finite orthogonal polynomial expansions. Currently we are attempting to develop a program for estimating force constants (or changes in force constants upon condensation) directly from measurements of equilibrium isotope effects and their temperature dependences (such as vapor pressure ratios of isotopic molecules) by the application of the same type of polynomial expansions.

Some preliminary experiments have been carried out on the fractionation of ^{13}C by the distillation of phosgene ($COCl_2$). An inverse isotope effect has been observed at 0°C, with ^{13}C concentrating in the distillate. These experiments will be continued and extended to determine the absolute and relative magnitudes of the vapor pressure ratios for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ in this compound, and to observe their temperature dependence. The feasibility of phosgene distillation for ^{13}C enrichment will be examined.

PUBLICATIONS

Bigeleisen, J., Takanobu Ishida, and William Spindel, Correlation of Isotope Effects with Molecular Forces. I. The Diatomic Molecule, Proc. Nat. Acad. Sci., 67: 113 (1970).

———, Takanobu Ishida, and William Spindel, Correlation of Isotope Effects with Molecular Forces. II. Triatomic Molecules, J. Chem. Phys., 55: 5021 (1971).

JeeVanandam, M., Vapor Pressure Isotope Effect Near the Triple Point, J. Chem. Phys., 55: 5735 (1971).

03:304 ISOTOPE EFFECTS ON RATE AND EQUILIBRIUM PROCESSES. Marvin J. Stern. (Yeshiva University, Department of Chemistry, Belfer Graduate School of Science, Amsterdam Avenue, New York, New York 10033).

The underlying and unifying theme of the researches carried out under this contract has been the study of isotope effects from a theoretical point of view in order: (i) to gain a better understanding of the causes and manifestations of the basic isotope effect phenomena that have both academic and practical applications and (ii) to develop methods for extracting, from experimental data, important physicochemical information such as the extent of quantum mechanical tunneling through a potential energy barrier and bonding-force changes occurring during a chemical reaction. Although the researches that have been carried out have been almost exclusively theoretical, it is now planned to change the nature of the program into a combined experimental–theoretical one. Current projects in this program are: (i) a theoretical study of the manifestations of quantum mechanical tunneling on kinetic isotope effects; (ii) the theoretical development of a method of extracting detailed information as to the force constant changes occurring during a reaction from secondary deuterium kinetic isotope effects; and (iii) an experimental study, using the stopped-flow method, of proton-transfer, ion-pair formation reactions. Future researches will include the use of the stopped-flow and temperature-jump methods to study the effects of quantum mechanical tunneling on kinetic isotope effects, especially as they relate to processes of fundamental biochemical and biophysical importance.

PUBLICATIONS

Vogel, P. C., and M. J. Stern, Temperature Dependences of Kinetic Isotope Effects, J. Chem. Phys., 54: 779-796 (1971).

Stern, M. J., and P. C. Vogel, Relative Tritium–Deuterium Isotope Effects in the Absence of Large Tunneling Factors, J. Amer. Chem. Soc., 93: 4664-4675 (1971).

———, and P. C. Vogel, Relative $^{14}C-^{13}C$ Kinetic Isotope Effects, J. Chem. Phys., 55: 2007-2013 (1971).

———, M. E. Schneider, and P. C. Vogel, Low-Magnitude, Pure-Primary, Hydrogen Kinetic Isotope Effects, J. Chem. Phys., 55: 4286-4290 (1971).

Schneider, M. E., and M. J. Stern, Arrhenius Preexponential Factors for Primary Hydrogen Kinetic Isotope Effects, J. Amer. Chem. Soc., 94: 1517-1522 (1972).

ALSO SEE Radiation Chemistry: Other; 03:142, 03:163, 03:167; Photochemistry and Energy Transfer: 03:170, 03:174, 03:177, 03:189; Hot Atom Chemistry: 03:206; Kinetics and Mechanisms: 03:211; Chemical Spectroscopy: 03:241; High-Temperature and Inorganic Chemistry: 03:363; Structural Chemistry: 03:384; Separations Chemistry: 03:419; Engineering Chemistry: 03:429, 03:432, 03:433, 03:435.

THERMODYNAMICS

Studies of the thermodynamics and thermochemistry of chemical substances.

03:305 THERMODYNAMIC AND MAGNETIC PROPERTIES OF SOLIDS. Gerstein, B. C. (Ames Laboratory, Chemistry Division).

The present work in this group involves investigations of the behavior of valence electrons in three types of simple model solids via heat capacity and susceptibility measurements, and tight binding band calculations. The systems chosen represent a broad range of interactions in solids. These are: (a) Double salts of the stoichiometry A_aMX_b in which chains or sheets of transition metal atoms, M, bridged by halogen atoms, X, are separated by alkylated ammonium atoms, A. An example of such a system is dimethylammoniumtetrachloromanganate(II), $((CH_3)_2NH_2)_2MnCl_4$, a two dimensional system. The thermodynamic behavior of these salts is used to test theoretical approximations to the fundamental interaction leading to cooperative magnetism, a phenomenon extensively utilized in devices such as computer memory cores and electric motors. (b) A_xMO_3 tungsten bronze-type nonstoichiometric oxides, in which a 5d transition metal, M, forms an oxide that is capable of being doped with another metal, A, (for example sodium) over a composition range, x. Examples are alkali metal tungsten bronzes, Na_xWO_3, with $0 \le x \le 0.9$. These compounds are valuable as model systems because they exhibit almost every known interaction of valence electrons in the solid state. (c) Rare earth alloys and compounds, in which the well-shielded 4f shell is used as a probe for determining the magnitude of interactions such as crystal field effects. These interactions are critical to the magnetic behavior of the rare earths. Work for the immediate future involves: (a) testing the two dimensionality of the interaction in $((CH_3)_2NH_2)_2MnCl_4$ by a thermal and magnetic study of the isostructural compound $((CH_3CH_2CH_2)_2NH_2)_2MnCl_4$ in which propylammonium groups lead to interlayer spacings larger than in the methylammonium compound; (b) revision of a currently operating program for tight binding band calculations of A_xMO_3 solids to include three and four center interactions; and (c) completion of initial susceptibility measurements on a Lu–Tm alloy to complement a thermal study of the crystal field interaction in rare earth metals.

PUBLICATIONS

Gerstein, B. C., and F. Olander, Initial Susceptibility Study of Thermal Hysteresis in Gd in the Neighborhood of the Curie Region; Frequency Dependence of the Magnetization, J. Appl. Phys., 42: 3438 (1971).

———, W. A. Taylor, W. D. Shickell, and F. H. Spedding, Heat Capacity of Scandium from 6 to 300°K, J. Chem. Phys., 54: 4723 (1971).

———, F. D. Gehring and R. D. Willett, Models and Magnetism in One Dimensional Systems; Low Temperature Magnetic Susceptibilities of Dimethylammonium Trichlorocuprate(II), and Tetramethylammonium Trichloronickelate(II), J. Appl. Phys., 42: 1932 (1972).

Taylor, W. A., B. C. Gerstein, W. D. Shickell, and F. H. Spedding, A Thermal and Magnetic Study of Crystal Field Splittings in Dilute Rare Earth Alloys I: $Lu_{0.9035}Er_{0.0965}$, J. Chem. Phys., 56: 2722 (1972).

Spedding, F. H., D. C. Rulf, and B. C. Gerstein, Thermal Study of Entropies and Crystal Field Splittings in Heavy Rare Earth Trichloride Hexahydrates. Heat Capacities from 5–300°K, J. Chem. Phys., 56: 1498 (1972).

03:306 THERMODYNAMIC PROPERTIES OF INORGANIC COMPOUNDS. Tevebaugh, A. D., and W. N. Hubbard. (Argonne National Laboratory, Chemical Engineering Division).

Thermodynamic properties of selected inorganic substances are being determined calorimetrically. The main thrust is to obtain data for compounds of special interest in nuclear technology and high-temperature chemistry. Two types of data are being sought: room temperature enthalpies of formation and high-temperature enthalpy increments. From these measurements, the high-temperature thermodynamic properties and the chemical equilibrium behavior of a large variety of substances can be predicted. Combustion bomb calorimetry, hypergolic reaction calorimetry, and flow reaction calorimetry, all with either oxygen or fluorine as oxidants, and solution calorimetry are used in enthalpy of formation measurements. High-temperature enthalpy measurements are being made by means of two drop calorimeters: one with a maximum operating temperature of about 1600°K and the other with a maximum operating temperature of about 2500°K.

Recent work has been the determination of the thermodynamic properties of Na_2C_2 in equilibrium with sodium and graphite up to 800°C. This work is important because Na_2C_2 is postulated as being the species that transports carbon between various steel structures in sodium-cooled reactors. Also of interest to the LMFBR program is the stability of Na_3UO_4, a compound that may form when fuel comes in contact with the sodium coolant. The enthalpy of this compound from 600 to 800°K was determined by drop calorimetry.

Plans are being made to determine the thermodynamic properties of a number of other compounds of interest to the LMFBR program. These compounds include $CsMoO_4$, $CsUO_4$, Rb_2MoO_4, Cs_3CrO_4, TeF_6, Tc_2O_3, Pu_2O_3, PuF_4, and PuF_6.

PUBLICATIONS

Fredrickson, D. R., and M. G. Chasanov, The Enthalpy of Molybdenum Disulfide to 1200°K by Drop Calorimetry, J. Chem. Thermodyn., 3: 693 (1971).

———, and M. G. Chasanov, The Enthalpy of Ruthenium Dioxide to 1200°K by Drop Calorimetry, J. Chem. Eng. Data, 17: 21 (January 1972).

Flotow, H. E., D. W. Osborne, P. A. G. O'Hare, J. L. Settle, F. C. Mrazek, and W. N. Hubbard, Uranium Diboride: Preparation, Enthalpy of Formation at 298.15°K, Heat Capacity from 1 to 350°K, and Some Derived Thermodynamic Properties, in

Proceedings of the First International Conference on Calorimetry and Thermodynamics, Warsaw, Poland, August 31–September 4, 1969, Polish Science Publishers, 1971, p. 197.

Greenberg, E., H. M. Feder, and W. N. Hubbard, The Thermochemistry of HF: The Enthalpy of Formation of Liquid HF, in Proceedings of the First International Conference on Calorimetry and Thermodynamics, Warsaw, Poland, August 31–September 4, 1969, Polish Science Publishers, p. 275.

O'Hare, P. A. G., and A. C. Wahl, Dissociation Energy, Ionization Potential, Electron Affinity, Dipole and Quadrupole Moments of Chlorine Monoxide (ClO,$^2\pi$) from Ab Initio Molecular Orbital Calculations, J. Chem. Phys., 54: 3770 (1971).

03:307 THE INVESTIGATION OF ELEMENTARY EXCITATIONS IN QUANTUM FLUIDS: THE THERMODYNAMICS AND TRANSPORT PROPERTIES OF LIQUID ^{3}He AND ^{4}He.

Abraham, B. M. (J. B. Ketterson and P. R. Roach, Solid State Sciences Division). (Argonne National Laboratory, Chemistry Division).

The objective of the program is to gather thermodynamic and transport data on liquid helium in the mK temperature range, which can be used to test the predictions and calculations derived from many-body theory. Many-body theory (quantum statistical mechanics of interacting systems) impinges on nearly all of modern physics, e.g., theories of the nucleus, of neutron stars, of metals, and of superconductors; and the study of the thermodynamic and transport properties of the two helium liquids (^{3}He and ^{4}He) has played a key role in the development of the theory.

If a detailed knowledge of the excitation spectrum (energy–momentum relation) is known, then the transport properties can be calculated. Accoustic waves are a very powerful microscopic probe to determine the low-momentum, long-wavelength part of the spectrum. In order to employ them we have had to develop a very sensitive ultrasonic interferometer. The measurements to date have uncovered serious discrepancies in the existing theory, and we have definitely eliminated one theoretical approach. Our goal is to establish unambiguously the excitation spectrum for ^{4}He in the long-wavelength limit. While our frequency capability is already unique for this sort of measurement, we now find it necessary to extend it from 200 to 2000 MHz.

Another aspect of the program is the determination of the quasiparticle–phonon interactions in solutions of ^{3}He–^{4}He and the determination of the quasiparticle–quasiparticle interactions in liquid ^{3}He. An error in the temperature scale, discovered by us, has brought into question some of the previous work on ^{3}He. We are currently trying to improve the temperature scale, refrigeration techniques, and heat transfer techniques, all of which are necessary before substantial progress can be made with the main problem stated above.

PUBLICATIONS

Abraham, B. M., O. G. Brandt, and Y. Eckstein, The Pressure Dependence of the Solubility of Liquid ^{3}He in Superfluid ^{4}He, in Proceedings of the 12th International Conference on Low Temperature Physics, Kyoto, Japan, September 4–10, 1970, E. Kanda (Ed.), Academic Press of Japan, 1971.

______, and D. W. Osborne, Experimental Determination of the Molar Volume and Derivation of the Expansion Coefficient, Entropy Change on Compression, Compressibility and First Sound Velocity for Liquid ^{3}He from 35 to 1200 mK and from the Saturation Pressure to 24 atm, J. Low Temp. Phys., 5: 335 (1971).

______, D. Chung, Y. Eckstein, J. B. Ketterson, and P. R. Roach, Sound Propagation, Density, and Viscosity in Liquid ^{3}He, J. Low Temp. Phys., 6: 521 (1972).

Roach, P. R., J. B. Ketterson, B. M. Abraham, and M. Kuchnir, Thermal Expansion of Liquid ^{4}He Between 0.1 and 0.7 K, Phys. Lett., A, 39: 251 (1972).

______, B. M. Abraham, J. B. Ketterson, and M. Kuchnir, Absence of a Quadratic Term in the ^{4}He Excitation Spectrum, Phys. Rev. Lett., 29: 32 (1972).

03:308 LOW-TEMPERATURE CALORIMETRY OF COMPOUNDS OF HEAVY ELEMENTS AND OF REACTOR MATERIALS.

Osborne, D. W., H. E. Flotow, and F. Schreiner. (Argonne National Laboratory, Chemistry Division).

The primary objective of this program is the determination of thermodynamic properties of selected substances of potential interest to the AEC. Among the substances currently being studied are: (a) compounds of plutonium and uranium such as $^{242}PuF_3$, $^{242}PuF_4$, Na_3UO_4, and UFSi; (b) compounds of important fission products such as cesium, molybdenum, and technetium (e.g., Cs_2O, Mo_2C, and TcF_6); and (c) other compounds of interest in reactor technology such as Na_2C_2.

The method is to measure the heat capacity (and related properties such as heats of transition and fusion) between room temperature and temperatures that are sufficiently low to permit a reliable extrapolation to 0°K. From the heat capacity data it is possible to calculate other properties important in chemical thermodynamics, such as entropy, enthalpy increments from 0°K, and Gibbs energy increments from 0°K. These results can be combined with measurements of enthalpies of reaction at room temperature and with heat capacity or enthalpy measurements extending to high temperatures, in order to predict stability, equilibrium constants, and electrode potentials that may be difficult or impossible to measure directly.

Low-temperature calorimetry can also provide information of interest in solid state physics and in theoretical chemistry. For example, Schottky anomalies and λ anomalies may occur in the heat capacity curve, which can be correlated with other properties such as magnetic susceptibility or which can yield the low-lying energy levels in the solid. The heat capacity curve may supplement results obtained from theoretical lattice dynamics or from inelastic scattering or from velocity-of-sound measurements. Another example is that a comparison of the entropy calculated from the calorimetric data with the entropy calculated from statistical mechanics can often be used to test a molecular model or to evaluate a missing vibrational frequency or to determine a barrier hindering internal rotations in the molecule.

PUBLICATIONS

Flotow, H. E., D. W. Osborne, and R. R. Walters, Thorium Monosulfide: Heat Capacity and Thermodynamic Properties from 1–350°K. Re-evaluation of the Magnetic Entropy of Uranium Monosulfide, J. Chem. Phys., 55: 880–886 (1971).

Osborne, D. W., F. Schreiner, and H. Selig, Calorimetric Study of Iodine Pentafluoride: Heat Capacity Between 5 and 350°K, Enthalpy of Fusion and Vaporization, Standard Entropy of the Vapor, and Other Thermodynamic Properties, J. Chem. Phys., 54: 3790-3798 (1971).

______, B. Weinstock, and J. H. Burns, Heat Capacity, Enthalpy of Fusion, and Thermodynamic Properties of NpF_6 from 7 to 350°K, J. Chem. Phys., 52: 1803-1810 (1970).

______, and F. Schreiner, Magnetic Anomaly in the Heat Capacity of TcF_6 at 3.12°K, in Proceedings of the 12th International Conference on Low Temperature Physics, Kyoto, Japan, September 4–10, 1970, E. Kanda (Ed.), Academic Press of Japan, 1971, pp. 797-798.

Schreiner, F., D. W. Osborne, A. V. Pocius, and E. H. Appelman, The Heat Capacity of Potassium Perbromate, $KBrO_4$, Between 5 and 350°K, Inorg. Chem., 9: 2320-2324 (1970).

03:309 CORRELATION OF ENTROPY AND ENERGY.

Thorn, R. J., and J. R. McCreary. (Argonne National Laboratory, Chemistry Division).

Two principles based on statistical thermodynamic studies have proven useful in guiding some of our efforts. The first may be stated somewhat as follows: With increasing energy, as the temperature increases without limit, the entropy approaches a finite value in a bound system which depends on the structure of the system.

The second states that for a sequence of similar chemical reactions (in particular where orbital symmetry is conserved at the reacting site) the change in entropy is monotonically related to the change in enthalpy.

The latter principle is particularly useful in distinguishing systematic from random errors and both are useful in developing systematics which permit interpolation and extrapolation of thermochemical data in a sequence of compounds.

As an example, we have rather complete information on the enthalpies and entropies of fusion and sublimation for the lanthanide trifluorides. Two linearly correlated subsets of data are found, corresponding to the two alternate crystal structures, triclinic and orthorhombic.

These properties can be further correlated with the actual energy levels found by photoelectron spectroscopy for this series.

PUBLICATIONS

Norman, J. H., P. Winchell, and R. J. Thorn, Fundamental Nature of the Correlation of ΔH vs. ΔS: Lanthanide Fluoride Complexes, Inorg. Chem., 10: 2365-2368 (1971).

Thorn, R. J., Analysis of Sets of Determination of ln p vs. T^{-1}: Correlation of ΔH^0 and ΔS^0, High Temp. Sci., 3(3): 197-218 (1971).

McCreary, J. R., and R. J. Thorn, Correlation of Entropy and Enthalpy in Analyses of Systematic Errors: Sublimation of Magnesium, High Temp. Sci., 3(4): 300-329 (1971).

3:310 COMPUTER EVALUATION OF EQUILIBRIUM CONSTANTS FROM SPECTROPHOTOMETRIC DATA: THE PALLADIUM CHLORIDE–BROMIDE SYSTEM.

Newman, L., S. Feldberg, and P. Klotz. (Brookhaven National Laboratory, Department of Applied Science).

A computer method of evaluating equilibrium constants from spectrophotometric data has been developed for the following type of chemical system:

$$MX_m + nY \overset{\dagger\beta_n}{\rightleftharpoons} MY_nX_{m-n} + nX$$

The basis of the technique is a novel and simple method of graphing the error surface in the region of minimum error. Extinction coefficients for all species are also evaluated. Uncertainties in log $\dagger\beta_n$ are estimated by comparison of values obtained in separate experiments.

Very precise spectrophotometric data (±0.001 absorbance units) for the $PdBr_nCl_4^{2-}$ tetrahedral complexes were obtained for a wide range of lithium/bromide/chloride concentration ratios. The calculated values of log $\dagger\beta_n$ are in reasonable agreement with graphically analyzed data of previous workers.

The computer method was also used along with a graphical method to evaluate equilibrium constants for measurements performed in acetonitrile. There is an almost statistical distribution of the species in both systems. However, the stability of $PdCl_4^{2-}$ is $10^{2.4}$ times greater than that of $PdBr_4^{2-}$ in acetonitrile. This is not only an inversion of the relative stability in water but a change of 6.5 orders of magnitude.

It was also found that the measurement of mixed ligand complexation appears to be a better method of determining the relative stability of simple ligand complexes than measurements involving the individual systems.

Other systems will be the subject of future investigations.

03:311 THE FORMATION CONSTANTS FOR THE MIXED METAL COMPLEXES BETWEEN INDIUM(III) AND URANIUM(VI) WITH MALIC, CITRIC, AND TARTARIC ACIDS.

Newman, L., and P. Klotz. (Brookhaven National Laboratory, Department of Applied Science).

The formation of mixed metal complexes has not been examined to any significant extent and very little quantitative data are available concerning their formation constants. Such constants have been determined for the mixed metal complexes between indium(III) and uranium(VI) with malic, citric, and tartaric acids. In the cases of malic and tartaric acids the equilibrium can be written as

$$UO_2^{2+} + In^{3+} + 2\ H_3L = UO_2InL_2^{-} + 6\ H^+.$$

The logarithms of the equilibrium constants are −7.62 for the malate system and −7.14 for the tartrate. In the case of citric acid the equilibrium is

$$UO_2^{2+} + In^{3+} + 2\ H_4L = UO_2InL_2^{3+} + 8\ H^+$$

where two of the protons come from the hydroxyl groups. The logarithm of the constant is −11.58. Infrared measurements on trilaurylamine (tridodecylamine) extracts of the mixed metal complexes have been made and are discussed.

The dimerization constant for the formation of $(UO_2\ \text{citrate})_2$ was determined potentiometrically and found to agree with the literature values. However, arguments are presented for the necessity of recalculating the values presented in the literature for the equilibrium

$$UO_2^{2+} + H_3L = UO_2L^- + 3\ H^+.$$

The logarithms of the recalculated values are −7.40 for malate, −6.30 for citrate, and −6.85 for tartrate.

03:312 STUDY OF CRITICAL PHENOMENA BY NEUTRON SCATTERING.

Corliss, L. M., and J. M. Hastings. (Brookhaven National Laboratory, Chemistry Department).

In the vicinity of magnetic ordering transitions, magnetic systems undergo large spontaneous spatial and temporal fluctuations in the degree of local magnetic order. These fluctuation phenomena are characteristic of all second order phase transitions and thus the critical point behavior of magnetic systems strongly resembles that found, for example, in gas–liquid systems, in binary liquid mixtures, and in order–disorder alloys. Second order phase transitions are partially understood at present in terms of microscopic models and theories of the general properties of correlation functions. Many of these ideas are highly speculative and consequently experimental confirmation is particularly important in guiding current theoretical efforts. Inelastic neutron spectrometry is now capable of providing detailed and quantitative information on critical point behavior; the space and time dependence of the fluctuations are obtained from the variation of scattered intensity with momentum and energy transfer. The neutron-scattering technique has already yielded valuable results on some prototype systems and will be applied to new materials such as ferrites. Investigations will also be carried out to test predictions of critical point behavior in certain pyrite structures exhibiting a new form of field-induced ferromagnetism.

PUBLICATIONS

Tucciarone, A., H. Y. Lau, L. M. Corliss, A. Delapalme, and J. M. Hastings, Quantitative Analysis of Inelastic Scattering in Two-Crystal and Three-Crystal Neutron Spectrometry; Critical Scattering from $RbMnF_3$, Phys. Rev., B, 4: 3206 (1971).

______, L. M. Corliss, and J. M. Hastings, Neutron Investigation of the Spin Dynamics in Paramagnetic $RbMnF_3$, J. Appl. Phys., 42: 1378 (1971).

______, J. M. Hastings, and L. M. Corliss, Theoretical and Experimental Spin Relaxation Functions in Paramagnetic $RbMnF_3$, Phys. Rev. Lett., 26: 257 (1971).

03:313 HIGH-PRESSURE CHEMISTRY.

Jura, George. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

At the present time two general fields of investigation are being pressed: the energetics of metals as a function of pressure and temperature and the infrared spectra of materials of interest as a function of pressure.

A technique for the determination of the heat capacity by a pulse technique in the microsecond range has been developed. The method can be used for heat capacity determination to very high pressures. The temperature range in principle can vary from 77°K upwards. The method is not restricted for use in pressure apparatus. It can be used at one atmosphere, and the preliminary work indicates that it is faster, and with the proper instrumentation could be as good as and faster than the presently available methods. Preliminary work has been done at one atmosphere to a temperature of 750°C. There is no indication in the experiments to indicate that this is an upper limit. In principle, the method should be applicable to the melting point of the pure or alloyed metal. The work has been done on metallic iron from about 100°K to room temperature and pressures of 100 kbar, and the results seem to be consistent within a few tenths of a percent. It is believed that even better results can be obtained with better voltage–time measurements. It also seems to be possible to determine the heats of transition between solid phases directly with the method. The heat leak in the system must be more carefully studied before any definitive results can be obtained. These experiments, whether performed at high pressures or at one atmosphere, are basic in the understanding of the energetics of metals and alloys.

It is possible to obtain infrared spectra of one atmosphere quality to a pressure of at least 40 kbars. Reflectivity measurements are also possible. Much information can be obtained in this manner concerning the internal modes of many molecules as the external potential is varied. This is of great importance in the understanding of the internal modes of motion.

03:314 LOW-TEMPERATURE PROPERTIES OF MATERIALS.

Phillips, Norman E. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

In this research information that contributes to an understanding of the properties of materials is obtained by heat capacity measurements at low temperatures. Several metal–insulator transitions, in V_2O_3 and SmS, are being studied by measurements of the heat capacity at pressures up to 20 kbar. These pressures are high enough to produce a metallic state in both substances. Similar apparatus will be used to study the pressure dependence of the heat capacity of cerium, lanthanum, and uranium. In these metals the experiments will give information related to the volume dependence of the energies of the 4f or 5f electrons and their role in the electronic and magnetic properties.

We are designing improved apparatus for the measurement of the heat capacity of liquid ^4He at temperatures to about 1°K. These experiments are expected to give more quantitative data on the phonon spectrum.

Experiments on the properties of dilute magnetic alloys are continuing. Among the systems being studied are dilute solutions of rare earth metals in noble metals.

A series of related experiments on the powdered CMN (cerium magnesium nitrate $(Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O)$) temperature scale and the Kapitza resistance between magnetic materials and ^3He

will be initiated. The first step will be to compare the powdered CMN temperature scale with a γ-ray anisotropy thermometer by adiabatic demagnetization of a cell containing liquid ^{3}He, powdered CMN, and a γ-ray thermometer attached to copper fins. Some preliminary information on the Cu$-^3$He Kapitza resistance will be obtained in the same experiment. In later experiments the field dependence of the CMN$-^3$He Kapitza resistance will be studied to test theories of the magnetic energy transfer. The experiments may then be extended to metallic systems containing magnetic impurities.

PUBLICATIONS

Triplett, B. B., and N. E. Phillips, Low Temperature Heat Capacity of $Ni_{0.62}Rh_{0.38}$, Phys. Lett., A, 37: 443 (1971).

______, and N. E. Phillips, Calorimetric Evidence for a Singlet Ground State in CuCr and CuFe, Phys. Rev. Lett., 27: 1001 (1971).

Thorp, T. L., B. B. Triplett, W. D. Brewer, M. L. Cohen, N. E. Phillips, D. A. Shirley, and J. E. Templeton, Search for Superconductivity in Lithium and Magnesium, J. Low Temp. Phys., 3: 589 (1970).

Lambert, M. H., J. C. J. Brock, and N. E. Phillips, Calorimetric Determination of Density of Electronic States in Alpha-Phase Indium Alloys. I. Alloys with Tin, Phys. Rev., B, 3: 1816 (1971).

Phillips, N. E., Low Temperature Heat Capacities of Metals, CRC Crit. Rev. Solid State Sci., 2: 467 (1972).

03:315 SOLVENT EXTRACTION OF STRONG ACIDS. Diamond, Richard M. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

There have been two main reasons for these investigations: (1) the identification and study of the various possible protonic species extracted, e.g., the solvated H_3O^+ ion; (2) a study of the factors influencing the solvent extraction of ionic species in general, e.g., the nature of the solvent, aggregation of ionic species, and properties of the extractant. The original work was with tributyl phosphate (TBP) in CCl_4 and isooctane; the existence of $H_3O^+ \cdot 3TBP$ was indicated with additional water molecules probably bridging between the protons and TBP. More recent studies with more polar solvents also showed a 2 : 1 TBP : H$^+$ species. We believe this is just an example of stepwise complexing of the H_3O^+ by TBP; and ir spectra indicate essentially the same (H_3O^+) structure. Our present work uses trioctylphosphine oxide (TOPO) as extractant. This is more basic than TBP, and so we find that two molecules of TOPO can abstract the proton from water to form an essentially anhydrous complex, TOPO$\cdots$H$^+\cdots$OPOT, with an ir spectrum entirely different from that of the TBP complexes. The proton is less well protected in this cation, and so the extraction is more sensitive to the nature of the diluent and anion than in the TBP case; but in both systems it has been possible to correlate the degree of extraction with the properties of the diluent and anion in a reasonable way. The increased ionic aggregation with the TOPO complex leads to interesting activity coefficient effects that are being studied independently by means of osmometric measurements, and it is hoped to continue this type of comparison with the more highly aggregated alkylammonium salt systems.

03:316 SEPARATIONS CHEMISTRY RESEARCH — FUNDAMENTAL CHEMISTRY. McDowell, W. J., J. W. Roddy, B. Weaver, R. D. Baybarz. (Oak Ridge National Laboratory, Chemical Technology Division).

The purpose of fundamental studies in the separations chemistry program is to increase the knowledge of the chemistry and mechanisms of separations methods, and thus to improve, extend, or define the limits of their process, analytical, and physicochemical applications. The scope includes the investigation and improvement of the physicochemical means used for these studies, development and use of some of the separations methods as versatile physicochemical tools, and collection of thermodynamic and other data for some important materials. Solvent extraction and chromatography are the major but not exclusive classes of separation methods studied.

Current work includes: (1) continued detailed study of selected extraction systems; (2) investigation of aqueous metal ion complexes, especially in the moderate to high-ionic-strength solutions that are essential to some separations systems, together with work on both theory and techniques for approximating the thermodynamic activities of ions and neutral species in such solutions; (3) kinetics measurements in extraction and chromatography, in systems displaying metal–metal interactions, as an adjunct to equilibrium measurements of complexing, and in the study of uranyl photochemistry; (4) properties of selected compounds of the transplutonium actinides; and (5) continued use and improvement of vapor pressure depression measurements to determine the organic phase activity coefficients and aggregation numbers needed in the study of various phase equilibrium systems.

PUBLICATIONS

Harmon, H. D., J. R. Peterson, W. J. McDowell, and C. F. Coleman, The Tetrad Effect: The Thiocyanate Complex Stability Constants of Some Trivalent Actinides, J. Inorg. Nucl. Chem., 34: 1381 (1972).

Roddy, J. W., C. F. Coleman, and S. Arai, Mechanism of the Slow Extraction of Iron(III) from Acid Perchlorate Solutions by Di(2-ethylhexyl)phosphoric Acid in n-Octane, J. Inorg. Nucl. Chem., 33: 1099 (1971).

Weaver, Boyd, and J. N. Stevenson, Relative Oxidation Potentials of the Bk(IV)–Bk(III) and Ce(IV)–Ce(III) Couples in Acid Solutions, J. Inorg. Nucl. Chem., 33: 1877 (1971).

Weaver, B., and R. R. Shoun, Basicities of Trivalent Actinides and Lanthanides and Solubilities of Their Hydroxides, in Proceedings of the 9th Rare Earth Research Conference, USAEC Report CONF-711001, p. 322, 1971.

McDowell, W. J., Equilibria in the System: Di(2-ethylhexyl) phosphoric Acid–Benzene–Water–Alkali (Hydroxide, Nitrate), J. Inorg. Nucl. Chem., 33: 1067 (1971).

03:317 THERMOCHEMISTRY. Busey, R. H., R. B. Bevan, and R. A. Gilbert. (Oak Ridge National Laboratory, Chemistry Division).

Thermochemical measurements of low-temperature heat capacities, high-temperature enthalpies, and heats of solution and reaction provide values of entropies, enthalpies, and free energies of formation of compounds of interest to chemistry and to technology. While serving the need for acquiring accurate values of chemical thermodynamic properties, these measurements frequently reveal phenomena of interest to theoretical chemistry and solid state physics. A newly designed and built solution–reaction calorimeter is being employed to determine the enthalpies of formation of Tc_2O_7, TcO_3, and TcO_4^-(aq). TcO_3 is a new compound of technetium synthesized in this laboratory for the first time. The high sensitivity and low noise level of the temperature sensor and its circuitry make this solution calorimeter suitable for observations on milligram amounts of material. It will thus be used to determine enthalpies of solution and formation of selected actinide compounds. Evaluation and work-up of high-temperature enthalpy data are being made on PbF_2, $KTcO_4$, and $KReO_4$, a series of compounds exhibiting interesting order–disorder transitions. The low-temperature calorimeter will be employed for measurements on rare earth halides, where the dearth of accurate values of the entropies derived from such low-temperature heat capacity observations makes their acquisition of importance.

PUBLICATION

Busey, R. H., R. B. Bevan, Jr., and R. H. Gilbert, The Heat Capacity of Potassium Pertechnetate from 10 to 310°K. Entropy and Gibbs Energy. Entropy of the Aqueous Pertechnetate Ion, J. Chem. Thermodyn., 4: 77–84 (1972).

03:318 FREE ENERGIES OF MULTICOMPONENT AQUEOUS ELECTROLYTE SOLUTIONS. Johnson, J. S., and R. M. Rush (Oak Ridge National Laboratory, Chemistry Division).

Knowledge of free energies of aqueous solutions containing more than one electrolyte, particularly at high concentrations, is necessary for understanding and rational control of chemical processes (such as solvent extraction and ion exchange) and for interpretation of fundamental studies of solution chemistry (elucidation of species in solution, for example). Solution thermodynamics also has intrinsic interest. We measure activities of water by the isopiestic technique and thus obtain activities of solutes in concentrated solutions containing more than one solute. Solutions selected usually contain ions commonly occurring both in natural and artificial solutions (such as sodium, chloride, magnesium, and sulfate) or ions of particular importance. In the latter class, perchlorate is the outstanding example, since it is frequently present in studies of species and kinetics in solution. We select perchlorate solutes to cover extremes of activity coefficient behavior with cation pairs of various charges, e.g., Na^+ and H^+, Ba^{2+} and UO_2^{2+}, as well as mixtures containing more than one charge type. We plan to obtain information on perchlorate solutions containing other anions. Another reason this class is interesting is that the high solubility of many perchlorates allows measurements under conditions in which ions interact in the presence of very little water.

PUBLICATIONS

Rush, R. M., and J. S. Johnson, Isopiestic Measurements of the Osmotic and Activity Coefficients for the Systems $HClO_4$ + $UO_2(ClO_4)_2$ + H_2O and $NaClO_4$ + $UO_2(ClO_4)_2$ + H_2O at 25°C, J. Chem. Thermodyn., 3: 779 (1971).

Scatchard, G., R. M. Rush, and J. S. Johnson, Osmotic and Activity Coefficients for Binary Mixtures of NaCl, Na_2SO_4, $MgSO_4$, and $MgCl_2$ in Water at 25°. III. Treatment with the Ions as Components, J. Phys. Chem., 74: 3786 (1970).

03:319 PROPERTIES OF AQUEOUS SOLUTIONS.

Lietzke, M. H., and R. W. Stoughton. (Oak Ridge National Laboratory, Chemistry Division).

The major objective of this project is a systematic investigation into the thermodynamic properties of water and of aqueous electrolyte solutions. Currently, primary emphasis is placed upon aqueous electrolyte mixtures. Electromotive force measurements on these solutions are being combined with either glass electrode or isopiestic measurements reported in the literature so that the partial molal free energy (or activity) of each component in the mixtures can be calculated. The results are of interest not only in solution chemistry but to workers in the fields of geochemistry, physical oceanography, desalination, and solvent extraction.

A study of the $HCl-MgCl_2$ system will complete a series covering aqueous solutions of alkali and alkaline earth chlorides with HCl. *Trends in the activity coefficient of each component* will be analyzed going both down and across the periodic table. Hopefully, these trends can be correlated with known physical parameters of the component ions.

Work will continue on the derivation of simple expressions for calculating the osmotic coefficient of electrolyte mixtures and the activity coefficient of each component in these mixtures. Several mixtures containing transition metal ions will be investigated to ascertain whether generalizations applicable to alkali and alkaline earth metal ions will hold for these ions also.

PUBLICATIONS

Lietzke, M. H., and R. J. Herdklotz, Electromotive Force Studies in Aqueous Solutions at Elevated Temperatures. XIII. The Thermodynamic Properties of $HCl-NaCl-MgCl_2$ Mixtures, *J. Inorg. Nucl. Chem.*, 33: 1649 (1971).

______, and R. J. Herdklotz, Activity Coefficient Behavior in Aqueous Binary Salt Mixtures, J. Tenn. Acad. Sci., 46: 133 (1971).

03:320 PHYSICAL CHEMISTRY OF POLYELECTROLYTE SOLUTIONS AND GELS.

Boyd, G. E., S. Lindenbaum, and Q. V. Larson. (Oak Ridge National Laboratory, Director's Division).

An important incentive in this program is the attainment of a fundamental understanding of the properties of polyelectrolyte solutions and gels. *Major attention is directed towards measurements* with synthetic organic polyelectrolytes; however, the behavior of naturally occurring charged and reactive polymers such as DNA and proteins, for example, is becoming of increasing relevance. The use of aqueous polyelectrolyte solutions, particularly of sodium polyacrylate, shows great promise for the economical recovery of waste and brackish water via reverse osmosis or hyperfiltration techniques. Polyelectrolyte gels, such as the organic ion exchangers, continue to be used extensively in AEC operations; for example, for the removal of radioactivity from aqueous coolants for pressurized water reactors, for the treatment and disposal of low-level radioactive wastes, and for the separation and isolation of the heavier transplutonium elements in the TRU production operations at ORNL.

The physicochemical techniques employed in this program include isopiestic vapor pressure measurements, microcalorimetry, partial molal volume determinations, self-diffusion measurements, single-ion electrodes for the estimation of ionic activities, and Raman and infrared spectral measurements. The experimental work is guided by the Lifson–Katchalsky cell theory of polyelectrolyte solutions, and the Rice–Harris theory of polyelectrolyte gels. Current emphasis is with solutions; however, we plan to return to the study of ion exchange gels because of their recent important applications in the preparation of an attractive new type of nuclear fuel particles for high-temperature, high-performance gas-cooled reactors.

PUBLICATIONS

Lindenbaum, S., Heats of Dilution of Aqueous Solutions of Sodium Salts of Carboxylic Acids, J. Chem. Thermodyn., 3: 625 (1971).

Boyd, G. E., S. Lindenbaum, and R. A. Robinson, Estimation of Solute Activity Coefficients in Dilute Aqueous Mixtures: Comparisons with Predictions from the Guggenheim Theory of Solutions, J. Phys. Chem., 75: 3153 (1971).

03:321 THERMODYNAMICS OF MOLTEN SALT SYSTEMS.

Bamberger, C. E., R. G. Ross, and C. F. Baes, Jr. (Oak Ridge National Laboratory, Reactor Chemistry Division).

The purpose of this continuing program is to extend and systematize the considerable amount of thermodynamic data available for various metal fluorides dissolved in molten mixtures of LiF and BeF_2. Such mixtures would serve as the fuel solvent in molten salt breeder reactors and are being considered in several other technological applications relevant to the AEC's energy programs. The principal experimental methods continue to be the measurement of heterogeneous equilibria and of EMF cells. Currently we are measuring the solubilities of the sparingly soluble oxides of structural metals (NiO, Cr_2O_3, MoO_2), fission products (Nb_2O_5), and actinides (ThO_2, PaO_2, Pa_2O_5, UO_2, PuO_2) as a function of melt composition and temperature. The results, along with available formation free energies and entropies for the solid oxides, will yield improved thermochemical values and activity coefficients for the corresponding dissolved fluorides. Oxy ions of the various metal cations generally are not formed, except for cations of small size and high charge; thus, Nb^{5+} seems to form an oxy ion but Pa^{5+} does not. The entropies of the dissolved fluorides have been found to correlate well with the entropies of the corresponding solid oxides. This should considerably improve our estimates of formation enthalpies of dissolved fluorides as well as the temperature coefficients of numerous heterogeneous equilibria in $LiF-BeF_2$ melts.

PUBLICATIONS

Bamberger, C. E., and C. F. Baes, Jr., The Exchange of U^{4+} and Th^{4+} Between Molten $LiF-BeF_2-ThF_4-UF_4$ and *$(U-Th)O_2$ Solid Solutions, J. Nucl. Mater., 35: 177 (1970).*

______, R. G. Ross, and C. F. Baes, Jr., The Oxide Chemistry of Plutonium in Molten Fluorides and the Free Energy of Formation of PuF_3 and PuF_4, J. Inorg. Nucl. Chem., 33: 767 (1971).

______, R. G. Ross, C. F. Baes, Jr., and J. P. Young, Absence of an Effect of Oxide on the Solubility and Absorption Spectra of PuF_3 in Molten $LiF-BeF_2-ThF_4$ and the Instability of Plutonium III Oxyfluorides, J. Inorg. Nucl. Chem., 33: 3591 (1971).

Hitch, B. F., and C. F. Baes, Jr., A Ni–NiO Reference Electrode *of the Third Kind for Molten Fluorides, J. Inorg. Nucl. Chem.,* 34: 163 (1972).

03:322 HIGHLY CONCENTRATED AQUEOUS ELECTROLYTES.

Braunstein, J., and H. Braunstein. (Oak Ridge National Laboratory, Reactor Chemistry Division).

The objectives of this program are to provide experimental data and theoretical interpretation in concentration regions of aqueous electrolytes that are critically important in bridging the gap between molten salt and dilute solution theories. The thermodynamic behavior of highly concentrated aqueous electrolytes is investigated and is correlated with the behavior of dilute solutions and of molten salts. Properties such as the vapor pressures are determined. The mutual interactions of added solutes are evaluated electrochemically. The kinds of particles that can carry electrical current through the solutions, and their relative speeds, are determined. Theoretical studies relate the observed behavior to more fundamental properties, such as the sizes and charges of the particles, and contribute to our understanding of the way in which highly concentrated electrolyte solutions behave in various technologically important processes, such as electroplating, water electrolysis, and corrosion. Isopiestic studies of water activity in hygroscopic salts, such as $Ca(NO_3)_2$, and their mixtures with weakly hydrated salts, such as KNO_3, will be extended to deuterium oxide, to aid in characterizing the ion–water, water–water, and ion–ion interactions. The water activities will be used also, with the EMF of cells with transference, to determine transference numbers. Measured association equilibria of Cd^{2+} with Br^- in $Ca(NO_3)_2 \cdot xH_2O$ electrolytes will be extended to a broader concentration range (both less than 4 and greater than 6 moles of water per mole salt) to elucidate the effects of water and different alkali metal concentrations on the equilibria, and to test the quasi-lattice model of competing hydration and association equilibria.

PUBLICATIONS

Braunstein, J., Statistical Thermodynamics of Molten Salts and Concentrated Aqueous Electrolytes, Chap. 4 in Ionic Interactions, Vol. 1, S. Petrucci (Ed.), Academic Press, Inc., New York, 1971.

______, and H. Braunstein, Association Constants for $CdCl^+$, $CdCl_2$, $CdBr^+$, and $CdBr_2$ in Molten $Ca(NO_3)_2 \cdot 4H_2O$, Chem. Comm., 565-567 (1971).

Braunstein, H., and J. Braunstein, Isopiestic Studies of Very Concentrated Aqueous Electrolyte Solutions of LiCl, LiBr, $LiNO_3$, $Ca(NO_3)_2$, $LiNO_3 + KNO_3$, $LiNO_3 + CsNO_3$ and $Ca(NO_3)_2 + CsNO_3$ at 100 to 150°C, J. Chem. Thermodyn., 3: 419-431 (1971).

03:323 TRANSPORT AND THERMODYNAMICS IN MOLTEN SALT MIXTURES. Braunstein, J., H. R. Bronstein, and J. Truitt. (Oak Ridge National Laboratory, Reactor Chemistry Division).

A genuine understanding of molten salt behavior is important in a wide variety of technologies. The purpose of this program is to provide experimental data and theoretical interpretation of transport and thermodynamic properties of molten salts. Properties such as the energy changes associated with mixing of different salts are related to the sizes and charges of the ions constituting the salts. The extent to which molten salts conduct electricity is measured and is related to other properties of these liquids involving transport of charge or mass. The detailed way in which species in the melt interact with one another and with electrodes is investigated. Proposed theories of transport and thermodynamic (equilibrium) properties are tested by correlation with the results of these investigations and those from other laboratories. The studies contribute to an understanding of factors affecting electrochemical processes in metallurgy and chemical separations, energy production and utilization, electrochemical methods of chemical analysis, corrosion of metals, and the development of electrochemical devices. New electrodes, including liquid metal alloys, are being developed for investigations of molten salts. Rapid electrochemical scanning methods are being used, especially in mixtures of alkali fluorides with beryllium fluoride, to characterize the detailed nature of transport in these systems whose properties span those of most molten salt mixtures.

PUBLICATIONS

Romberger, K. A., J. Braunstein, and R. E. Thoma, New Electrochemical Measurements of the Liquidus in the $LiF-BeF_2$ System, J. Phys. Chem., 76: 1154-1159 (1972).

______, and J. Braunstein, Transference Numbers and Mobilities in Molten Mixtures of Beryllium Fluoride and Lithium Fluoride, Inorg. Chem., 9: 1273-1275 (1970).

Braunstein, J., Comment on Dinuclear Complexes in Molten Salts, J. Electroanal. Chem., 33: 235-241 (1971).

______, and G. D. Robbins, Electrolytic Conductance Measurements and Capacitive Balance, J. Chem. Educ., 48: 52-59 (1971).

______, K. A. Romberger, and R. Ezell, Chemical Potential Interaction Parameters in Charge-Unsymmetric Molten Salt Mixtures, J. Phys. Chem., 74: 4383-4385 (1970).

03:324 PHYSICAL AND THERMAL PROPERTIES OF MOLTEN SALTS. Cantor, Stanley. (Oak Ridge National Laboratory, Reactor Chemistry Division).

The chief objective of this project is to determine thermodynamic activities of fluoride ion in molten fluorides by measuring the solubility of $BF_3(g)$. This gas acts as a thermodynamic probe, reacting with fluoride ions in the melt to form tetrafluoroborate (BF_4^-) ions. Specifically, BF_3 solubility measurement is a direct means for determining the activity of alkali fluoride in multicomponent fluoride systems. In the range, 50 to 80 mole % LiF in the system $LiF-BeF_2$, solubility of BF_3 per unit pressure (Henry's Law constant) is linear with the activity of LiF. Measurements are in progress to determine whether this proportionality holds over the entire composition range in $LiF-BeF_2$.

In $LiF-BeF_2-ThF_4$ (72–16–12 mole %), solubility measurements showed that LiF activities were about one-half those in 72–28 mole % $LiF-BeF_2$. Further study in $LiF-BeF_2-ThF_4$ mixtures will be used to compare interactions of $LiF-ThF_4$ with those of $LiF-BeF_2$.

A second objective of this project is to provide methods for predicting values of physical properties of molten salts, especially those properties that are difficult to measure. Recently we published methods, based on the Debye theory of specific heats, for estimating sonic velocity in single component molten salts. Presently we are reviewing data on thermal conductivities for the purposes of identifying the phonon free path (or its equivalent in an ionic melt) with a molecular dimension characteristic of the salt.

PUBLICATION

Cantor, S., Relationship Between Sonic Velocity and Entropy in Molten Salts, J. Appl. Phys., 43: 706 (1972).

03:325 HIGH-TEMPERATURE AQUEOUS SOLUTION CHEMISTRY. Marshall, W. L., and L. B. Yeatts. (Oak Ridge National Laboratory, Reactor Chemistry Division).

This program is directed toward a further understanding of aqueous electrolyte solutions to high temperatures (0 to 800°C) and pressures (1 to 4000 atm) through studies of electric conductance and solubility behavior with unique apparatus developed at ORNL. Extents of solute ionization, solubility relations, evaluations of solute–solvent interactions, and thermodynamic properties of solutes are obtained. These studies show that at high temperatures ion transport in conducting electric currents is 7 to 10 times faster, electrolytes are much weaker, water is a more simply structured liquid, and solubilities and conductances adhere to electrolyte theory better than at low temperatures. From this information, interpretations are obtained that allow predictions of aqueous electrolyte behavior to be made over the wide ranges of temperature and pressure. These predictions are important for better understanding the effect of electrolytes in corrosion processes and the behavior of salts in polluted and natural waters, for achieving better economy in water desalination, and for predicting the behavior of salts of geochemical and oceanographic interest. The present studies are concerned with finding a systematic description of concentrated electrolytes (a region of great concern) and obtaining electric conductances of several additional salts, for example, $CaCl_2$ and $MgCl_2$. These latter salts, of a charge type different from that of the salts previously investigated, are important to further understanding of aqueous solution behavior to high temperatures and pressures. They are of particular interest to geochemistry.

PUBLICATIONS

Yeatts, L. B., and W. L. Marshall, Electrical Conductance and Ionization Behavior of Sodium Chloride in Dioxane–Water Solutions at 300°C and Pressures to 4000 Bars, J. Phys. Chem., 76: 1053 (1972).

______, and W. L. Marshall, Solubility of Calcium Sulfate Dihydrate and Association Equilibria in Several Mixed Electrolyte Salt Systems at 25°C, J. Chem. Eng. Data, 17: 163 (1972).

______, L. A. Dunn, and W. L. Marshall, Electrical Conductance and Ionization Behavior of Sodium Chloride in Dioxane–water Solutions at 100°C and Pressures to 4000 Bars, J. Phys. Chem., 75: 1099 (1971).

Marshall, W. L., A Further Description of Complete Equilibrium Constants, J. Phys. Chem., 76: 720 (1972).

______, Complete Equilibrium Constants, Electrolyte Equilibria, and Reaction Rates, J. Phys. Chem., 74: 346 (1970).

03:326 HYDROLYSIS AND EMF STUDIES AT ELEVATED TEMPERATURES. Mesmer, R. E., B. F. Hitch, and C. F. Baes, Jr. (Oak Ridge National Laboratory, Reactor Chemistry Division).

EMF techniques will continue to be applied to the study of the hydrolysis behavior of metal ions and other protolytic equilibria of interest in reactor technology. Studies are carried out up to 300°C in two hydrogen electrode concentration cell assemblies developed as part of this program. At the present time the phosphoric acid and ammonia systems are being investigated in KCl media.

Results now available show the behavior of the first two ionization steps for phosphoric acid in 1.9, 0.5, 0.25, and 0.1 m KCl up to 300°C. The third ionization step has been studied up to 150°C in 1 and 0.5 m KCl only since it cannot be accurately determined at low concentrations or at higher temperatures. Polymerization of phosphate and reduction by hydrogen have been shown to be unimportant factors in these experiments.

The ionization of ammonia has now been examined at 1.0, 0.4, 0.2, and 0.04 m KCl at temperatures up to 300°C. With the completion of this work and the selection of a suitable fitting function we will be able to describe both of these important systems occurring in reactor coolants and in boiler water. Such information will also provide a valuable extension of the useful temperature range of these buffer systems for other applications.

After completion of this work we plan to study other protolytic equilibria involving H_2CO_3, silicic acid, the alkaline earth cations and also more complex solubility behavior of transition metal oxide systems.

PUBLICATIONS

Mesmer, R. E., and C. F. Baes, Jr., Acidity Measurements at Elevated Temperatures. V. Aluminum Ion Hydrolysis, Inorg. Chem., 10: 2290 (1971).

______, C. F. Baes, Jr., and F. H. Sweeton, Acidity Measurements at Elevated Temperatures. VI. Boric Acid Equilibria, Inorg. Chem., 11: 537 (1972).

______, C. F. Baes, Jr., and F. H. Sweeton, Acidity Measurements at Elevated Temperature. IV. Apparent Dissociation Product of Water in 1 m Potassium Chloride up to 292°, J. Phys. Chem., 74: 1937 (1970).

Sweeton, F. H., and C. F. Baes, Jr., The Solubility of Magnetite and Hydrolysis of Ferrous Ion in Aqueous Solutions at Elevated Temperatures, Thermodynamics, 2: 479 (1970).

ALSO SEE Heavy Element Chemistry: 03:78, 03:93, 03:94; Kinetics and Mechanisms: 03:219; Chemical Spectroscopy: 03:236, 03:263; Theoretical Chemistry: 03:272, 03:280, 03:286; Isotope Chemistry: 03:294, 03:299, 03:301, 03:302; High-Temperature and Inorganic Chemistry: 03:328, 03:329, 03:334, 03:339, 03:343, 03:344, 03:346, 03:347, 03:350, 03:352, 03:354, 03:355, 03:357, 03:358, 03:359, 03:360; Structural Chemistry: 03:373, 03:385; Analytical Chemistry: 03:395, 03:401; Separations Chemistry: 03:409, 03:417; Engineering Chemistry: 03:428, 03:432, 03:433; Miscellaneous Chemical Studies: 03:452, 03:453, 03:454, 03:461.

HIGH-TEMPERATURE AND INORGANIC CHEMISTRY

Studies of the preparation, properties, and reactions of inorganic compounds; coordination chemistry; the chemistry of high-temperature systems including molten salts.

03:327 SPECTRAL EMITTANCE AND EMISSIVITY STUDIES. Bautista, Renato G. (Ames Laboratory, Chemical Engineering Division).

The determination of temperatures beyond the range of thermocouples or in situations where the placement of a thermocouple is not possible can best be handled by the use of an optical radiation pyrometer. Precise temperature measurement requires information on the spectral emittance of the solid surfaces and the spectral emissivity of the liquid surfaces at a known wavelength.

The spectral emittance and emissivity of metal samples are presently being determined by direct comparison of the brightness temperature of the sample surface to the true temperature of the sample at a wavelength of 0.645 μ. An automatic optical pyrometer is focused on the sample to determine the brightness temperature and is then focused on a blackbody approximation cavity located in the sample crucible. The spectral emittances of solid surfaces strongly depend on the condition of the surfaces but vary only slightly with changes in temperature. The spectral emissivities of the liquid metals are essentially constant with respect to changes in temperatures.

The very high vapor pressures of some materials prevent the accurate measurement of their spectral emittances. For some materials, the presence of even small amounts of gases that are released during the heating causes formation of other compounds such as oxides and nitrides. The solution of these problems will be attempted through better vacuum by use of an ion pump and by development of a technique whereby the presence of an inert atmosphere will prevent the formation of other chemical compounds.

03:328 THERMOCHEMICAL PROPERTIES OF MATERIALS AT HIGH TEMPERATURES. Bautista, Renato G. (Ames Laboratory, Chemical Engineering Division).

The mechanism of decomposition of compounds that vaporize in a complex manner can be determined by the simultaneous Torque Knudsen technique. The decomposition vapor pressures are determined directly by simultaneous measurements of the torsional recoil of a suspended effusion cell and indirectly by weight loss measurements through Knudsen effusion. The average molecular weight of all the vaporizing species is then calculated without identification of each effusing species. This makes possible the calculation of the absolute vapor pressure of any compound vaporizing in a complex manner and the determination of its heat of vaporization and entropy of vaporization. The decomposition of the noble metal halides and the newly synthesized rare earth polymers of di(2-ethylhexyl)phosphoric acid is presently being studied.

The transpiration technique is used for measuring vapor pressures above 10^{-3} mm Hg. This apparatus, which is capable of temperatures up to about 1450°C, will be most useful in determining vapor pressures of refractory and high-melting metals, alloys, and other compounds, such as oxides, carbides, and nitrides.

The levitation of conductive samples in an r-f field eliminates the need of a crucible before being dropped into a calorimeter. Levitation calorimetry will make available precise heat capacity data up to the liquid phase of high-melting substances.

PUBLICATIONS

Harada, Takeo, Morton Smutz, and Renato G. Bautista, Polymers of Iron and Rare Earths and Di-(2-ethylhexyl)phosphoric Acid, in Proceedings of the International Solvent Extraction Conference, April 1971, The Hague, Netherlands, Society of Chemical Industry, England, Vol. II, pp. 950-956, 1971.

______, Morton Smutz, and Renato G. Bautista, Characterization of the Iron and Rare Earth Polymers of Di-(2-ethylhexyl)phosphoric Acid, J. Chem. Eng. Data, 17(2): 203-204 (1972).

03:329 THERMODYNAMIC PROPERTIES OF LIQUID METAL SYSTEMS. Stevenson, F. D. (Ames Laboratory, Chemical Engineering Division).

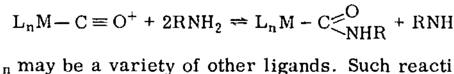
As a result of work just completed on the lead and indium–lead systems using Langmuir vaporization, which demonstrated the utility of cell design modifications, work is being extended to the measurement of low vapor pressures of the higher-boiling elements. The successful application of the Langmuir method makes possible the measurement of such thermodynamic properties at the lowest possible temperatures where the hostility of the environment is at a minimum. The results obtained for the indium–lead system, which showed that diffusion controlled the vaporization in the binary, have provided the impetus to a continued study of the conditions which lead to the stability and instability of binary and multicomponent vaporizing systems. This work is in the initial stages and is expected to answer questions concerning frequently observed low distillation rates from liquid metal systems.

PUBLICATION

Ulrichson, Dean L., and F. D. Stevenson, Ind. Eng. Chem., Fundam., 11: 287 (1972).

03:330 TRANSITION METAL-CATALYZED REACTIONS OF CARBON MONOXIDE AND AMINES. *Angelici, Robert J.* (Ames Laboratory, Chemistry Division).

The purpose of this project has been to elucidate mechanisms whereby transition metal compounds catalyze the reactions of carbon monoxide and amines to form organic formamides, ureas, and isocyanates. In our search for key intermediates in these reactions, we have found that CO, when bound to certain transition metals will react with amines to give carboxamido complexes,



$$L_nM-C\equiv O^+ + 2RNH_2 \rightleftharpoons L_nM-C\begin{smallmatrix}\nearrow O\\ \searrow NHR\end{smallmatrix} + RNH_3^+$$

where L_n may be a variety of other ligands. Such reactions occur with $[(C_6H_5)_3P]_2Pt(Cl)(CO)^+$, $(C_5H_5)Fe(CO)_3^+$, $(C_5H_5)Ru(CO)_3^+$, $(CH_3NH_2)Mn(CO)_5^+$, $(CH_3NH_2)Re(CO_5^+)$, $(C_5H_5)Mo(CO)_4^+$, and $(C_5H_5)W(CO)_4^+$ while others such as $(arene)Mn(CO)_3^+$ and $[(C_6H_5)_3P]_2Mn(CO)_4^+$ form equilibrium mixtures of starting complex and carboxamido product. Finally, there are carbonyl complexes that do not react with amines at all; representatives are $(RNH_2)_3Mn(CO)_3^+$, $(RNH_2)_3Re(CO)_3^+$, and $(C_5H_5)Mn(CO)_3$. We have correlated the reactivities of these diverse complexes with the C–O stretching force constants of the reacting CO groups. Those CO groups with force constants greater than 17.0 mdynes/Å readily form carboxamido complexes; those with force constants between 16.0 and 17.0 give equilibrium mixtures; while those with constants below 16.0 show no evidence for carboxamido formation. Although this correlation may be rationalized theoretically, its greatest use at present is in predicting the formation of carboxamido intermediates that may be essential to these catalytic reactions. In the future we will pursue reactions that result in the conversion of carboxamido complexes to formamides, ureas, and isocyanates.

03:331 HOMOPOLYATOMIC IONS OF THE POST-TRANSITION ELEMENTS. Corbett, John D. (Ames Laboratory, Chemistry Division).

Homopolyatomic or cluster ions containing only one type of atom, e.g., Cd_2^{2+}, Bi_9^{5+}, I_3^+, appear limited to the post-transition elements. As such they provide significant examples of localized metal–metal bonding, simple structural and bonding models, and new chemistry.

Large anions have been found to enhance the stability of these polyatomic cations, and the ion $AlCl_4^-$ has proved to be particularly convenient for use in synthetic routes involving molten salt media. Nuclear quadrupole resonance (NQR) data are being accumulated for ^{35}Cl in such salts to determine easily whether free $AlCl_4^-$ ions are present in the compounds or not; the approach avoids the ambiguity present in vibrational data and the expense and time involved in a structural determination by x-ray methods. NQR data for ^{127}I and ^{35}Cl are also being obtained for the structural characterization of cations such as ICl_2^+, I_2Cl^+, I_3^+, and I_5^+ in their $AlCl_4^-$ salts.

Synthesis of bromine and of other interhalide cations such as Br_3^+ and ICl_4^+ as well as investigations with counter-anions other than $AlCl_4^-$ are underway. A synthetic, NQR, and x-ray study of compounds reputed to contain the $Ga_2Cl_6^{2-}$ anion is also in progress since other formulations seem not to have been excluded. The x-ray characterization of the cation in $Bi_5^{3+}(AlCl_4^-)_3$ has been frustrated by twinning problems, and details of the structure are now being sought utilizing other anions and with infrared–Raman methods. There is a small amount of evidence for anions of certain elements (Hg, Pb, Sn, Bi) that are isoelectronic with known cations; further investigations are in progress.

PUBLICATIONS

Prince, David J., John D. Corbett, and Bruce Garbisch, Polyatomic Cations of Tellurium and Selenium in Chloroaluminate Salts. A Study of the Systems M- ($MCl_4 + 4AlCl_3$), Inorg. Chem., 9: 2731 (1970).

Friedman, Robert Mark, and John D. Corbett, Bismuth(I) in the Solid State. The Crystal Structure of $(Bi^+)(Bi_9^{5+})(HfCl_6^{2-})_3$, Chem. Commun., 422 (1971).

McMullan, Richard K., David J. Prince, and John D. Corbett, The Crystal Structure of Octaselenium(2+) Tetrachloroaluminate, $Se_8^{2+}(AlCl_4^-)_2$, Inorg. Chem., 10: 1749 (1971).

Corbett, John D., James F. Rounsaville, and Kenneth R. Poeppelmeier, Miscibility in the Systems Sodium Iodide–Trisodium Bismuthide and Sodium Iodide–Trisodium Antimonide, Inorg. Chem., 10: 1830 (1971).

Couch, Thomas W., Donald A. Lokken, and John D. Corbett, The Crystal Structures of Tetratellurium(2+) Tetrachloroaluminate and Heptachlorodialuminate, $Te_4^{2+}(AlCl_4^-)_2$ and $Te_4^{2+}(Al_2Cl_7^-)_2$, Inorg. Chem., 11: 357 (1972).

03:332 THE LOWER HALIDES OF SOME TRANSITION AND INNER-TRANSITION ELEMENTS. Corbett, John D. (Ames Laboratory, Chemistry Division).

The identification and characterization of the lowest halides formed by transition and inner-transition elements under strongly reducing conditions is pertinent (a) to their occurrence on oxidatior of structural metals, during preparative metallurgy reactions, and in molten salt solvents, and (b) as examples of unique structures, bonding, and stability that occur in the solid state or in solvents under unusual conditions.

Sesquihalides of scandium and gadolinium are under continuing investigation. Magnetic susceptibility data on high-purity Gd_2Cl_3 are being taken at low temperatures in order to establish more about the nature of the electronic conduction in the remarkable metal–metal chains therein. Synthesis, crystal growth, and x-ray studies are underway on Sc_2Br_3 and Sc_2Cl_3 in order to establish their structural relationship to that of the gadolinium chloride.

Three other rare earth metal–molten trihalide systems are being investigated: Ho–$HoCl_3$ to ascertain whether a reduced solid halide exists; Tm–$TmCl_3$ to establish better the number and stability of the many intermediate phases ($2.04 < Cl/Tm < 2.15$); and Lu–$LuCl_3$ as a possible source of analog of Gd_2Cl_3.

Monochlorides of zirconium and hafnium are unique in their stoichiometry among Group IV elements and in their metallic conductivity among all metal chlorides. Synthesis of monocrystals suitable for structural work is underway. Further magnetic susceptibility measurements are anticipated as well.

PUBLICATIONS

Johnson, David A., and John D. Corbett, The Relative Stabilities of the Rare Earth Metal Diiodides. The Metal–Metal Triiodide Systems for Terbium, Dysprosium, and Holmium, in Colloque International du C.N.R.S., Les Elements des Terres Rares, 429, 1970.

Lokken, Donald A., and John D. Corbett, Gadolinium Sesquichloride, An Unusual Example of Metal–Metal Bonding, J. Amer. Chem. Soc., 92: 1799 (1970).

Struss, Arthur W., and John D. Corbett, A Study of the Lower Chlorides of Zirconium and Hafnium. The Formation of Stable Monochlorides, Inorg. Chem., 9: 1373 (1970).

Corbett, John D., High Purity Rare Earth Metal Iodides—Preparation and Reaction with Silica Containers, Inorg. Nucl. Chem. Lett., 8: 337 (1972).

03:333 INORGANIC REACTION MECHANISMS. Espenson, J. H. (Ames Laboratory, Chemistry Division).

Studies are in progress dealing with several types of group substitution and oxidation–reduction reactions of metal complexes. The basic objective of this work is the understanding of the detailed molecular processes by which certain types of chemical reactions occur. To further this goal, the methods of chemical kinetics, radioactive tracers, and spectroscopy are applied to a study of these reactions. The primary interest of this group has focused on transition metal complexes. One group of compounds on which a considerable quantity of work is being done are the alkyl complexes of chromium(III), typified by the dichloromethyl complex $Cr(H_2O)_5CHCl_2^{2+}$. This complex undergoes three basic groups of reactions on which kinetic and mechanistic studies are in progress:

(a) Ligand substitution of one water molecule trans to the alkyl; e.g.:

$$Cr(H_2O)_5CHCl_2^{2+} + SCN^- \rightarrow trans\text{-}Cr(H_2O)_4(NCS)CHCl_2^{2+} + H_2O$$

(b) Reductive reactions of the alkyl fragment:

$$Cr(H_2O)_5CHCl_2^{2+} + 2Cr^{2+} + H^+ \rightarrow CrCH_2Cl^{2+} + CrCl^{2+} + Cr^{3+}$$

(c) Oxidative electrophilic dealkylation:

$$Cr(H_2O)_5CHCl_2^{2+} + Br_2 + H_2O \rightarrow Cr(H_2O)_6^{3+} + CHCl_2Br + Br^-.$$

Radiotracer studies using ^{51}Cr are planned in the near future to clarify the nature of the multistep process found to occur in reaction (b).

The oxidation–reduction chemistry of iron porphyrins is being examined. The role of iron(II) in catalyzing the demetallation of iron(III) porphyrins in acetic acid is being studied, with indications that the Fe(II)–Fe(III) electron transfer step is rate determining. Studies have recently been begun on the oxidation of iron(II) porphyrins by ferricyanide ion. We also hope soon to begin studies of electron transfer between an Fe(II) porphyrin and an Fe(III) porphyrin.

PUBLICATIONS

Espenson, J. H., and R. T. Wang, The Oxidation of Uranium(IV) by Chromium(VI) and the Induced Oxidation of Iodide Ions, Inorg. Chem., 11: 955 (1972).

______, and W. R. Bushey, Kinetic Studies on the Formation of a Cyanide-Bridged Adduct of Two Cationic Metal Complexes, Inorg. Chem., 10: 2457 (1971).

Adin, A., and J. H. Espenson, Kinetics of Some Oxidation Reactions of Diaquocobaloxime(II), Inorg. Chem., 11: 686 (1972).

______, and J. H. Espenson, Dealkylation Reactions of Alkylcobaloxime Compounds with Mercury(II), J. Chem. Soc., D: 653 (1971).

Pladziewicz, J. R., and J. H. Espenson, Electron Transfer Reactions of Ferrocenes, J. Phys. Chem., 75: 3381 (1971).

03:334 HIGH-TEMPERATURE CHEMISTRY. Franzen, Hugo F. (Ames Laboratory, Chemistry Division).

Research work by the members of this group is directed toward the determination of the nature and structure of chemical substances important in systems at high temperatures. The thermodynamics and stoichiometries of substances and processes in high-temperature systems are characterized by mass spectrometry, x-ray diffraction, and chemical analysis. The structures of new solids are determined by x-ray diffraction and the structures of vapor molecules are investigated by infrared matrix-isolation spectroscopy.

In the area of vaporization thermodynamics the vaporization of vanadium monosulfide is in progress. The vaporization is being studied using a quadrupole mass spectrometer to examine the vapor in a Knudsen effusion experiment. Initial results demonstrated the existence of two previously uncharacterized vapor molecules, VS and VS_2. Thermodynamic properties of these vapor species will be determined, and attempts will be made to examine these molecules by matrix-isolation spectroscopy.

In the area of condensed phase studies, a new subsulfide of titanium has been prepared and is under study, methods of single-crystal preparation are being investigated for several refractory sulfide systems, attempts are being made to prepare new refractory metal-rich selenides of transition metals and studies of the preparation, structure, and properties of mixed sulfide–phosphide systems are in progress.

PUBLICATIONS

Conard, B. R., and H. F. Franzen, The Zirconium–Sulfur System at High Temperatures, High Temp. Sci. 3: 49 (1971).

Strachan, D. M., R. G. Barnes, and H. F. Franzen, Knight Shift and Spin-Lattice Relaxation Time Measurements in the Phosphides with the Ti_3P Structure Type, J. Solid State Chem., 3: 293 (1971).

Brom, J. M., Jr., and H. F. Franzen, Infrared Spectra and Structure of Matrix Isolated Thallous Halides, J. Chem. Phys., 54: 2874 (1971).

Edwards, Jimmie G., Hugo F. Franzen, and Paul W. Gilles, High-Temperature Mass Spectrometry, Vaporization, and Thermodynamics of Titanium Monosulfide, J. Chem. Phys., 54: 545 (1971).

Franzen, H. F., and J. G. Smeggil, The Crystal Structure of Ta_6S, Acta Crystallogr., Sect. B, 26: 125 (1970).

03:335 THE CHEMISTRY OF HEAVY TRANSITION METAL COMPOUNDS. McCarley, Robert E. (Ames Laboratory, Chemistry Division).

This research is concerned with the chemistry of heavy transition elements, principally Nb, Ta, Mo, and W, in their lower oxidation states. Compounds containing these elements in lower oxidation states, e.g., Nb(II,III), Ta(II,III,IV), and W(III,IV), are either unknown or poorly characterized. Hence, understanding the occurrence, reactions, and structure of such compounds has fundamental significance, but also will be important to practical applications in diverse areas.

Current work can be divided into two general areas, viz., new synthetic chemistry and development of more useful methods for physical characterization of compounds. Successful development of methods for the predictable synthesis of metal–metal bonded cluster species is a significant achievement. Reactions in fused salt media have provided efficient routes to $Mo_6X_8^{4+}$ and $W_6X_8^{4+}$ (X = halogen) cluster species, whereas previously unknown metal–metal bonded dimers, $Nb_2X_6(C_4H_8S)_3$, $Ta_2X_6(C_4H_8S)_3$, and $MoW(CH_3CO_2)_4$, have been obtained via reactions in more conventional nonaqueous solvents. These studies will be continued with the objective of developing methods for producing more complicated mixed metal cluster compounds by stepwise addition of metal atoms to simpler species.

Nuclear quadrupole resonance (NQR) studies show great promise as a powerful tool for characterizing metal halide compounds of the type discussed above. Recent work in this laboratory has demonstrated that metal–metal bonding results in large electric field gradients at the metal atoms which can be measured by NQR spectroscopy. Fortunately, ^{93}Nb, ^{181}Ta, ^{185}Re, and ^{187}Re, which commonly form metal–metal bonds, all may be studied by this technique. The first pure NQR spectra for any compounds of ^{181}Ta recently were observed during this work. A major effort in the future will be directed to the use of NQR for structure determination, correlation of metal–metal bond order with NQR coupling constants, and development of other methods for physical characterization.

PUBLICATIONS

Koknat, F. W., and R. E. McCarley, Chemistry of Polynuclear Metal Halides. IX. The Crystal and Molecular Structure of Bis(tetramethylammonium)Hexachloro(dodeca-μ-chloro-hexaniobate), $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$, Inorg. Chem., 11: 812 (1972).

Edwards, P. A., R. E. McCarley, and D. R. Torgeson, Chemistry of Polynuclear Metal Halides. X. Nuclear Quadrupole Resonance Study of Bis(tetramethylammonium)Hexachloro-dodeca-μ-chloro-hexaniobate, Inorg. Chem., 11: 1185 (1972).

03:336 PHASE RELATIONS IN LITHIUM–CHALCOGEN SYSTEMS. Cunningham, P. (Argonne National Laboratory, Chemical Engineering Division).

The electrochemical couples of lithium and the chalcogens show promise for use as energy storage and conversion devices. The phase diagrams of the lithium–sulfur and lithium–tellurium systems have been delineated. The lithium–sulfur system has only one intermediate phase, Li_2S (mp 1372°C). A miscibility gap, with a critical temperature above 600°C, extends from about 0.2 to 37.0 atom percent lithium above a montectic temperature of 364.8°C. The eutectic reaction [liquid → $Li_2S(s) + \beta\text{-}S(s)$] occurs at 115.5°C.

The lithium–tellurium system has two intermediate phases, LiTe (mp 1202°C) and $LiTe_3$ (mp 459.3°C). The $LiTe_3$ phase has not been reported previously. Two eutectic reactions occur: one at 423.5°C [liquid → $LiTe_3(s) + Te(s)$] and the other at 448.5°C [liquid → $Li_2Te(s) + LiTe_3(s)$].

PUBLICATIONS

Johnson, C. E., and E. J. Hathaway, Solid–Liquid Phase Equilibria for the Ternary Systems Li(F,Cl,I) and Na(F,Cl,I), J. Electrochem. Soc., 118: 631 (1971).

Cunningham, P. T., S. A. Johnson, and E. J. Cairns, Phase Equilibria in Lithium–Chalcogen Systems. I. Lithium–Selenium, J. Electrochem. Soc., 118: 1941 (1971).

03:337 PHASE EQUILIBRIA AT HIGH TEMPERATURES. Ackermann, R. J. and Rauh, E. G. (Argonne National Laboratory Chemistry Division).

Melting points, eutectic temperatures, and solubilities for the U–W, U–Ta, Th–W, Th–Ta, U–Th–W, Zr–W, and Hf–W systems have been determined by novel but simple techniques in the temperature range 1500 to 3000°K. The important experimental aspect involves the successful containment of 100- to 300-mg samples of liquid metals and alloys in single-crystal crucibles of tungsten and tantalum.

The respective solubility curves for tungsten and tantalum in liquid thorium and uranium approach linear behavior only at the lower temperatures; at higher temperatures the solubility curves acquire a strong positive curvature. The derived partial molar excess enthalpies and entropies tend toward, but do not achieve, regular solution behavior at the lower temperatures. The intermetallic compound $ThTa_2$ has been observed. The correlation of the measured solubilities with enthalpies of vaporization, atomic volumes, and solubility parameters predicts decreasing solubilities of solid refractory metals in liquid actinide metals beyond plutonium. Although the chemical behavior of thorium in the +4 valence state appears to closely resemble that of zirconium and hafnium, the metallic behavior of thorium is anomalous and suggests the metallic valence is less than 4 which is generally ascribed to zirconium and hafnium based on metallic radii.

Phase transformations and thermal expansion at temperatures up to 2500°C have been studied by means of a high-temperature, controlled-atmosphere diffractometer (with C. A. Sorrell, University of Missouri, Rholla). The orthorhombic–tetragonal transition in WO_3 that is associated with a lambda-type heat capacity curve has been shown to be structurally continuous in the z-direction but discontinuous in the x- and y-directions. The $\alpha-\beta$ transition in quartz has been demonstrated to be a continuous, lambda-type transition contrary to many of the earlier studies. *The study of thermal expansion of quartz from 573 to 1400°C has* shown negative expansion coefficients that become progressively pronounced with the onset of β-crystobalite. Such behavior indicates strong anisotropic vibration showing a preference for the transverse rather than longitudinal modes, resulting in the movement of atoms into the empty spaces of the relatively open β-quartz structure.

The existence of holes in structures at high temperatures provides the necessary ingredient for the mechanism of diffusion. The compounds UO_2 and PuO_2, which possess the fluorite structure, show premelting phenomena that are manifested by lambda-type heat capacity curves several hundred degrees below their respective melting points. Similarly, fluorite (CaF_2) itself displays this premelting behavior. The latter is being studied to ascertain whether and how the anion sub-lattice becomes disordered prior to melting.

PUBLICATION

Ackermann, R. J., and C. A. Sorrell, The Thermal Expansion and Orthorhombic–Tetragonal Transition of the Tungsten Trioxide Phase, High Temp. Sci., 2: 119 (1970).

03:338 THE CHEMISTRY OF UNUSUAL AND POWERFULLY OXIDIZING INORGANIC COMPOUNDS. Appelman, E. H. (Argonne National Laboratory, Chemistry Division).

This project consists of studies in the broad area of the chemistry of reactive and relatively unfamiliar inorganic compounds.

Into this category fall such materials as the noble gas compounds, higher-valent actinide compounds, perbromic acid and the perbromates, astatine compounds, and a variety of reactive fluorine-containing compounds, such as the recently synthesized hypofluorous acid.

We are now completing work on the infrared, NMR, photoionization, and photoelectron spectra of hypofluorous acid, in collaboration with H. Kim (U. of Missouri), J. C. Hindman, and J. Berkowitz. The results should provide a great deal of useful information about this unusual molecule. We expect in the near future to study the reaction chemistry of HOF and the mechanism by which it is formed from the reaction of fluorine with water.

We are continuing a collaborative effort with T. Anderson of Aarhus University, Denmark, on the radiation chemistry of the perbromates, and in collaboration with D. Cohen and S. Fried, we have just begun a study of the Raman spectra of high-valent neptunium compounds in aqueous solution that should permit us to confirm the structures of the ions present.

We expect to pursue further studies of the redox reactions of xenon compounds in aqueous solution, and we hope to explore the possibility of synthesizing some still-missing compounds of seven-valent bromine, such as $BrOF_5$.

PUBLICATIONS

Studier, M. H., and E. H. Appelman, Hypofluorous Acid, J. Amer. Chem. Soc., 93: 2349 (1971).

Appelman, E. H., The Oxidation of Halates to Perhalates by Xenon Difluoride in Aqueous Solution, Inorg. Chem., 10: 1881 (1971).

Goleb, J. A., H. H. Claassen, M. H. Studier, and E. H. Appelman, Infrared Spectrum of Matrix-Isolated HOF, Spectrochim. Acta, Part A, 28: 65 (1972).

Kim, H., E. F. Pearson, and E. H. Appelman, Millimeter-Wave Spectrum and Structure of Hypofluorous Acid: HOF and DOF, J. Chem. Phys., 56: 1 (1972).

Johnson, G. K., P. A. G. O'Hare, and E. H. Appelman, Thermodynamic Properties of Perbromyl Fluoride, BrO_3F, Inorg. Chem., 11: 800 (1972).

03:339 STUDIES OF CHEMICAL SPUTTERING, DEUTERIDE AND TRITIDE MOLECULE FORMATION AND TRAPPING IN THERMONUCLEAR REACTORS. Gruen, D. M. (Argonne National Laboratory, Chemistry Division).

Tritium inventory and holdup are serious considerations for the safe and economic operation of a thermonuclear reactor. Since deuterium and tritium are chemically reactive gases, their inventory in a fusion reactor will be strongly influenced by chemical compound formation. Some of the areas where compound formation is likely to occur are neutral beam dumps and injector sources, as well as divertor and vacuum wall structures.

For many types of fusion reactors, the plasma must be thermalized at some state of the operation of the machine so that the unburned D and T can be recovered, processed and prepared for reinjection into the device. Trapping on metal surfaces has been suggested as a useful way of pumping a significant fraction of the energetic ion flux. However, many of the consequences of this concept have not been explored seriously.

Ion flux trapping of D^+ and T^+ on metal surfaces is efficient over only a small temperature range because of saturation of surface layers at the lower temperatures and hydride decomposition at the higher temperatures. The estimated flux of 2×10^{17} ions/cm^2/sec at the trapping surface for a 5000-MW reactor is sufficient to cause gross chemical effects such as deuteride and tritide formation. Compound formation, sputtering rates, and mechanisms of trapping on metal surfaces under saturation conditions will, therefore, be entirely different from rates determined on clean surfaces. It is, therefore, important, for example, to evaluate a wide range of materials for their trapping efficiency and to define their optimum operating parameters.

An apparatus has been developed that allows sputtered atoms and molecules to be collected, matrix isolated, and studied spectroscopically. Chemical sputtering has been observed with this device. In very recent experiments the matrix isolation technique has been used in conjunction with an isotope separator that produces monoenergetic mass-selected particles. This work is aimed at developing a new, sensitive, and quantitative method of measuring sputtering yields. Because of the known difficulties in measuring sputtering yields of the hydrogen getter metals niobium, molybdenum, and vanadium, the new method, which does not involve target weight loss data, will be applied to these metals.

Studies of the gas phase reactions $2M(g) + H_2(g) = 2MH(g)$ are aimed at establishing the thermodynamics of such reactions so as to be able to calculate partial pressures of gaseous metal hydrides coexisting with metal vapor partial pressures under any set of conditions. This work is to be extended to metals of interest to fusion reactor development and is clearly of importance for controlling plasma contamination.

Work is also underway on a chemical accelerator (with S. Wexler and E. K. Parks) to study a variety of problems including the scattering of ionized and neutral D_2 and T_2 molecules and D and T atoms from Nb surfaces as a function of surface coverage and temperature, collision energy, exchange of energetic neutrals with surface atoms, and the formation of MH molecules in collisions of sputtered metal atoms with D_2 and T_2 molecules.

Theoretical calculations (with A. C. Wahl) have already yielded preliminary confirmation for the existence of chemically bound excited states of TiH and VH molecules, which had also been predicted on the basis of chemical systematics. This work is to be extended to include correlation effects so as to get more reliable values for the dissociation energies of these molecules.

03:340 INORGANIC CHEMISTRY OF URANIUM. Hoekstra, H. R. (Argonne National Laboratory, Chemistry Division).

The objective of this project is to obtain detailed information on the uranium–oxygen and related systems (e.g., ternary systems incorporating additional anions or cations). The scope of the investigation includes the synthesis of pure phases, a delineation of their stability regions, and a study of their properties. Hydrothermal and combined high-temperature–high-pressure methods are included among the preparative techniques employed. Variations in uranium bonding as a function of oxidation state and of other ions in the system are investigated by x-ray diffraction, infrared, Raman, and thermoanalytical methods. The utility of photoelectron spectroscopy (ESCA) to this project will be determined as it becomes available.

A recently completed study of the UO_3-H_2O system has supplied new data on each of the six phases in this system, including complete structural determinations (with S. Siegel) on two of them — $\gamma UO_2(OH)_2$ and $H_2U_3O_{10}$. A related study on the rare earth uranates is in progress. Several series of compounds have been identified in these systems.

The program for the near future will be directed toward an investigation of several UO_2-MO_X systems where M represents fission product elements that will become prominent in breeder reactor fuels at high burnup, i.e., Cs, Ba, Nd, and Zr.

PUBLICATIONS

Hoekstra, H. R., and S. Siegel, Preparation and Properties of Cr_2UO_6, J. Inorg. Nucl. Chem., 33: 2867-2873 (1971).

______, S. Siegel, and F. X. Gallagher, Reaction of Platinum Dioxide with Some Metal Oxides, Advan. Chem. Ser., 98: 39-53 (1971).

03:341 THE CHEMISTRY OF REACTIVE FLUORIDES. Hyman, H. H.; Malm, J. G.; Quarterman, L. A.; and Sheft, I. (Argonne National Laboratory, Chemistry Division).

An attempt to recompute the monomer–polymer equilibria in hydrogen fluoride has revealed anomalies that have necessitated the redetermination of a number of properties of this compound. In spite of the inherent simplicity of hydrogen fluoride and its heavy tonnage use in industry, such basic data as liquid density, boiling point, and vapor density have been known with relatively poor precision.

They have now been redetermined and a laser-Raman study initiated to determine the monomer concentrations directly.

The determination of the Raman spectrum with a laser source for quantitative measurement of the concentration of both molecules and ionic species has been applied to a number of halogen fluoride and hydrogen fluoride solutions. Equilibrium constants for reactions such as $BrF_3 + HF \rightarrow BrF_2^+ + HF_2^-$ have been determined and approximate acid (or base) strengths are being tabulated for a number of fluoride ion donor or acceptor molecules. Solutes include halogen fluorides, noble gas fluorides, and a number of salts containing hexafluoro anions.

A number of synthetic fluorine chemistry projects are underway or planned for the near future. 50 g of ^{242}Pu are now available and the low rate of radioactive decay makes possible low-temperature heat capacity measurements on compounds synthesized from this nuclide.

The preparation of new fluorides and oxyfluorides of the higher actinide elements will be attempted with particular emphasis on the synthesis of volatile compounds.

Since the chemistry of xenon hexafluoride poses continuing problems of fundamental interest, we foresee a continued need for the synthesis of pure material and samples with controlled impurity levels for critical experiments utilizing NMR and molecular spectroscopy, or whatever techniques offer the hope of increased understanding.

03:342 STUDIES OF CHEMICAL METHODS FOR REMOVING RADON AND XENON FROM AIR.

Stein, L. (Argonne National Laboratory, Chemistry Division).

Reactions of radon and xenon with solid and liquid fluorinating agents are being studied at Argonne in an effort to develop practical methods for removing radioactive isotopes of these elements from air. ^{222}Rn (half-life 3.82 days) is a naturally occurring air contaminant in uranium mines, and ^{133}Xe (half-life 5.27 days) and ^{135}Xe (half-life 9.2 hours) are fission product gases that are released to the atmosphere by fuel processing plants during the decladding and dissolution of uranium fuel elements. Liquid bromine trifluoride and a number of solid halogen fluoride–metal fluoride complexes, such as ClF_2SbF_6, BrF_2SbF_6, $BrF_4Sb_2F_{11}$, and BrF_2BiF_6, have been shown to remove radon from air efficiently at 23 to 25° (through the formation of nonvolatile radon ions or compounds). The solid complexes are decomposed by moisture but can probably be used in combination with desiccants for removal of ^{222}Rn from recirculated (secondary) air in mines and for analysis of ^{222}Rn in air. An oxygenyl complex, O_2SbF_6, containing the O_2^+ cation, has been shown to react with both radon and xenon at 23 to 25°. This appears very promising as a reagent for removing the heavy noble gases from air because it has a low vapor pressure at 25° and produces only oxygen as a gaseous reaction product. Efforts are now being made to separate krypton–xenon mixtures with O_2SbF_6 and to determine optimum conditions for preparing O_2SbF_6 by photochemical methods.

PUBLICATIONS

Stein, L., Ionic Radon Solutions, Science, 168: 362 (1970).

——, Chemical Properties of Radon, Yale Sci. Mag., 44: 2 (1970).

——, Chemical Methods for Removing Radon and Radon Daughters from Air, Science, 175: 1463 (1972).

03:343 THERMOCHEMISTRY AT HIGH TEMPERATURES.

Thorn, R. J.; Ackermann, R. J.; Hoekstra, H. R.; McCreary, J. R.; Rauh, E. G.; and Winslow, G. H. (Argonne National Laboratory, Chemistry Division).

The program in high-temperature chemistry at Argonne National Laboratory consists essentially of thermodynamic and thermochemical investigations of inorganic compounds of the transition metal, lanthanide, and actinide elements at temperatures ranging from 500 to 3000°C.

Current investigations are directed toward understanding the structures of material that may be of interest in both fission and fusion reactors, the vaporization process, and the thermochemistry of the simple gaseous molecules that result.

Research in this field is proceeding at three levels, the development of experimental techniques, their utilization for accumulation of the pertinent data, and finally an attempt to develop a fundamental understanding of the underlying principles or at least a systematics that will permit both interpolation and extrapolation to new systems or unavailable conditions of temperature, pressure, and material composition.

Developments in three significant experimental techniques are of current interest; improved temperature-measuring and controlling devices, simultaneous measurement of the mass effusion from a Knudsen cell and mass spectrometric analysis of the effusate, and the introduction of photoelectron spectrometry.

Historically, the standard temperature instrument above 1000°C has been the disappearing filament optical pyrometer using visual matching and, therefore, individually calibrated by each experimenter. A camera lens assembly has now been substituted in an L&N automatic reading and recording pyrometer to permit the measurement of the temperature of an area smaller than the standard effusion cell orifice (<60-mil diameter). Coupled to a proportional controller and induction heater, an overall precision of up to 0.02°C for the Knudsen cell seems to be attainable and temperature measurement and control are no longer limiting.

A recording microvacuum balance and a quadrupole mass spectrometer valved off within an ion pump and thus maintained at high vacuum (10^{-8} torr) have been coupled to permit simultaneous measurement of the rate of effusion from a Knudsen cell and an analysis of the effusate. The data are fed directly to the Division's Sigma V computer for rapid automatic data acquisition and reduction.

Finally, we are planning to acquire and use a photoelectron spectrometer (ESCA) particularly with the goal of studying the valence states in nonstoichiometric lanthanide and actinide compounds (e.g., UO_{2+x}, CeO_{2-x}), solids with mixed central atoms (e.g., $(UPU)O_{2\pm x}$), conduction and valence bands in solids, molecular orbitals in high-temperature molecules, and a variety of surface phenomena that are particularly amenable to this technique.

PUBLICATIONS

Thorn, R. J., Some Theoretical Significances of High Temperature Chemistry, Advan. High Temp. Chem., 3: 1-33 (1971).

McCreary, J. R., and R. J. Thorn, Statistical Procedures of Calculation Enthalpies of Sublimation from Vapor Pressures, High Temp. Sci., 3(4): 330-339 (1971).

Holt, B. D., R. J. Thorn, and P. G. Wahlbeck, Non-Equilibrium Condensation of a $NiCl_2$ Molecular Beam on Metal Surfaces, High Temp. Sci., 3: 10-25 (1971).

03:344 SIMPLE GASEOUS MOLECULES AT HIGH TEMPERATURE.

Thorn, R. J.; Ackermann, R. J.; and Rauh, E. G. (Argonne National Laboratory, Chemistry Division).

Systematic studies of simple vapors of a single type of compound (for example, gaseous monoxides) that spans the periodic table are of fundamental importance in general studies of chemical bonding.

Precise systematic relations among monoxides are derived from measurements of isomolecular exchange reactions such as $Y(g) + ZrO(g) \rightarrow YO(g) + Zr(g)$. Completed studies from which we have derived accurate dissociation energies include YO, ZrO, HfO, ThO, UO, CeO, and LaO. Thermochemical quantities for these gases are used to derive thermochemical properties for nonstoichiometric oxides. We have shown that simple ab initio calculations of dissociation energies of the monoxides do not predict the observed decrease with increasing atomic number for the transition metal and alkaline earth monoxides, presumably because they neglect the contribution of excited states.

A calibrated mass spectrometric analysis of the effusate yields both enthalpies and entropies for each equilibrium studied. Again we expect to initiate photoelectron spectroscopic studies to supplement our existing measurement facilities.

Studies in progress or planned include additional oxides and lanthanide and actinide fluorides.

PUBLICATIONS

Ackermann, R. J., and E. G. Rauh, A High-Temperature Study of the Stoichiometry, Phase Behavior, Vaporization Characteristics, and Thermodynamic Properties of the Cerium–Oxygen System, J. Chem. Thermodyn., 3: 609-624 (1971).

——, and E. G. Rauh, A High-Temperature Study of the Stoichiometry, Phase Behavior, Vaporization Characteristics, and Thermodynamic Properties of the Lanthanum–Oxygen System, J. Chem. Thermodyn., 3: 445-460 (1971).

03:345 VALENCE STATES IN SOLIDS.

Thorn, R. J.; Ackermann, R. J.; and Siegel, S. (Argonne National Laboratory, Chemistry Division).

It is well recognized that oxidation potentials as used in aqueous solutions should have a counterpart in solid compounds. Unfortunately, there is no single solid phase standard environment in which to study valence changes for a single element. We have found it useful to compare some structural and thermochemical parameters for a series of solid compounds, particularly the lanthanides. For example, for the lanthanide monosulfides, monoselenides, and monotellurides, the atomic radii for Sm, Eu, and Yb correspond to the +2 state, those for the remainder of the lanthanides correspond to +3. Those in this latter category exhibit metallic conduction, whereas Sm, Eu, and Yb compounds do not. Europium and ytterbium even show anomalous radii associated with a lower valence in the metallic state.

We expect to find photoelectron spectroscopy a most powerful tool in assigning valence states. Our plans include studying a sequence of compounds containing the same element, e.g., gaseous europium, metallic europium, intermetallic europium compounds, europium oxides, sulfides, the dihalides, and trihalides, and an analogous series with a more typical lanthanide.

A systematics which permitted prediction of valence states for trace elements in specific solid phases would be most useful in predicting fission product behavior in fuel elements, and to some extent our program is pointed in this direction for the reference breeder reactor fuel ($U_{0.8}Pu_{0.2}O_{2-x}$).

03:346 NONSTOICHIOMETRIC SOLID STATE BEHAVIOR AT HIGH TEMPERATURES.

Thorn, R. J.; Ackermann, R. J., and Winslow, G. H. (Argonne National Laboratory, Chemistry Division).

The lattice defects associated with nonstoichiometric solids in the form of vacancies and interstitial atoms grow in number with increasing temperature. The relationship between such thermodynamic quantities as the partial molar vapor pressure, enthalpy, and entropy of sublimation and the creation of such lattice defects is intrinsically interesting and most useful in analyzing the behavior of nonstoichiometric phases characteristically found in actinide oxide fuel elements in nuclear reactors.

Recent studies have shown that such defects are not randomly distributed but are clustered in a relatively ordered way, and an appropriate cluster model has been developed recently to derive an equation of state for ThO_2 and correlate lattice parameters as a function of temperature and thermochemical measurement for both UO_{2+x} and the substoichiometric UO_{2-x}, a phase of great importance in fuel elements for nuclear reactors (often as $U_{(a)}Pu_{(1-a)}O_{2-x}$).

While present analyses are based on oxygen sub-lattice defects, a more complete model including cation vacancies is being developed to improve predictions of mass transport, and experiments are planned on diffusion under temperature gradients to test the models. This program is aimed at an improved description of the fuel element performance in the reference design fast breeder reactor.

It is anticipated that nonstoichiometric phases of interest will be among the solids scheduled for photoelectron spectroscopy studies now being planned.

PUBLICATIONS

Winslow, G. H., Thermomechanical Properties of Real Materials: The Thermal Expansions of UO_2 and ThO_2, High Temp. Sci., 3(5): 361-380 (1971).

Thorn, R. J., Statistical Thermodynamic Analysis of Residual Structures in Compositional Homogeneity, in The Chemistry of Extended Defects in Non-Metallic Solids, L. Eyring and M. O'Keeffe (Eds.), North Holland Publishing Company, Amsterdam, 1970, p. 395.

03:347 HIGH-TEMPERATURE PHYSICAL CHEMISTRY.

Egan, J. J. (Brookhaven National Laboratory, Department of Applied Science).

The objective of this program is the study of the thermodynamic and transport properties of nuclear materials at high temperatures.

The thermodynamic properties of liquid and solid alloys are being studied by means of solid electrolytes. Also, a new technique involving the formation of F-centers in alkali and alkaline earth halides equilibrated with the alloys is being used. Many of the systems studied are liquid semiconductors and results obtained have been used to show how the thermodynamics of mixing are influenced by the concentration of electrons and electron holes. Systems of current interest include Mg–Bi, Mg–Sb, Mg–Sn, Na–Bi, and Ca–Bi as well as others.

Electronic conductivity of molten salts is being studied. An experimental technique has been developed to measure the electronic component of the conductivity independently of the ionic component. The results are used to interpret polarography, chronopotentiometry, electrolysis, and double layer measurements in molten salt systems.

PUBLICATIONS

Heus, R. J., and J. J. Egan, Thermodynamic Studies of Liquid Mg_3Bi_2 Using CaF_2 Solid Electrolytes, Z. Phys. Chem. (Frankfurt), 74: 108 (1971).

Bookless, J. S., and J. J. Egan, Use of F Centers for the Investigation of Alloy Thermodynamics. The Potassium–Lead System. J. Phys. Chem., 76: 1202 (1972).

03:348 INTERMEDIATES IN OXIDATION–REDUCTION REACTIONS. THALLIUM(II).

Dodson, R. W. and Schwarz, H. A.

Thallium(II) is often invoked as an oxidation–reduction intermediate. The aim of this work is to obtain quantitative information about its properties.

The anticipated induction of the thallium(I)–thallium(III) electron exchange by reducing agents that generate thallium(II) was found with iron(II). The results give an indirect estimate of ca $4 \times 10^6\ M^{-1}\ sec^{-1}$ for the specific rate at which Tl(II) oxidizes iron(II) in 1M $HClO_4$. Direct measurement by pulse radiolysis techniques gives $6.7 \times 10^6\ M^{-1}\ sec^{-1}$. Other reactions measured by pulse radiolysis were: $OH + Tl^+$; $H + Tl^{3+}$; and $2Tl^{2+} \rightarrow Tl^+ + Tl^{3+}$. The absorption spectrum of Tl^{2+} in 1M $HClO_4$ was determined from 225 to 370 nm. The kinetic results, in conjunction with other data, show that the reaction $Tl^+ + Tl^{3+} \rightarrow 2Tl^{2+}$ is too slow, by many orders of magnitude, to play a significant role in the normal thallium(I)–thallium(III) electron exchange.

Exploratory experiments showed that vanadium(IV) accelerates the exchange. The kinetics of the induced reaction will be studied. Chloride complexing has been found to have a profound influence on the kinetics of the oxidation of iron(II) by thallium(III). Pulse radiolysis studies indicated that complexes of thallium(II) with chloride are observable. These entities will be investigated with the aim of placing the results in relation to the properties of thallium(III) as an oxidant in chloride media.

PUBLICATIONS

Warnqvist, B., and R. W. Dodson, Induction of the Thallium(I)–Thallium(III) Exchange by Iron(II), Inorg. Chem., 10: 2624 (1971).

03:349 KINETIC STUDIES OF SUBSTITUTION AND OXIDATION–REDUCTION REACTIONS INVOLVING COMPLEX IONS IN SOLUTION.

Sutin, N. (Brookhaven National Laboratory, Chemistry Department).

The rate of electron transfer between two metal centers can be markedly increased by the addition of anions. These anion-catalyzed reactions do not occur in a single step but proceed instead in a number of stages. A major objective of this work is to obtain detailed information about the individual steps leading from reactants to products. Some of these steps involve substitution into the inner coordination shell of the metal center and for this reason ligand replacement reactions are being investigated in conjunction with the electron-transfer work. Current work involves studies of the effect of added chloride, azide, and thiocyanate ions on the rate of reduction of $Fe(phen)_3^{3+}$, $Co(phen)_3^{3+}$, $Co(en)_3^{3+}$, and porphyrin complexes of iron(III) by Cr^{2+}, V^{2+}, and Fe^{2+} ions. These studies are elucidating the effect of the changes of orbital symmetry of the transferring electron on the rate of the oxidation–reduction, and provide useful models of the electron-transfer site in more complex systems.

PUBLICATIONS

Jaffe, M. R., D. P. Fay, M. Cefola, and N. Sutin, The Kinetics and Mechanism of the Formation of the Monothenoyltrifluoroacetone Complexes of Nickel(II), Cobalt(II), Copper(II), and Iron(III), J. Amer. Chem. Soc., 93: 2878 (1971).

Fay, D. P., A. R. Nichols, Jr., and N. Sutin, The Kinetics and Mechanisms of the Reactions of Iron(III) with Beta-Diketones. The Formation of Monoacetylacetonatoiron(III) and the Effect of Copper(II) on the Formation of Monothenoyltrifluoroacetonatoiron(III), Inorg. Chem., 10: 2096 (1971).

Turner, D. H., G. W. Flynn, N. Sutin, and J. V. Beitz, Laser Raman Temperature-Jump Study of the Kinetics of the Triiodide Equilibrium; Relaxation Times in the 10^{-8}–10^{-7} Second Range, J. Amer. Chem. Soc., 94: 1554 (1972).

Sutin, N., and J. K. Yandell, Kinetic and Equilibrium Studies of the Reactions of Iron(III) and Iron(IV) Dithiolate Complexes with Organic Bases, Inorg. Chem., 3: 448 (1972).

______, and A. Forman, Some Unusual Anion Effects on the Rate of Reduction of Iron(III) Complexes, J. Amer. Chem. Soc., 93: 5274 (1971).

03:350 HIGH-TEMPERATURE THERMAL PROPERTIES OF REACTOR COOLANTS.

Bonilla, Charles F. (Columbia University, Liquid Metals Research Laboratory, Department of Chemical Engineering and Applied Chemistry, New York, New York 10027).

With the putting into service this year of improved high-temperature equipment and techniques, more rapid and more accurate determination of high-temperature thermodynamic properties of reactor coolants and power cycle working fluids has been accomplished. In particular, by an original pressure tube technique, the vapor pressure of potassium up to its critical point has been measured directly in repeated self-consistent runs, yielding the critical pressure as 2380 ± 2 psia and the critical temperature as 3642 ± 2°F. The vapor pressure fits a new four-constant equation all the way to the critical point with a standard deviation of only 0.5%. These results are of value in understanding the liquid and vapor state of metals, in predicting other high-temperature thermodynamic and transport properties of potassium and other alkali metals, and in optimizing the design of potassium vapor turbines and power cycles for space and other nuclear power missions for which potassium is the indicated working fluid.

With the success of the potassium program, the method is to be extended in the next contract year to sodium, of importance in the LMFBR program, as well as back to cesium, on which somewhat inconsistent critical point data were obtained in 1968, and probably to rubidium, on which additional data are indicated. When possible, and to the extent possible, the method and equipment will also be applied to lithium, a favorable reactor coolant under extreme conditions.

Employing a different original tilting capsule technique, the critical density of rubidium was found to be 0.347 g/cc. The critical temperature was obtained as 3331°F, in rather good agreement with 3315°F obtained earlier by the entirely different pressure tube method for an average of 3323°F, probably correct to ±0.2%.

PUBLICATIONS

Oster, G. F., and C. F. Bonilla, The High Temperature Saturated Phase Densities and the Critical Density and Temperature of Cesium, in Proceedings of the Fifth International Symposium on Thermophysical Properties, American Society of Mechanical Engineers, 1970, p. 468.

Silver, I. L., and C. F. Bonilla, The High Temperature Vapor Pressure and the Critical Pressure and Temperature of Cesium by Direct Measurement, in Proceedings of the Fifth International Symposium on Thermophysical Properties, American Society of Mechanical Engineers, 1970, p. 461.

03:351 KINETIC, MAGNETIC, AND MOSSBAUER STUDIES ON PORPHYRIN SYSTEMS. Hambright, Peter. (Howard University, Department of Chemistry, Washington, D. C. 20001).

The aim of this project is to understand the basic coordination chemistry involved in the interaction of metal ions with porphyrin-type molecules. In addition to the biological and possible astrochemical importance of porphyrin-like metal complexes, their selective tumor distribution properties, especially in combination with toxic and radioactive metal ions, make them attractive potential chemotherapeutic agents. The chemistry of such large, rigid macrocyclic ligands and the unusual oxidation states stabilized are of general interest.

To this end, the kinetics of the addition and acid-catalyzed removal of metal ions from porphyrins and the mechanisms of replacement of one metal ion by another from such ligands are being studied. Electron transfer and electron exchange reactions, as well as fast axial ligand substitution processes, are being studied by rapid mixing and relaxation methods, in both aqueous and nonaqueous solutions.

Low-temperature magnetic and Mössbauer studies on iron and manganese complexes will determine the validity of the Griffith–Kotani theories for obtaining zero-field splitting parameters from low-temperature magnetic measurements.

PUBLICATIONS

Hambright, P., Coordination Chemistry of Metalloporphyrins, Coord. Chem. Rev., 6: 247 (1971).

Shears, B., and P. Hambright, Acid Catalyzed Solvolysis Reactions of Zinc Porphyrins Having Various Basicities and Zinc N-Methyl Porphyrins, J. Amer. Chem. Soc., 93: 776 (1971).

Khosropour, R., and P. Hambright, A General Mechanism for Metal Ion Incorporation into Porphyrin Molecules, Chem. Commun., 13: (1972).

Shah, B., B. Shears, and P. Hambright, Kinetic Differences Between the Incorporation of Cd(II) and Zn(II) into Porphyrins and N-Methyl Porphyrins, Inorg. Chem., 10: 1828 (1971).

Higginbotham, E., and P. Hambright, Stability Constants of Vanadyl Porphyrins with Pyridine and Evidence for Antiferromagnetic Association, Inorg. Nucl. Chem. Lett., 747 (1972).

03:352 HIGH-TEMPERATURE CHEMISTRY. Gilles, Paul W. (University of Kansas, Department of Chemistry, Lawrence, Kansas 66044).

The goals of the research are to establish the compositions and structures of high-temperature substances and to measure the thermodynamics and kinetics of their high-temperature reactions.

Measurements of the vaporization properties of the titanium oxides are leading to an establishment of the compositional width of the Ti_3O_5 phase at high temperature and to a resolution of the controversy on the dissociation energies of TiO(g) and TiO_2(g). Studies will be undertaken to measure the fragmentation patterns of TiO(g) and TiO_2(g), to measure the oxygen potential throughout wide regions of the TiO system, and to explore the use of the mass spectrometrically determined TiO_2/TiO ratio for measuring oxygen potentials in high-temperature fuel systems.

Studies of the vaporization properties of the rare earth sulfides are leading to values for the dissociation energies of simple gaseous molecules and to the elucidation of the conditions necessary for equilibrium in Knudsen cells. Future studies will be directed toward ternary sulfide systems.

The kinetics of vaporization of cuprous chloride is being investigated by a combined Knudsen–torsion apparatus, supplemented by high-temperature mass spectrometry in an effort to deduce the detailed mechanism of vaporization. Future studies will involve characterization of the surface structure of vaporizing single crystals as well as measurements of their vaporization rates.

PUBLICATIONS

Edwards, Jimmie G., Hugo F. Franzen, and Paul W. Gilles, High Temperature Mass Spectrometry, Vaporization, and Thermodynamics of Titanium Monosulfide, J. Chem. Phys., 54: 545 (1971).

______, James M. Leitnaker, Heribert Wiedemeier, and Paul W. Gilles, High Molecular Weight Boron Sulfides. VII. Lower Temperature Studies and Metastable Decompositions, J. Phys. Chem., 75: 2410 (1971).

Hampson, Peter J., and Paul W. Gilles, High Temperature Vaporization and Thermodynamics of the Titanium Oxides. VII. Mass Spectrometry and Dissociation Energies of TiO(g) and TiO_2(g), J. Chem. Phys., 55: 3712 (1971).

Gilles, Paul W., and Peter J. Hampson, High Temperature Vaporization and Thermodynamics of the Titanium Oxides. VIII. Thermodynamics of the Titanium Oxides, in Advances in Mass Spectrometry, Vol. 5, A. Quayle (Ed.), The Institute of Petroleum, London, and the Elsevier Publishing Company, New York, 1971, p. 374.

Chen, H., and P. W. Gilles, High Molecular Weight Boron Sulfides. VIII. Vapor Pressures of B_2S_3(g) and B_4S_6(g) over Stoichiometric B_2S_3, J. Phys. Chem., 76: 2035 (1972).

03:353 HIGH OXIDATION STATE FLUORIDES AND OXYFLUORIDES: SYNTHESIS AND STRUCTURE. Bartlett, Neil. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

The search for new noble gas compounds, particularly ArF^+ and new XeF^+ salts, continues but the major emphasis is on the use of known compounds as synthetic reagents. The thermally stable salt $KrF^+[Sb_2F_{11}]^-$ is a powerful oxidizer and is being used in efforts to make BrF_6^+, ClF_6^-, and $XeOF_5^+$ salts. Our crystallographic studies have proved that the XeF_5^+ cation occurs in the compounds $[XeF_5]^+[AsF_6]^-$; $[XeF_5]^+[RuF_6]^-$; and $[XeF_5]_2^+[PdF_6]^{2-}$. We have also established the salts $[Xe_2F_7]^+[SbF_6]^-$; $[XeF_3]^+[SbF_6]^-$; $[XeF_3]^+[Sb_2F_{11}]^-$; $[XeOF_3]^+[SbF_6]^-$; and $[XeOF_3]^+[Sb_2F_{11}]^-$ and shown that of the binary xenon fluorides, XeF_6 is the best fluoride ion donor. Since XeF_6 is a good base and a good ionizing solvent, it promises to be an excellent reagent (with elemental fluorine) in the generation of hitherto unknown (or uncertain) oxidation states (e.g., Au(IV), Hg(IV); Pu(VII); and Np(VII)).

Recently we have established that IrF_4 exists and is isomorphous with PtF_4 and PdF_4 (all apparently structurally related to UCl_4). The Ir(IV) is low spin d^5. There is some evidence for a higher fluoride of gold than Au(III). AuF_6, should it exist, would be more powerfully oxidizing than PtF_6. Even IrF_6 and PtF_6, however, promise to be useful in generating new cations and radicals.

PUBLICATIONS

Bartlett, N., and M. Wechsberg, The Xenon Difluoride Complexes of $XeF_2 \cdot XeOF_4$; $XeF_2 \cdot XeF_6 \cdot AsF_5$ and $XeF_2 \cdot 2XeF_6 \cdot 2AsF_5$ and Their Relevance to Bond Polarity and Fluoride Ion Donor Ability of XeF_2 and XeF_5, Z. Anorg. Allg. Chem., 385: 5-17 (1971).

______, M. Wechsberg, G. R. Jones, and R. D. Burbank, The Crystal Structure of Xenon(II) Fluoride Fluorosulfate, $FXeOSO_2F$, Inorg. Chem., 11: 1124 (1972).

______, Dannie-Heineman Prize Address—Noble-Gas Chemistry and Its Significance, Göttingen Akademie–Jahrbuch, pp. 22-23, 1971.

03:354 THEORETICAL AND EXPERIMENTAL SPECTROSCOPIC AND THERMODYNAMIC STUDIES DIRECTED TOWARD CHARACTERIZATION OF THE HIGH-TEMPERATURE BEHAVIOR OF GASES AND CONDENSED PHASES. Brewer, Leo. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

The determination of thermodynamic data for high-temperature molecules is difficult and most methods do not yield sufficiently accurate results. The development of a combination of radiative lifetime measurements on a molecular beam with absorption or emission intensity measurements in a high-temperature King-type furnace will be continued in the hope of obtaining an accurate method utilizing the third law of thermodynamics. King furnace measurements are being taken for TiO and VO and molecular beam measurements are being attempted with TiO and high-temperature atomic vapors.

Alloys of solutions of transition metals of the third to sixth groups with the noble metals are of interest because of the unusually strong interactions that are attributed to electron donations by the noble metals to the transition metals with vacant d orbitals. The proper representation of the variation of the thermodynamic properties with concentration is not known and presents a particularly important challenge. Vaporization measurements as well as other high-temperature equilibration studies are planned to characterize the variation of Gibbs energy with concentration.

PUBLICATIONS

Brewer, L., Energies of the Electronic Configurations of the Singly, Doubly, and Triply Ionized Lanthanides and Actinides, J. Opt. Soc. Amer., 61: 1666-1681 (1971).

______, and J. L. Wang, Absorption Spectrum of the Mg_2 Molecules in Solid Rare Gases, J. Mol. Spectrosc., 40: 95-102 (1971).

______, and C. A. Chang, Matrix Isolation of Pb and Pb_2, J. Chem. Phys., 56: 1728-1740 (1972).

______, and J. Tellinghuisen, Quantum Yield for Unimolecular Dissociation of I_2 in Visible Absorption, J. Chem. Phys., 56: 3929-3938 (1972).

______, and J. L. Wang, Ground State of Gaseous CaO; A Study of the Matrix Spectra of Ca and CaO, J. Chem. Phys., 56: 4305-4309 (1972).

03:355 SOLID STATE MATERIALS SYNTHESIS. Donaghey, Lee F. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

Synthesis and processing phenomena in solid state materials are under study to determine optimum conditions for synthesis and crystal growth, as well as effect of processing variables on structure-dependent physical properties.

High-temperature galvanic cell techniques utilizing solid electrolytes are applied to measure phase stability and thermodynamic properties of Group III to V ternary alloys, where data obtained by other methods is contradictory. In addition, sources of error and methods of overcoming solid oxide electrolyte limitations in EMF cells are subject to critical study using isolated-electrode techniques.

Measurements of chemical transport and deposition of inorganic compounds are studied to determine optimum transport and product efficiency conditions. Thermodynamic conditions for the transport of $GaAs_{1-x}P_x$ and several chromium chalcogenide spinels have been studied theoretically and subjected to quantitative evaluation.

The kinetics of solidification is given theoretical and experimental study to determine rate-limiting processes and instabilities during crystal growth. Solidification kinetic mechanisms for unconstrained growth are measured through isothermal velocity profiles. The growth habits and kinetics of several iodides and phosphates are being explored through crystallization in gel matrices. The hydrodynamics of simultaneous forced and natural convection during Czochralski crystal growth are measured experimentally to ascertain these effects on mass transport.

Future programs include (1) the completion of a magnetometer for low-temperature measurement of magnetic susceptibility of spinels and (2) the study of electronic and ionic transport in thin films produced by sputtering and liquid phase epitaxy.

03:356 SYNTHETIC CHEMISTRY. Jolly, William L. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

Germanium and tin analogs of organic compounds are prepared to permit direct comparison of the chemistries of germanium and tin with carbon. Intermediates in the hydrolysis of boron hydrides and borohydrides are identified and isolated. The chemistry of compounds containing sulfur–nitrogen bonds is systematized by the synthesis and characterization of unusual sulfur–nitrogen compounds.

We plan to continue our present efforts to prepare compounds containing Ge–B bonds. In preliminary studies, to avoid some of the difficulties of working with the GeH_3^- ion, the $Ge(CH_3)_3^-$ ion will be used as a reagent.

We shall attempt to quench some of the reactive intermediates formed in the acid hydrolysis of BH_4^- by treatment of the intermediates with OH^- ion. Probably a continuous-flow reactor can be devised for preparing such adducts on a large scale. Indeed such a reactor may be applicable to many similar syntheses in inorganic chemistry.

The ring S_7N^- ion isomerizes to a blue species that may correspond to the open-chain S_7N^- ion. We plan to study the equilibrium between these species as a function of concentration and temperature by visible–UV spectrophotometry.

PUBLICATIONS

Jolly, W. L., The Structures of Sulfur–Nitrogen Compounds, Advan. Chem. Ser., 110: 92 (1972).

Dreyfuss, R. M., and W. L. Jolly, The Reaction of Potassium Germyl with Organic Halides, Inorg. Chem., 10: 2567 (1971).

Webster, J. R., M. M. Millard, and W. L. Jolly, The Synthesis and Characterization of the Halostannanes, Inorg. Chem., 10: 879 (1971).

Webster, J. R., and W. L. Jolly, The Stannonium Ion in Acid Solutions, Inorg. Chem., 10: 877 (1971).

Lipp, S. A., and W. L. Jolly, The Reaction of Tetrasulfur Tetranitride with Sulfuric Acid, Inorg. Chem., 10: 33 (1971).

03:357 AN INVESTIGATION OF SOME LANTHANIDE CARBON, NITROGEN, CHALCOGEN, AND HALOGEN SYSTEMS AT ELEVATED TEMPERATURES. Eick, Harry A. (Michigan State University, Department of Chemistry, East Lansing, Michigan 48823).

The goal of this project is to characterize the decomposition and structural behavior of lanthanide refractories—in particular, those lanthanides that exhibit multiple oxidation states.

A current project involves determination of the decomposition/vaporization mode of samarium oxide bromide. Complete elucidation of this decomposition process has required vaporization studies across the lanthanide series—TmOBr and YbOBr at the heavy end, NdOBr at the light end, and $SmBr_3$. Cursory vaporization studies of YbF_2 and EuSe are in progress; a detailed study of TmF_2 will be undertaken. Future studies will involve other halides and oxide halides of Sm, Eu, Yb, and Tm. Related lanthanides will be studied when necessary to aid elucidation of the entire vaporization process.

Structural studies of $Yb_3Si_2O_8Cl$, a phase that forms when Yb_2O_3 and $YbCl_3$ are sealed in quartz under a Cl_2 atmosphere, of YbOCl, and of an apparently ordered $LaErF_6$ are in progress, as are studies of other phases observed in mixed-metal fluoride systems. Use of mixed-metal studies enables preparation in pure form of phases observed otherwise only as trace components of mixtures.

The structure of $La_2O_2C_2$, which contains acetylinic units, is in final refinement stages. Preparative studies on europium and ytterbium mixed halides have yielded as yet unidentified products. Correlative studies are effected whenever possible, and future structural undertakings will relate to those cited above.

PUBLICATIONS

Hariharan, A. V., and H. A. Eick, Vaporization Thermodynamics of $EuCl_2$, High Temp. Sci., 4: 91 (1972).

______, and H. A. Eick, Vaporization Thermodynamics of Europium(II) Sulfide, High Temp. Sci., 3: 123 (1971).

Work, D. E., and H. A. Eick, On the Preparation of Condensed ScO, J. Less-Common Metals, 26: 413 (1972).

Seiver, R. L., and H. A. Eick, Vapor Pressure Measurements in the Samarium Dicarbide–Carbon and Thulium Dicarbide–Carbon Systems, High Temp. Sci., 3: 292 (1971).

Smeggil, J. G., and H. A. Eick, The Crystal Structure of Strontium Dibromide, Inorg. Chem., 10: 1458 (1971).

03:358 EQUILIBRIA INVOLVING FUSED SALTS AND LIQUID METAL ALLOYS. Ferris, L. M. and Smith, F. J. (Oak Ridge National Laboratory, Chemical Technology Division).

The purpose of this program is to obtain basic chemical data relating to the separation of rare earths from thorium in the chemical processing of molten salt breeder reactors (MSBRs). Current studies support the development of a metal-transfer process for achieving this separation. The individual and mutual solubilities of thorium and selected rare earths in liquid lithium–bismuth and lithium–lead alloys are being determined. The solubility products of the compounds formed when mutual solubilities have been exceeded are being derived from the data. The equilibrium distribution of lithium and bismuth between liquid lithium–bismuth alloys and molten LiCl or LiBr is being determined over the temperature range 650 to 800°C. The data are being interpreted in terms of the distribution of the saltlike species Li_3Bi between the fused salt and the liquid alloy phases. In the future, similar studies using liquid lithium–lead alloys will be conducted. Spectrophotometric studies of the fused salts in equilibrium with the various liquid alloys will be made in an effort to identify the heavy-metal species present in the salt.

PUBLICATIONS

Schilling, C. E., and L. M. Ferris, The Solubility of Thorium in Liquid Bismuth, J. Less-Common Metals, 20: 155 (1970).

Smith, F. J., and L. M. Ferris, Mutual Interactions of Thorium, Nickel, and Bismuth in Th–Ni–Bi Solutions, J. Inorg. Nucl. Chem., 32: 2863 (1970).

———, The Solubilities of Thorium and Neodymium in Liquid Lithium–Bismuth Solutions, J. Less-Common Metals, 27: 195 (1972).

03:359 PROTACTINIUM CHEMISTRY IN MOLTEN SALT SYSTEMS. Ferris, L. M. and O. K. Tallent. (Oak Ridge National Laboratory, Chemical Technology Division).

The purpose of this program is to obtain basic information on the chemistry of protactinium relating to the isolation of protactinium in the chemical processing of molten salt breeder reactors (MSBRs). The equilibrium distribution of protactinium between liquid lithium–bismuth alloys and selected lithium-containing halide salts was determined. Results of these studies were used in conjunction with other data to estimate Gibbs free energies of formation for several protactinium halides. Presently, the precipitation of solid Pa_2O_5 from molten $LiF-BeF_2-ThF_4-UF_4$ solutions by equilibration with $H_2O-HF-Ar$ gas mixtures is being studied, using a transpiration method. Equilibrium quotients for the precipitation reaction are being determined in the temperature range 525 to 700°C. Preliminary results show that a large fraction of the protactinium can be precipitated as Pa_2O_5 before the attendant precipitation of uranium or thorium oxides occurs. The precipitation can be effected with gas mixtures in which the partial pressures of HF and H_2O are both less than about 0.2 atm. In future work, the conditions under which both protactinium and uranium oxides precipitate will be defined with more accuracy. When salt mixtures are in equilibrium with solid Pa_2O_5 and the appropriate H_2-HF-H_2O-Ar gas mixture, both PaF_5 and PaF_4 can exist in the salt. The transpiration method will, therefore, also be used to determine the equilibrium constants for the reaction $PaF_5 + \frac{1}{2} H_2 = PaF_4 + HF$. This equilibrium constant, when used with other available information, allows estimation of the maximum oxide concentration permissible in an MSBR at a given temperature.

PUBLICATIONS

Mailen, J. C., and L. M. Ferris, Distribution of Transuranium Elements Between Molten Lithium Chloride and Lithium–Bismuth Solutions: Evidence for Californium(II), Inorg. Nucl. Chem. Lett., 7: 431 (1971).

Ferris, L. M., J. C. Mailen, and F. J. Smith, Chemistry and Thermodynamics of the Distribution of Lanthanide and Actinide Elements Between Molten $LiF-BeF_2$ and Liquid Bismuth Solutions, J. Inorg. Nucl. Chem., 33: 1325 (1971).

———, Estimated Free Energies of Formation of $PaCl_4$, $PaBr_4$, PaF_4, and Activity Coefficients for Protactinium in Liquid Bismuth Solutions, Inorg. Nucl. Chem. Lett., 7: 791 (1971).

———, J. C. Mailen, and F. J. Smith, Estimation of Activity Coefficients of Barium and Several Lanthanide Elements in Liquid Bismuth from Distribution Coefficient and Thermochemical Data, J. Less-Common Metals, 25: 83 (1971).

———, J. C. Mailen, and F. J. Smith, Estimated Free Energies of Formation of Some Lanthanide and Actinide Halides at 600–800°C Using Molten Salt–Liquid Metal Distribution Coefficient Data, J. Inorg. Nucl. Chem., 34: 491 (1972).

03:360 CHEMISTRY OF NONAQUEOUS SYSTEMS AT HIGH TEMPERATURES. Bredig, M. A.; Bronstein, H. R.; Dworkin, A. S. (Oak Ridge National Laboratory, Chemistry Division).

This program is concerned with the properties in the liquid and solid state at high temperature of materials pertinent to nuclear and nonnuclear energy. The following topics are under study: thermodynamic properties of melts containing BeF_4^{2-} or BF_4^- ions, important as constituents of potential nuclear fuel and coolant salt mixtures, using EMF, phase equilibria, and calorimetric measurements; and the thermodynamic systematics of the lanthanide halides using high temperature enthalpy, low-temperature specific heat, and high-temperature EMF measurements.

A continuing study of the diffuse, order–disorder transition at elevated temperatures in compounds of the fluorite and antifluorite type of structure. If we confirm our prediction of high electric conductivity in the solid between the transition and melting points, this type of compound (e.g., PbF_2 or $SrCl_2$) has a potential as a solid electrolyte in high-temperature batteries. The thermal conductivity of disordered UO_2 (fluorite structure) at 2000 to 3000°C is difficult to measure or to predict. Therefore, other compounds of fluorite structure (e.g., BaF_2) will be sought in which the conductivity at lower temperatures will model that in UO_2 at high temperatures.

Use of the novel potentiostatic voltage-step technique (developed in this laboratory) with a metal capillary to measure the electric conductivity of molten fluorides corrosive to ceramic insulators.

PUBLICATIONS

Dworkin, A. S., and M. A. Bredig, Enthalpy of Lanthanide Chlorides, Bromides, and Iodides from 298–1300°K. Enthalpies of Fusion and Transition, High Temp. Sci. 3: 81 (1971).

———, and M. A. Bredig, Miscibility of Liquid Metals with Salts X. Various Studies in Alkaline Earth Metal–Metal Fluoride and Rare Earth Metal–Metal Di- and Trifluoride Systems, J. Phys. Chem., 75: 2340 (1971).

———, Enthalpy of Uranium Tetrafluoride from 298–1400°K, Enthalpy and Entropy of Fusion, J. Inorg. Nucl. Chem., 34: 135 (1972).

Bronstein, H. R., and D. L. Manning, Lanthanum Trifluoride as a Membrane in a Reference Electrode for Use in Certain Molten Fluorides, J. Electrochem. Soc., 119: 125 (1972).

03:361 A STUDY OF THE MOLECULAR SYMMETRY OF TRANSITION METAL HALIDES AND THEIR REACTIONS WITH SMALL MOLECULES IN LOW-TEMPERATURE MATRICES. DeKock, Carroll W. (Oregon State University, Department of Chemistry, Corvallis, Oregon 97331).

The molecular geometry and force constants of simple transition metal halide molecules provide information about the bonding in these compounds. With few exceptions these molecular species do not exist at room temperature but must be prepared by vaporizing the appropriate solid transition metal halide. These high-temperature gas-phase species may be conveniently studied by trapping them in an argon matrix at 14 to 20°K and observing their infrared and laser-Raman spectra. These spectra lead to a determination of the molecular geometry and force constants for these molecules. The program to date has concentrated on studies of the rare earth fluorides and the 3d transition metal chlorides and fluorides.

In addition, studies of the reactions of these transition metal halides with small molecules, such as CO, N_2, O_2, and NO, have been made. We have observed reactions with all of the above small molecules with matrix-isolated NiF_2 and $NiCl_2$. In all cases the species formed, $NiX_2(YZ)$, were previously unknown. We anticipate continued studies in this area with emphasis on trapping transition metal catalytic intermediates.

PUBLICATIONS

DeKock, C. W., and D. A. Van Leirsburg, Preparation and Identification of CO and N_2 Complexes of NiF_2 and $NiCl_2$, J. Amer. Chem. Soc., 94: 3235 (1972).

———, R. D. Wesley, and D. D. Radtke, Infrared Spectra and Geometries of Rare-Earth Dihalides: SmF_2, $SmCl_2$, EuF_2, $EuCl_2$, YbF_2, and $YbCl_2$, High Temp. Sci., 4: 41 (1972).

———, and D. D. Radtke, Synthesis of the Dichlorides of Samarium, Europium, and Ytterbium, J. Inorg. Nucl. Chem., 32: 3687 (1970).

Wesley, R. D., and C. W. DeKock, Geometry and Infrared Spectra of Matrix-Isolated Rare-Earth Halides. I. LaF_3, CeF_3, PrF_3, NdF_3, SmF_3, and EuF_3, J. Chem. Phys., 55: 3866 (1971).

03:362 CHELATION OF TRANSITION METALS BY DERIVATIVES OF 3-NITROSO-2-PYRIDINOL AND 5-NITROSO-4-PYRIMIDOL. McDonald, Curtis, W. and Rhodes, Thornton. (Southern University, Department of Chemistry, Baton Rouge, Louisiana 70813).

The major objectives of this investigation are to study the various types of spectra, determine reaction ratios and structures, investigate solution equilibria, and ascertain the analytical applications of metal chelates formed by the reaction of transition metal ions with derivatives of o-nitrosopyridinols and o-nitrosopyrimidinols. In order to carry out the proposed objectives, some o-nitrosopyridinols and o-nitrosopyrimidinols will be purchased commercially and others will be synthesized. The investigation will include a study of the effect that various fundamental groups at certain positions on the pyridine and pyrimidine rings would have on the chelating properties of the organic reagents. If a metal chelate is formed that shows exceptional analytical importance, a method will be developed for the determination of the metal involved. In all cases, the reaction ratios in solution and structures of the metal complexes will be of primary importance.

The usual conventional methods of determining reaction ratios in solution and structures of metal complexes will be utilized. These include molar ratio studies, continuous variations methods, infrared spectrophotometry, elemental analysis, and others. Formation constants of the various metal complex ions in solution will be determined from spectral data.

PUBLICATION

McDonald, C. W., and J. Rhodes, The Chelation of o-Nitrosopyrimidinols I, Mikrochim. Acta, 767-771 (1971).

03:363 UNUSUAL OXIDATION STATES OF TRANSITIONAL METALS. Watt, George W. (The University of Texas, Department of Chemistry, Austin, Texas 78712).

This program is concerned with a broad investigation of the chemistry of transitional metals (both d- and f-series) in (particularly) abnormally low oxidation states, the stabilization of these states via coordination with appropriate ligands, and the effect of coordination on the properties of the associated ligands. Although past work has emphasized primarily the d-series elements, current and future work is and will be concerned with the f-series actinides, thorium and uranium. For example, the higher oxidation states of uranium have been studied extensively while the (II), (I), and (O) species as components of coordination compounds are virtually unknown. We propose to generate the monoxide, UO, by the reduction of $UOCl_2$ with either potassium in liquid ammonia or sodium naphthalenide in tetrahydrofuran and $(C_5H_5)_2U$ by the similar reduction of the known corresponding dichloride. If these and related species can be produced and characterized, they will then be combined with ligands chosen with a view to producing volatile compounds of thorium and uranium in the hope that they—or analogous compounds of the higher actinides—might be of interest in connection with isotope separations using the gas centrifuge.

PUBLICATIONS

Watt, George W., L. K. Thompson, and A. J. Pappas, Tetrakis and Bis Platinum(II) Iodide Complexes with Pyridine and Substituted Pyridine Ligands, Inorg. Chem., 11: 747 (1972).

———, and William R. Strait, The Synthesis of Complexes of 2-, 3-, and 4-Cyanopyridine-N-Oxide with Copper(II) and Iron(II) and (III), J. Inorg. Nucl. Chem., 34: 947 (1972).

———, and John E. Cuddeback, The Synthesis of Mixed Ligand Complexes of Platinum(II), J. Inorg. Nucl. Chem., 33: 259 (1971).

———, and John S. Thompson, Jr., The Interaction of Liquid Ammonia and Urea and Thiourea Complexes of Copper(I) and (II), Silver(I), Zinc(II), Nickel(II), and Palladium(II), J. Inorg. Nucl. Chem., 33: 1319 (1971).

———, and Robert L. Hood, Reactions of Deprotonated Ligands—VI Beta-Aminoethylamido-(ethylenediamine) Palladium(II) Iodide, J. Inorg. Nucl. Chem., 32: 3359 (1970).

ALSO SEE Heavy Element Chemistry: 03:69, 03:71, 03:76, 03:78, 03:80, 03:87; Radiation Chemistry: Other; 03:142; Kinetics and Mechanisms: 03:209, 03:228, 03:238; Chemical Spectroscopy: 03:230, 03:234, 03:238, 03:239, 03:252, 03:254, 03:261, 03:263; Thermodynamics: 03:306, 03:309, 03:310, 03:311, 03:313, 03:316, 03:317, 03:321, 03:323, 03:324, 03:325, 03:326; Structural Chemistry: 03:373; Analytical Chemistry: 03:405; Separations Chemistry: 03:410, 03:416, 03:417, 03:418; Engineering Chemistry: 03:424, 03:425, 03:426, 03:428, 03:429, 03:432, 03:433, 03:434, 03:435; Miscellaneous Chemical Studies: 03:452, 03:453, 03:454, 03:460.

STRUCTURAL CHEMISTRY

Studies of the structure of matter, principally by neutron and x-ray diffraction.

03:364 X-RAY-DIFFRACTION STUDIES OF MOLECULAR STRUCTURE. Clardy, Jon. (Ames Laboratory, Chemistry Division).

The goal of our program is the application of x-ray diffraction to the elucidation of molecular structures of biochemical, mechanistic, or theoretical importance.

Biological molecules now under investigation include aminousnic acid, a key fungal metabolite of unknown structure; synthetic and natural dimeric alkaloids related to the clinically important anticancer alkaloids vinblastine and leurocristine; a potent toxin from A. gravis; and oleandomycin, a macrolide antibiotic. In conjunction with these problems we are working on crystallographic techniques, such as the use of higher order phase relationships, to determine structure invariants and the practical use of anomalous dispersion data early in the phase-determining process.

Mechanistic problems of special emphasis are those related to reactions of molecules with strained carbon–carbon bonds or fluxional structures. We are investigating the bromination products of semibullvalene and bullvalene. We are completing the structure of the first dimer of a strained-bridgehead olefin. Work is also in progress on structures involving silver-catalyzed rearrangements of strained hydrocarbons.

Theoretically interesting structures now being worked on include the first silepin, and its consequences for $d\pi - p\pi$ delocalization; a crystalline homotropylium derivative; an accurate determination of all carbon–carbon bond lengths in bihomocubane; model propellanes; a bishomoaromatic naphthlene and azabullvalene.

PUBLICATIONS

Clardy, Jon, Leonard K. Read, Michael J. Broadhurst, and Leo A. Paquette, Crystal and Molecular Structure of cis-Bicyclo[6.1.0] nonatriene Cycloadducts, J. Amer. Chem. Soc., 94: 2904 (1972).

———, J. A. Chan, and W. C. Wildman, The Structure of Lycorenine and the 7-Hydroxy Alkaloids Derived from the [2]Benzopyrano [3,4-g] Indole Nucleus, J. Org. Chem., 37: 49 (1972).

———, and T. J. Barton, Novel Solid-State Molecular Complex of Diphenylacetylene and 1,1-dimethyl-2,5-diphenyl silacyclopentadiene, J. Chem. Soc., (D) 11: 690 (1972).

———, G. K. McEwen, J. A. Mosbo, and J. G. Verkade, The Structure of the Product Obtained from an Unusual Phosphine Halogenation Reaction, J. Amer. Chem. Soc., 93, 6937 (1971).

Paquette, Leo A., Michael J. Broadhurst, Chee-man Lee, and Jon Clardy, The Stereochemistry of Uniparticulate Electrophilic Additions to cis-Bicyclo[6.1.0]nonatriene, J. Amer. Chem. Soc., 94: 630 (1972).

03:365 DEVELOPMENT OF IMPROVED DIFFRACTION TECHNIQUES. Jacobson, Robert A. (Ames Laboratory, Chemistry Division).

The past few years have seen a pronounced increase in use of diffraction techniques by the novice. Although a reasonable fraction of structures can now be solved by rather straightforward methods, diffraction techniques are still rather expensive in time and effort. New approaches that offer greater efficiencies are still needed.

We have recently developed a computer program for rapid Fourier series computation, based on the fast Fourier (Cooley–Tukey) algorithm, and this program is now being distributed to interested crystallographers around the world. With this program electron density maps and other similar crystallographic three-dimensional Fourier series can be calculated in one-fifth to one-twenty-fifth the time necessary for other general programs previously available. Moreover, the speed advantage increases as the size of the problem increases.

Research is also continuing into the use of a polychromatic neutron beam for diffraction investigations. Use of such a white beam provides almost a 100-fold increase, or permits the use of much smaller crystals. Current successful refinement of potassium antimony tartrate has now further demonstrated the usefulness of this approach. Investigations are also in progress on a modification of this technique employing simultaneously three to four orders of reflection from a graphite monochromating crystal.

With the rapidity of electron density map calculations afforded by the fast Fourier program, it now becomes possible to attempt to couple some of the existing structure determination methods for complex molecules, namely Patterson superposition and symbolic addition methods, in order to obtain a more powerful technique than either alone. Such investigations have begun and initial results are promising enough that further research in this area is planned.

PUBLICATIONS

Hubbard, C. R., C. O. Quicksall, and R. A. Jacobson, A New Technique for Neutron Diffraction—Use of White Radiation, Nucl. Instrum. Methods, 94: 185 (1971).

———, C. O. Quicksall, and R. A. Jacobson, A Highly Efficient Neutron Diffraction Technique: Use of White Radiation, Acta Cryst., A 28: 236 (1972).

Hackert, M. L. and R. A. Jacobson, A Method for Partial Structure Evaluation, Acta Cryst., B, 26: 1682 (1970).

03:366 INFLUENCE OF WEAK INTERACTIONS ON SOLID STATE STRUCTURES. Jacobson, Robert A. (Ames Laboratory, *Chemistry Division*).

Strong interactions of the type associated with the formation of molecules from their constituent atoms are now reasonably well understood. However, the weaker interactions involved in the formation of many moieties in solution and especially in the solid phase are certainly much less well understood. The purpose of this research is to study by x-ray- and neutron-diffraction techniques the structures of solid state systems where weak interactions are important. It must be remembered that in many solids, although the interactions are weak, they are so numerous as to dictate many of the macroscopic properties of the solid.

Current emphasis in this program is placed on the study of two such model systems: the antimony halide and the copper bipyridylamine complexes. By varying the cation in the first case and the anion in the second, many different complexes can be isolated. For example, results just obtained for $Co(NH_3)_6SbCl_6$ indicate that the $SbCl_6^{3-}$ anion has undistorted octahedral shape with no evidence of lone pair distortion; however, preliminary results on $Co(NH_3)_6$-Sb_2F_9 indicate that the $Sb_2F_9^{3-}$ species consists of two square pyramids sharing a vertex through an asymmetric bridge. The coordination suggests the lone pair occupies the sixth position in each polyhedron to complete the distorted octahedron. The difference in these two structures containing identical cations could be ascribed to differences in electronegativity between fluorine and chlorine or to a size difference between the two halogens. Future plans include extensions of these structural studies including investigations of $KSbCl_5$ and $Cs_3Sb_2Br_9$.

Refinement of the $(CuL_2I)_2IClO_4$ structural data (L = 2,2'-bipyridylamine) indicates a distorted five-coordinate trigonal bipyramidal geometry where the distortion is toward a square pyramidal geometry with one of the L-nitrogens at the apex. (It should be noted that a trans planar configuration of the two amine ligands is essentially eliminated because of ligand–ligand repulsions.) Previous geometries found by us for such Cu–L complexes with other anions (ClO_4, SCN) include distorted tetrahedral, distorted square pyramidal, and distorted octahedral. Studies of tripyridylamine complexes of copper such as $[Cu(tripyam)_2I]ClO_4$ and $[Cu(tripyam)_2SCN]ClO_4$ are planned.

PUBLICATIONS

Lawton, S. L., and R. A. Jacobson, The Crystal Structure of Quinuclidinium Dodecabromoantimon(III) antimon(V)ate-2-Dibromine, $(C_7H_{12}NH)_4Sb(III)Sb(V)Br_{12} \cdot 2Br_2$, Inorg. Chem., 10: 709 (1971).

______, R. A. Jacobson, and R. S. Frye, The Crystal Structure of Pyridinium Tetracosabromoantimon(III) triantimon(V)ate, $(C_5H_5NH)_6Sb^{III}Sb_3^{V}Br_{24}$, Inorg. Chem., 10: 701 (1971).

Johnson, J. E., T. A. Beineke, and R. A. Jacobson, Crystal and Molecular Structure of Bis-(2,2-bipyridylamine) copper(II) perchlorate, J. Chem. Soc., A: 2124 (1971).

Hackert, M. L., R. A. Jacobson, and T. A. Keiderling, The Crystal Structure of Tetraethylammonium hexabromoantimonate(V), $(C_2H_5)_4NSbBr_6$, Inorg. Chem., 10: 1975 (1971).

______, and R. A. Jacobson, The Crystal Structure of 4-Ethylpyridinium tetrabromoferrate(III), Acta Cryst., B, 27: 1658 (1971).

03:367 NEUTRON MAGNETIC DIFFRACTION PROGRAM. Atoji, M. (Argonne National Laboratory, Chemistry Division).

Our principal objective is to study the nature of unpaired electrons associated with chemical and metallic bonds in solids. More specifically, the magnetic moment distribution of the unpaired electrons in the rare earth compounds and their actinide analogs are being investigated using neutron diffraction techniques with the applied magnetic field of up to 25 kilogauss at temperatures between 2°K and 1500°C. The program includes the determination of the crystal structures in order to relate them to the magnetic structures. Our neutron studies of the isostructural series, RC_2, RAu_2, and RAg_2 (R = rare earth elements), are revealing the fascinating variety of the magnetic configurations due to the anisotropic exchange interaction and the equally strong crystal field effect. This work will be extended to similar rare earth and uranium compounds so as to provide further information regarding the electronic spin interaction. By the same token, the intermetallics in the U–Fe, U–Co and U–Ni systems may also be included in the future program. An extensive experimental work on metallic erbium has just been completed, and the data are being analyzed with a specific emphasis on the spin density waves in the thermally and magnetically excited states. The solid solution systems, US–UC and UO_2–CeO_2, which may well be of interest in a systematic study of refractory uranium compounds, are scheduled for investigation, though not in the immediate future.

PUBLICATIONS

Atoji, M., Magnetic Structures of Tb_2C_3 and Ho_2C_3, J. Appl. Phys., 42: 1630 (1971).

______, Magnetic Structure of α-Tb_2C_3, J. Chem. Phys., 54: 3504-3509 (1971).

______, Magnetic Structure of α-Ho_2C_3, J. Chem. Phys., 54: 3510-3513 (1971).

______, Neutron Diffraction Study of Ce_2S_3 at 300°–5°K, J. Chem. Phys., 54: 3226-3227 (1971).

______, Neutron Structure Analyses of the Cubic CaC_2 and KCN, J. Chem. Phys., 54: 3514-3516 (1971).

03:368 STUDY OF HYDROGEN IN METAL HYDRIDES BY NEUTRON-SCATTERING MEASUREMENTS. Flotow, H. E. (Argonne National Laboratory, Chemistry Division).

In recent years neutron-diffraction and inelastic-neutron-scattering techniques have been used to study both the structure and proton dynamics in transition metal hydrides. Quasielastic scattering of a well-resolved beam of cold neutrons as a function of momentum transfer can be used to provide detailed information about hydrogen diffusion rates, activation energies, and in some cases, hydrogen jump distances.

We have studied the diffusion process of hydrogen in vanadium hydride by quasielastic thermal neutron scattering. Neutron line widths associated with diffusion broadening have been determined at 485K for $VH_{0.198}$ and $VH_{0.570}$. These measurements cover a range of momentum transfers for elastic scattering up to $4.1 A^{-1}$. The line width results are compared with proposed models involving diffusive jumps between octahedral and tetrahedral sites. Although no complete agreement was obtained, this comparison leads to the conclusion that jumps between tetrahedral sites seem to predominate in the diffusion process for $VH_{0.570}$. The results also suggest that the large Debye–Waller factors found in the present and previous neutron-scattering experiments on VH_x are connected with the relative magnitudes of diffusion relaxation time and jump time between sites.

Neutron line widths associated with diffusion broadening have now been obtained for $TaH_{0.15}$ from 295 to 613°K. These data are now being analyzed and additional data are being obtained for $TaH_{0.50}$.

It is now apparent that the theory has to be extended to include finite jump times and possibly other effects. However, detailed analysis of these effects and the influence of possible multiple jumps and mixed-site occupancy would require many more parameters in the cross section expressions. We are now preparing to make more accurate, high-resolution measurements on a single crystal of TaH_x to compare the usefulness of a more detailed theory for analyses of our experiments.

Inelastic-neutron-scattering measurements on $PdH_{0.68}$ are now in progress. Previous electric resistivity measurements and heat capacity data have shown anomalous behavior near 50°K. The neutron-scattering study will provide information on proton dynamics in the species and may help explain the anomalous behavior near 50°K.

PUBLICATIONS

Rowe, J. M., K. Shold, H. E. Flotow, and J. J. Rush, Quasi-Elastic Neutron Scattering by Hydrogen in the Alpha and Beta Phases of Vanadium Hydride, J. Phys. Chem. Solids, 32: 41-54 (January 1971).

deGraaf, L. A., J. J. Rush, H. E. Flotow, and J. M. Rowe, Quasi-Elastic Thermal Neutron Scattering by Hydrogen in Alpha-Vanadium Hydride, J. Chem. Phys., 56: 4574 (1972).

______, J. J. Rush, R. C. Livingston, H. E. Flotow, and J. M. Rowe, Study of Hydrogen Diffusion in Vanadium and Tantalum by Quasi-Elastic Thermal Neutron Scattering, in Proceedings of the International Meeting on Hydrogen in Metals, Kernforschungsanlage, Jülich, Germany, March 20–24, 1972.

03:369 NEUTRON CRYSTALLOGRAPHY. Peterson, S. W., and Williams, J. M. (Argonne National Laboratory, Chemistry Division).

The current program of the neutron crystallography group emphasizes structural studies of compounds with strong hydrogen bonds. The aim of this work is to provide the detailed structural basis for the understanding of function and mechanism in complex hydrogen bonded systems.

Work to date has been largely confined to O–H–O bonds and has concentrated on a very interesting series of strong acid hydrates in which the H_2O to ionizable proton ratio is greater than one. In all cases studied, the ionizable protons are found to be associated with H_2O molecules forming the new hydrated proton species $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$. These intriguing species are characterized by unusually short O–H–O bonds and the key H bonds involving the acid protons are the shortest ones and are typically double-minimum or flat potential-well, single-minimum types. Associated with these novel bonding structures are high proton mobilities and, presumably, facile modes for proton transfer. Thus, these highly hydrated proton species, which can be observed in detail in the well-ordered solid state, may provide useful models for protonic conduction and transfer phenomena of importance in aqueous liquid and biochemical systems.

Current hydrated proton studies include $H_2PtCl_6 \cdot 6H_2O$, nitranilic acid hexahydrate, sulfosalicylic acid trihydrate, and p-toluenesulfonic acid trihydrate. Isotope studies using partially and fully deuterated materials, in order to obtain isotope distribution and hydrogen bond isotope effect information, are also in progress. Extensions to such compounds as $HBr \cdot 2H_2O$, $HBr \cdot 4H_2O$, and $H_4Mo(CN)_8 \cdot 6H_2O$ are planned for the near future.

A broader range of neutron investigations will include structure studies of the currently important niobium and tantalum hydride system as well as the hydrogen bonded $(ClHCl)^-$, $(BrHBr)^-$, and $(F \cdot (HF)_n)^-$ ions. Longer range plans envisage a shift of attention to systems of biological importance.

PUBLICATIONS

Williams, J. M., and S. W. Peterson, Molecular Structure Determination by Neutron and X-Ray Diffraction, Chap. 1, in Spectroscopy in Inorganic Chemistry, Vol. II, Academic Press, Inc., New York, 1971.

O'Reilly, D. E., E. M. Peterson, C. E. Scheir, and J. M. Williams, Nuclear Magnetic Resonance of the Aquated Proton II: Chloroauric Acid Tetrahydrate, J. Chem. Phys., 55: 5629 (1971).

Peterson, S. W., J. M. Holloway, B. A. Coyle, and J. M. Williams, Antiprismatic Coordination About Xenon: The Structure of Nitrosonium Octafluoroxenate(VI), Science, 173: 1238 (1971).

Swanson, J. S., and J. M. Williams, Bichloride Ion Geometry in Tetramethyl Ammonium Bichloride, Inorg. Nucl. Chem. Lett., 6: 271 (1970)

03:370 STRUCTURAL AND SPECTRAL CHARACTERIZATION OF SOME ANHYDROUS DOUBLE NITRATE SALTS OF THE LANTHANIDES. Siegel, S., Carnall, W., Ferraro, J., and Gebert, E. (Argonne National Laboratory, Chemistry Division).

Structural investigations employing x-ray-crystallographic and molecular-spectroscopic techniques are being carried out in order to aid in relating hypersensitive transitions in the electronic spectra of the rare earth ion to its site symmetry.

The first compound to be investigated is $K_3Pr_2(NO_3)_9$. The symmetry of the crystal is cubic with a = 13.52 Å and the space group is O^6.

A Pr atom on a threefold axis is surrounded by twelve oxygen atoms belonging to six nitrate ions. The nitrate configurations fall into two groups. In each group, the Pr atom is shared by two oxygen atoms of a nitrate ion. However, in one nitrate configuration, one oxygen atom is shared by two Pr atoms and the two remaining oxygens by a Pr and K atom, respectively, while in the second nitrate configuration, one oxygen atom is bound to two K atoms while the other two oxygen atoms are shared between a Pr and K atom.

Preliminary investigations (W. Carnall) indicate a strong correlation between the intensities of the transitions and the site symmetry of the rare earth ion. As a result, more structures are to be investigated in detail. $K_3Er_2(NO_3)_9$, which is monoclinic, is currently under study. Similar studies, possibly with actinide sulfates, are also being contemplated.

03:371 CRYSTALLOGRAPHIC AND RELATED CHEMICAL STUDIES OF URANIUM COMPOUNDS. Siegel, S., Hoekstra, H., and Sherry, E. (Argonne National Laboratory, Chemistry Division).

Current emphasis has been directed towards a study of the UO_3–H_2O system, covering elucidation of structure and the nature of the hydrogen bonding.

The structure of $UO_3 \cdot \frac{1}{3}H_2O(H_2U_3O_{10})$ has been completed. The configuration shows chains of shared octahedra and bipyramids, with each configuration beginning and terminating in an octahedral array of oxygen atoms. Utilizing bond-strength and infrared data, it has been shown that hydrogen atoms are associated with these octahedra. CuU_3O_{10} is believed to exhibit a similar grouping, but with the Cu atoms bonded to the oxygen configuration. A morphological relationship to α-UO_3 has been found.

The structure of γ-$UO_3 \cdot H_2O(UO_2(OH)_2)$ has been determined. The configuration about a uranium atom is a distorted octahedron with secondary oxygens forming extended puckered layers. Each uranyl oxygen of an octahedron is hydrogen-bonded to a secondary oxygen in an adjacent layer. This structure explains the origin of what we consider to be a shear relationship governing a phase transformation between the β- and γ-forms of $UO_2(OH)_2$. With proper choice of orientation, orthorhombic β-$UO_2(OH)_2$ exhibits pseudo monoclinic symmetry with cell dimensions close to those of monoclinic γ-$UO_2(OH)_2$. However, the β-angle of the pseudo cell is about 10° larger than that in the γ-phase. This causes a one Ångstrom translational difference between the two structures. It is believed that a one Ångstrom shear causes a slight rotation of the U-6(O) octahedron, permitting a shift in two of the four hydrogen bonding directions. A report [Bannister and Taylor, Acta Cryst., B 26: 1775 (1970)] indicates that above room temperature, the octahedra of the β-modification exhibit rotation. Grinding experiments demonstrate the presence of this shear relationship. Two other phases in the $UO_3 \cdot H_2O$ system are being considered for future study.

Siegel, S., A. Viste, H. R. Hoekstra, and B. Tani, The Structure of Hydrogen Triuranate, Acta Cryst., B 28: 117 (1972).

______, and H. Hoekstra, An Examination of the Symmetry of Alpha-UO_3, Inorg. Nucl. Chem. Lett., 7: 497 (1971).

______, and H. Hoekstra, Bond Lengths in Gamma-UO_3, Inorg. Nucl. Chem. Lett., 7: 455 (1971).

Hoekstra, H., S. Siegel, and F. X. Gallagher, Reaction of PtO_2 with Some Metal Oxides, Chap. 4, Advan. Chem. Ser., No. 98 (1971).

______, and S. Siegel, Preparation and Properties of Cr_2UO_6, J. Inorg. Nucl. Chem., 33: 2867 (1971).

03:372 STRUCTURAL PROBLEMS IN POTENTIAL BREEDER FUELS. Siegel, S., Thorn, R., and Gebert, E. (Argonne National Laboratory, Chemistry Division).

Two problems are being considered in connection with a study of breeder fuels.

The first will be an attempt to determine the structure of UO_{2+x} in order to derive the site occupancy of the oxygen atoms. This would permit a measure of the occupancy of vacancies with anions and would lead to a structural evaluation of the nature of the defects. If such a study gave reasonable results, the technique could be applied to the mixed U–O/Pu–O fuel itself. The second problem under consideration is a study of the diffusion of uranium in UO_{2+x} and the relationship to structure.

03:373 SOLID STATE CHEMISTRY OF RARE OXIDE SYSTEMS. Eyring, LeRoy. (Arizona State University, Department of Chemistry, Tempe, Arizona, 85281).

All solid substances, at temperatures above the absolute zero, possess defects in their structures. Nonstoichiometric compounds or solids exposed to high temperatures and/or radiation fields such as nuclear power fuels and supporting materials for fusion devices have a high concentration of extended defects.

This research project seeks to build upon extensive investigations into the thermodynamic and dynamic properties of the closely related fluorite-type rare earth oxides as model systems for the actinide oxides and for solids with extended defects in general. Further understanding of these related materials requires definitive structure determination of key phases and the divination of the structural principle that relates them. Their complexities include polymorphism in single phases, homologous series of intermediate compounds, order–disorder transformations from intermediate phases of narrow composition to truly nonstoichiometric phases of wide composition range, chemical hysteresis, and pseudo-phase behavior.

The structural studies on single crystals are to be accomplished by the most advanced techniques including automated x-ray diffractometry and especially high-resolution electron microscopy and selected area electron diffraction. The latter method may lead to direct imaging of the lattice with point-to-point display of normal and defect structural intergrowth.

PUBLICATIONS

Sawyer, J. O., P. Caro, and L. Eyring, Preparation, Analysis and X-Ray Identification of the Dioxymonocarbonates of Lanthanum and the Lanthanide Elements, Monatsh. Chem., 102: 333 (1971)).

Haschke, John, and LeRoy Eyring, Hydrothermal Equilibria and Crystal Growth of Rare Earth Oxides, Hydroxides, Hydroxynitrates, and Hydroxycarbonates, Inorg. Chem., 10: 2267 (1971).

Turcotte, R. P., T. D. Chikalla, and L. Eyring, Oxygen Decomposition Pressures and Thermodynamic Data for Nonstoichiometric Berkelium Oxide, J. Inorg. Nucl. Chem., 33: 3749 (1971).

Weber, Gary, and LeRoy Eyring, Self-Diffusion of Oxygen in Iota Phase Praseodymium Oxide, in Advances in Chemical Physics, Vol. 21, Chemical Dynamics, J. Hirschfelder and D. Henderson (Eds.), Wiley–Interscience, Inc., New York, p. 253 (1971).

Turcotte, Rheal, Joyce Warmkessel, Richard J. D. Tilley, and LeRoy Eyring, On the Phase Interval $PrO_{1.50}$ to $PrO_{1.71}$ in the Praseodymium Oxide–Oxygen Systems, J. Solid State Chem., 3: 265 (1971).

03:374 STRUCTURAL STUDIES OF ORGANIC POLYSULFIDES.

Bernal, I. (Brookhaven National Laboratory, Chemistry Department).

As part of a broad program of studies of the structural chemistry of organosulfur compounds at Brookhaven the crystal structure of N,N′-dimethyl-3,6-epi-tetrathio-2,5-piperazinedione was determined. This is a synthetic compound, the tetrasulfide analogue of a 2,5-piperazinedione ring with an epi-dithio bridge across the 3,6-positions, the latter being a structural fragment common to gliotoxin, virus-inhibiting antibiotics of the aranotin type, sporidesmins, and the cancerostatic antibiotic chaetocin. The synthetic compound was prepared in the hope that it would give leads to the nature of the biogenetic processes by which some soil bacteria synthesize a certain class of substances.

The presence of disulfide linkages in biologically important molecules is well known. An important example is the disulfide compound sporidesmin, produced by the fungus Pithomyces chartarum, which is very harmful to sheep. That biological polysulfide analogues of the disulfide exist was not known until early 1972 when A. Taylor, et al., announced that this same fungus also produces the tetrasulfide compound Sporidesmin G, and that the latter has the same potency as Sporidesmin in damaging sheep. The Brookhaven crystal structure determination of the synthetic tetrasulfide compound provides a structural description of the biologically active center of Sporidesmin G. A natural question to ask is: Are there tri- or tetrasulfide analogues of other natural disulfide compounds (e.g., enzymes), and, if so, what are their biological effects and potencies? An answer to this question will be sought in a study of oxytocin to be run in collaboration with an investigator at Mount Sinai School of Medicine.

PUBLICATIONS

Ganguli, K. K., G. O. Carlisle, H. J. Hu, L. J. Theriot, and I. Bernal, Cobalt and Iron Complexes of Quinoxalinedithiol, J. Inorg. Nucl. Chem., 33: 3579 (1971).

Davis, B. R., I. Bernal, and H. Kopf, The Crystal and Molecular Structure of Di-π-Cyclopentadienyl Tungsten Tetrasulfide-$(\pi\text{-}C_5H_5)_2WS_4$, Angew. Chem., 83: 1018 (1971).

______, and I. Bernal, The Crystal and Molecular Structure of Syn-2, 11-dithia-9, 18-dimethyl-[3.3]metacyclophane, J. Chem. Soc., B: 2307 (1971).

Ricci, J. S., and I. Bernal, The Crystal Structure of 7, 15, 17, 19-Tetraethoxy-2,3,4,5,10,11,12,13-octathiatricyclo-[12,2,2, $2^{6,9}$]-eicosa-6,8,14,16,17,19-hexane, A Sulfur Analogue of the Paracyclophanes, J. Chem. Soc., B: 1928 (1971).

03:375 MAGNETIC STRUCTURE DETERMINATION BY NEUTRON DIFFRACTION.

Corliss, L. M., and Hastings, J. M. (Brookhaven National Laboratory, Chemistry Department).

Neutron diffraction is the most powerful of modern tools for determining the arrangement of atomic magnetic moments in solids. The interaction of neutrons with an ordered array of spins gives rise to coherent scattering and a characteristic diffraction pattern analogous to that obtained with x rays. From these magnetic diffraction effects one can derive the spatial repeat pattern of atomic spins. In addition, one can generally obtain the magnitude and orientation of individual moments as well as the spatial distribution of spin density within the atom. This information is basic to the understanding of magnetic properties: it provides a description of the magnetic state and an essential framework for theoretical calculations. Studies now under way or planned include the following:

1) A class of newly prepared iron-group fluorides crystallizing with the bronze and pyrochlore structures is being investigated. 2) The system $FeTa_2O_6$–$FeTaO_4$ has been found to exhibit ferromagnetism in a limited composition range and this observation will be further explored by systematic magnetic structure studies. 3) Investigation of the analogous antimonate system is also planned. 4) The magnetism of rare earth borides has been poorly understood despite extensive study. Magnetic structure determinations are being undertaken to provide a basic description of the magnetic state of these compounds.

PUBLICATIONS

Oesterreicher, H., L. M. Corliss, and J. M. Hastings, A Neutron Diffraction Study of the Pseudobinary System $ErCo_2$–$ErAl_2$, J. Appl. Phys. 41: 2326 (1970).

Shaked, H., J. M. Hastings, and L. M. Corliss, Magnetic Structure of Magnesium Chromite, Phys. Rev., B 1: 3116 (1970).

Hastings, J. M., and L. M. Corliss, Ordered Moment of NiS_2, IBM J. Res. Devel. 14: 227 (1970).

______, L. M. Corliss, M. Blume, and M. Pasternak, Spin Arrangement in the Pyrite, $MnTe_2$, Phys. Rev., B 1: 3209 (1970).

03:376 MAGNETIC PROPERTIES OF CRYSTALLINE COMPOUNDS.

Elliott, N. (Brookhaven National Laboratory, Chemistry Department).

Magnetic susceptibility measurements supplement x-ray crystal structure determinations in arriving at an understanding of the structures and chemical bonding in compounds of the transition metals. In this program attention is given to the effects of symmetry and of magnetic coupling via nonmagnetic ions. Among the results are the following:

An x-ray and magnetic study showed that in (bip H_2)$MnCl_5$ (bip H_2 = biphenyl) the anion $MnCl_5^{2-}$ is square pyramidal and monomeric.

Similar studies on $(NH_4)_2MnCl_6$, K_2MnCl_6, and Rb_2MnCl_6 showed that the observed magnetic interactions were in good agreement with those calculated from a model involving the covalent configuration $Mn^+ - Cl^0 - Cl^0 - Mn^+$, and the ionic form, $Mn^{2+} - Cl^- - Cl^- - Mn^{2+}$.

In magnetic susceptibility studies of some o-phenanthroline complexes of Fe(II) and Co(II) it was found that the moment of $[Fe(II)(mphen)_2](C10_4)_2 \cdot 2H_2O$ changes from 5.6 β at 295°K to 2.4 β at 61°K. A change in symmetry is thought to be the cause.

A study of some triple nitrites of transition metals is under way and an investigation of the magnetic behavior of transition metal phthalocyanines is planned.

PUBLICATIONS

Bernal, I., N. Elliott, and R. Lalancette, Molecular Configuration of the Anion $MnCl_5^{2-}$—A Square Pyramidal Pentahalide of the 3d Transition Series, Chem. Comm., 803 (1971).

03:377 PEPTIDE SEQUENCING BY ION IMPACT MASS SPECTROMETRY.

Friedman, L. (with L. Greene, Biology Department). (Brookhaven National Laboratory, Chemistry Department).

Techniques developed in the study of gaseous ion chemistry have been focused on problems of structural mass spectrometry of biochemically interesting molecules. The goal of this program is to develop a high-sensitivity technique for the generation of spectra that will provide amino acid sequence information on peptides and their derivatives and that will also permit the quantitative assay of mixtures of peptides, amino acids, and their derivatives. The two fundamental problems in structural mass spectrometry are the ionization process and sample volatility. The ionization problem has been virtually solved by the use of a low-pressure ionization chamber in which proton transfer takes place in a single ion–molecular collision. The tandem mass spectrometer system developed in the BNL Chemistry Department has been adapted to produce intense low-energy beams of a variety of protonated molecules. Subsequent proton transfer takes place with controlled amounts of internal energy deposited in the product ion. Serious background problems in the ionization of amino acids and peptides can be minimized by selection of appropriate ion reagents. Sample volatility can be enhanced with surface desorption methods. The use of inert surfaces reduces the energy required for the phase transition from adsorbed to gaseous molecules by tens of kilocalories per mole. Samples of less than one nanomole of underivatized tri- and tetraalanine and Thyrotropin Releasing Hormone have been evaporated from a teflon probe in a teflon collision chamber to provide mass spectra suitable for structural identification and quantitative assay.

The mass spectrometer system is currently being modified for computer control and data acquisition to permit investigations with even smaller samples of peptides and their derivatives. This will also facilitate the investigation of volatility problems.

PUBLICATIONS

Beuhler, R. J., L. J. Greene, and L. Friedman, Solvated Proton Mass Spectra of a Tripeptide Derivative, J. Amer. Chem. Soc., 93: 4307 (1971).

______, Flanigan, E., L. J. Green, and L. Friedman, Volatility Enhancement of Thyrotropin Releasing Hormone for Mass Spectrometric Studies, Biochem. Biophys. Res. Commun., 46: 1082 (1972).

03:378 CHEMICAL CRYSTALLOGRAPHY STUDIES BY NEUTRON AND X-RAY DIFFRACTION.

Hamilton, W. C. (Brookhaven National Laboratory, Chemistry Department).

X-ray and neutron crystallography often offer the quickest and most economical methods for the determination of fine points of molecular structure. Neutron diffraction is especially valuable for the determination of light atom positions in the presence of very heavy atoms—usually a difficult problem in x-ray crystallography. These techniques are being used to attack a large variety of problems in molecular and crystal structure, many of them in collaboration with chemists or physicists from other institutions.

Neutron-diffraction refinements of the structures of $U(BH_4)_4$ and $Hf(BH_4)_4$ have provided the only reliable information on the mode of attachment of borohydride groups to metal atoms.

Neutron-diffraction investigations of feldspars are being carried out to determine substitution ratios and precise Debye–Waller factors at several temperatures in order to obtain thermodynamic quantities that may be important in theories of mineral formation.

A long-standing project on precision refinements of the structures of the several solid phases of ice will be completed soon with the analysis of a new set of data on ordinary Ice I.

X-ray diffraction work is directed mainly toward the study of compounds with possible biological significance. These include peptide–nucleoside compounds, one of which is a demonstrated antiviral agent. The geometry of pentacoordinate phosphorus is thought to be important in understanding the mechanisms of important biochemical reactions, and work is now under way on some pentacoordinate phosphorus compounds containing adamantane-like ring systems.

PUBLICATIONS

Kamb, B., W. C. Hamilton, S. J. La Placa, and A. Prakash, Ordered Proton Configuration in Ice II, from Single-Crystal Neutron Diffraction, J. Chem. Phys., 55: 1934 (1971).

Ross, F. K., W. C. Hamilton, and F. Ramirez, Crystal and Molecular Structure of Ethylene-1,1-bis(triphenylphosphonium)-2,2-bis(phenylamide): $[(C_6H_5)_3P]_2C.C(N.C_6H_5)_2$, Acta Cryst. B, 27: 2331 (1971).

03:379 PRECISION NEUTRON DIFFRACTION STUDIES OF AMINO ACID AND NUCLEIC ACID COMPONENTS. Hamilton, W. C., Koetzle, T. F. (Brookhaven National Laboratory, Chemistry Department).

The structures of amino acids and nucleosides and small polymers of these important biological building blocks are being accurately determined by neutron diffraction.

The structures of fifteen naturally occurring amino acids have been refined, and hydrogen atom positions have been determined to a precision of 0.002 Å. This amino acid work is drawing to a close with the refinement of a few remaining structures and the analysis of the wealth of information obtained on N–H ... O hydrogen bonds in terms of a semi-empirical potential function. This potential function and the other information on hydrogen atom configurations being derived will be of importance to those interested in the prediction of the structures of polypeptides and in the variability of amino acid structures as they occur in proteins.

Neutron-diffraction data are being collected for a complex formed between a purine and pyrimidine base so that the possibility of disorder in the hydrogen bond can be carefully examined. The possibility of proton transfer across the hydrogen bonds in these genetic materials has been suggested as being part of the mechanism for mutations in living organisms. The work will continue with the analysis of a number of other base pairs, nucleotides, and oligonucleotides.

PUBLICATIONS

Lehmann, M. S., T. F. Koetzle, and W. C. Hamilton, Precision Neutron Diffraction Structure Determination of Protein and Nucleic Acid Components: I. The Crystal and Molecular Structure of the Amino Acid L-Alanine, J. Amer. Chem. Soc., 94: 2657 (1972).

Verbist, J. J., M. S. Lehmann, T. F. Koetzle, and W. C. Hamilton, Direct Methods in Neutron Crystallography: The Solution of the Structure of L-Proline Monohydrate by Symbolic Addition and Tangent Refinement, Nature, 235: 328 (1972).

03:380 PARALLEL DATA COLLECTION SYSTEMS FOR DIFFRACTION STUDIES. Thomas, R. (Brookhaven National Laboratory, Chemistry Department).

A new parallel data acquisition system for single crystal x-ray crystallographic studies has been designed and constructed at Brookhaven. It is called AESOP—an Automatic Equi-inclination Spectrometer Operating in Parallel. AESOP will have a special usefulness for biological macromolecular structural studies where, because of sensitivity to x-ray exposure, data must be collected rapidly or not at all. The x-ray detectors in AESOP consist of a linear array of 128 discrete quantum counters. All simultaneous reflections in one reciprocal lattice layer are measured in parallel, rather than serially as in single counter, conventional x-ray diffractometers.

The construction of AESOP is complete and the entire instrumentation system has been operational. Minor and final modifications deemed necessary as a result of experience to date are under way and AESOP is expected to be in continuous operation during the summer of 1972.

AESOP will first be tested for speed and accuracy of data acquisition. It is hoped that an improvement factor of 20 to 40 in speed over conventional instruments can be realized. The accuracy of the measurements should be at least equal to that of conventional four-circle instruments.

The first study using AESOP will be that of a bacterial enzyme, streptococcal proteinase, in collaboration with BNL biologists. Efforts are under way to obtain suitable single crystals of this enzyme. It is expected that this work will establish AESOP as an important national facility.

03:381 MOLECULAR BEAMS. Street, K., Hebert, A. J. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

The gas phase geometry of the metal dihalides, MX_2, poses an interesting problem in bonding theory, in that experimental results indicate that some of these molecules are bent and others are linear. A particularly interesting case is that of the alkaline earth dihalides, where whether a molecule is bent or linear depends in some cases on the nature of the halide ligand rather than on the central metal atom. Electric deflection experiments are being done on the alkaline earth dihalides in order to better define the demarkation between bent and linear species. Preliminary results indicate that the rare earth halides may also exhibit this ambivalence, some being linear (or planar) and others bent. Investigation of the rare earths will be a major part of the future program.

Work will continue to improve the theoretical models that correlate and predict the properties of these molecules. The distribution of uranium, thorium, and other trace elements in igneous rocks derived from active and fossil subduction zones are being studied. Rocks from the Aleutian arc (an active zone) will be compared with those of the western U.S. where one or more fossil zones have been hypothesized.

Investigation of trace element distributions in California alpine-type ultramafic complexes will continue. These are thought to represent sections of oceanic crust and upper mantle.

03:382 X-RAY CRYSTALLOGRAPHY. Templeton, David H. and Zalkin, Allan. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

Crystal structures of numerous substances are being determined by x-ray-diffraction methods, chemical principles which control structure are being studied, and the methods for such investigations are being improved. One area of study is hydrogen bonding in salt hydrates and in organic crystals where it is often important to the structure and to the thermodynamic properties. Disorder of hydrogen bonds in a sodium phosphate hydrate and its contribution to the entropy is being investigated. Better mathematical models for the description of hydrogen atoms are under study; specifically, use of complex form factors in least-squares refinement of structure permits estimation of the proton position more precisely than the traditional method does. The application of anomalous dispersion effects to improve the power of structure-determination methods is being tested with a difficult example of a natural product from citrus fruits. Studies of diverse metal complexes and compounds of xenon fluorides continue to establish the constitution and chemical nature of these new materials. A search continues for crystals likely to be of general interest and importance for understanding chemistry or for practical applications.

PUBLICATIONS

Fisher, Mark S., David H. Templeton, Allan Zalkin, and Melvin Calvin, Structure and Chemistry of the Porphyrins. The Crystal and Molecular Structure of the Monohydrated Dipyrinated Magnesium Phthalocyanin Complex, J. Amer. Chem. Soc., 93: 2622 (1971).

St. Clair, David, Allan Zalkin, and David H. Templeton. The Crystal Structure of Cesium 3, 3′-commo-Bis[nonahydro-1, 2-dimethyl-1,2-dicarba-3-chroma-closo-dodecaborate] Hydrate, a Hydrate of a Chromium Metallocarborane Salt, Inorg. Chem., 10: 2587 (1971).

______, Zalkin, Allan and David H. Templeton, The Crystal Structure of Tetraethylammonium 2,2′-commo-Bis(nonahydrodicarba-2-cobalta-closo-decaborate), a Salt of the Cobalt Derivative of the Nonahydridodicarbononaborate(2)-Ligand Inorg. Chem., 11: 377 (1972).

Avdeef, Alex, Kenneth N. Raymond, Keith O. Hodgson, and Zalkin, Allan, Two Isostructural Actinide π Complexes. The Crystal and Molecular Structure of Bis(cyclooctatetraenyl) uranium(IV), U(C_8H_8)$_2$, and Bis(cyclooctatetraenyl)thorium(IV), Th(C_8H_8)$_2$, Inorg. Chem., 11: 1083 (1972).

Fischer, Mark S., David H. Templeton, Allan Zalkin, and Melvin Calvin, Crystal and Molecular Structure of Methyl Pheophorbide with Applications to the Chlorophyll Arrangement in Photosynthetic Lamellae, J. Amer. Chem. Soc., 94: 3613 (1972).

03:383 INTERATOMIC AND INTERMOLECULAR FORCES DERIVED FROM CRYSTAL STRUCTURES. Busing, W. R. (Oak Ridge National Laboratory, Chemistry Division).

The elucidation of the nature of interatomic and intermolecular forces is the central problem underlying the theory of chemical reactions. The geometric measurements available through x-ray and neutron diffraction furnish an anchor point for deducing the forces, and modern electronic computers provide a means of carrying out the necessary analysis. A computer program has been prepared that represents a crystal or an isolated molecule by a potential energy model. Three areas of research to which it is applicable will be mentioned.

Because of interest in $LiF-BeF_2$ systems, we have recently shown that the crystal structure of Li_2BeF_4 can be represented reasonably well by a Born–Mayer ionic model. This work will be extended to include short-range polarization effects in an effort to explain the distortion of certain crystal structures such as that of $CaCl_2$.

Calculations of the conformations of large organic molecules, both in crystals and in an isolated state, indicate that the geometry of five-membered rings may be affected significantly by intermolecular forces. An x-ray study of crystalline cyclopentane will be made to test these conclusions.

Calculations of the frequencies and normal modes of vibrations in crystals will permit a comparison of observed and calculated anisotropic thermal motion as well as a more precise interpretation of experimental interatomic distances.

PUBLICATIONS

Busing, W. R., An Interpretation of the Structures of Alkaline Earth Chlorides in Terms of Interionic Forces, Trans. Amer. Crystallogr. Assoc., 6: 57 (1970).

03:384 NEUTRON AND X-RAY CRYSTAL STRUCTURE ANALYSIS. Levy, H. A., Brown, G. M., Busing, W. R., Johnson, C. K., Thiessen, W. E. (Oak Ridge National Laboratory, Chemistry Division).

This project aims to furnish for selected crystals the accurate knowledge of structure required for basic chemical understanding in a number of areas: energetics of crystal packing, hydrogen bonding and distribution of hydrogen isotopes among different locations, unusual chemical bonding, relationships between structure and reactivity, carcinogenesis, and anti-carcinogenesis, and enzyme–substrate relations and other biochemical processes. It includes development of theory, computer programs, and instruments. The superb neutron facilities at ORNL are utilized whenever precise location of hydrogen atoms or the degree of hydrogen isotope substitution is required, as in current work on isotope partitioning in crystals of $Y(H_2O-H-OH_2)(C_2O_4)_2 \cdot H_2O$, which contain the rather rare diaquated proton $(H_2O\text{-}H\text{-}OH_2)^+$, and on hydroxamic acids, such as hydroxyurea, $H_2NCONHOH$, which has been shown to have a pyramidal nitrogen in the –NHOH group. Other compounds under study include lithium hydroxide monohydrate, the 1 : 1 complex of urea and phosphoric acid, metallocenes, terpenoids, steroids, and natural pigments. Specific topics for the near future are neutron diffraction studies in relation to nucleoside and nucleotide structure and to sugar transport in physiological systems, and x-ray studies related to the structure of chlorophyll and of certain bile pigments known to have helical configurations in solution. For the longer term, the applicability of neutron resonance scattering to the solution of crystal structures of proteins or other molecules of high molecular weight will be explored.

PUBLICATIONS

Brown, G. M., F. L. Hedberg, and H. Rosenberg, Crystal Structure of Decachlororuthenocene. Noncoplanarity of Carbon and Chlorine Atoms Arising From Valence Forces, J. Chem. Soc., D, 5: (1972).

Busing, W. R., A Convenient Way of Applying Constraints in Structure-Factor Least-Squares Refinement, Acta Crystallogr., Sect. A, 27: 683 (1971).

Desiderato, R., J. C. Terry, G. R. Freeman, and H. A. Levy, The Molecular and Crystal Structure of 8-Hydroxyquinoline-N-oxide, Acta Crystallogr., Sect. B, 27: 2443 (1971).

Ellison, R. D., H. A. Levy, and K. W. Fung, Crystal and Molecular Structure of Trimercury Chloroaluminate, $Hg_3(AlCl_4)_2$, Inorg. Chem., 11: 833 (1972).

Thiessen, W. E., H. A. Levy, W. G. Dauben, G. H. Beasley, and D. A. Cox, A Highly Twisted Double Bond, J. Amer. Chem. Soc., 93: 4312 (1971).

03:385 STRUCTURAL CHEMISTRY: STRUCTURE IN LIQUIDS AND GLASSES. Levy, H. A., Narten, A. H., Vaslow, F. (Oak Ridge National Laboratory, Chemistry Division).

Although liquids are involved in virtually all technological fields—energy, environment, biology—the liquid state is poorly understood on the atomic and molecular scale. Consequently, much knowledge about liquids is empirical, and sound methods of prediction and extrapolation are lacking. This program attacks the problem at three levels: (a) determination of atomic and molecular arrangements by neutron and x-ray diffraction, (b) development and application of methods of obtaining intermolecular forces consistent with observed arrangements, and (c) application of intermolecular forces to compute, predict, and extrapolate physical properties.

X-ray- and neutron-diffraction studies of the system BeF_2-LiF over wide ranges of temperature and composition have yielded high-precision correlation functions. Molecular dynamics calculations based on purely ionic interaction potentials derived from crystal data have yielded ion pair correlation functions that agree well with those derived from diffraction. More refined calculations are expected to provide thermodynamic and transport properties under conditions difficult to realize in the laboratory. This work is to be extended to the molten alkali metals.

Combined x-ray- and neutron-diffraction studies of liquid water and aqueous LiCl and HCl have provided direct evidence for well-oriented hydration shells about Li^+, Cl^-, and H_3O^+ ions. The data are being analyzed to obtain a realistic potential of interaction between water molecules.

Diffraction studies of glassy BeF_2 and SiF_2 have been interpreted in terms of a new model that has successfully predicted the observed Raman scattering. The effects of radiation damage on amorphous materials are being studied by x-ray and neutron diffraction.

PUBLICATIONS

Narten, A. H., and H. A. Levy, Liquid Water: Molecular Correlation Functions from X-ray Diffraction, J. Chem. Phys., 55: 2263 (1971).

______, Liquid Gallium: Comparison of X-Ray and Neutron Diffraction Data, J. Chem. Phys., 56: 1185 (1971).

______, Diffraction Pattern and Structure of Noncrystalline BeF_2 and SiO_2 at 25°C, J. Chem. Phys., 56: 1905 (1972).

______, Liquid Water: Atom Pair Correlation Functions from Neutron and X-Ray Diffraction, J. Chem. Phys., 56: 5681 (1972).

Blum, L., and A. H. Narten, Mean Spherical Model for the Structure of Liquid Metals, J. Chem. Phys., 56: 5197 (1972).

03:386 CRYSTAL CHEMISTRY OF FLUORIDES. Brunton, G. D. (Oak Ridge National Laboratory, Reactor Chemistry Division).

This program has historically been concerned with crystal structures and coordination chemistry of simple and complex fluoride compounds such as those discovered and produced in pure form by the several ORNL programs devoted to fundamental and applied chemistry of molten fluoride mixtures. Emphasis upon such compounds continues, but, in recent times, the scope of this program has broadened to include studies of special inorganic compounds whose structures are of unique interest: e.g., $Y(H_5O_2)(C_2O_4)_2 \cdot H_2O$; or of compounds, e.g., $Na_2LIB_2F_7$ and $K_2Cr_2O_7$, whose crystal structures and interatomic distances provide the basic parameters for fundamental studies funded by other AEC activities. The results of the neutron-diffraction study of $YH_5O_2(C_2O_4)_2 \cdot H_2O$ will be published as soon as the work on the thermal models is completed. We hope that the improvement in accuracy of diffraction data collection, made possible by the installation of a new Si solid state detector, will resolve the ambiguities in the partially solved structures of $LiTh_2F_9$, $NaBeTh_3F_{15}$, and $Cs_2U_3F_{14}$. Data for the structures of Li_3ThF_4, and $LiTh_4F_{17}$ will be collected with the new instrument. The spectroscopy group under G. E. Boyd is interested in the structures of $CsBe_2F_5$ and $LiBF_4$ and we will investigate these two compounds when crystals are available.

PUBLICATIONS

Brunton, G., The Crystal Structure of CsU_6F_{25}, Acta Cryst., B, 27: 245 (1971).

______, The Crystal Structure of Li_2MoF_6, Mater. Res. Bull., 6: 555 (1971).
______, The Crystal Structure of $RbTh_3F_{13}$, Acta Cryst., B, 27: 1823 (1971).
______, The Crystal Structure of $Rb_5Zr_4F_{21}$, Acta Cryst., B, 27: 1944, (1971).
______, The Crystal Structure of $K_7Th_6F_{31}$, Acta Cryst., B, 27: 2290 (1971).

ALSO SEE Nuclear Spectroscopy: 03:7; Heavy Element Chemistry: 03:71, 03:80, 03:87, 03:94; Radiation Chemistry: Other; 03:132, 03:144; Photochemistry and Energy Transfer: 03:175; Hot Atom Chemistry: 03:196; Chemical Spectroscopy: 03:231, 03:236, 03:240, 03:246, 03:248, 03:254, 03:255, 03:266; Theoretical Chemistry: 03:281; Thermodynamics: 03:312; High-Temperature and Inorganic Chemistry: 03:331, 03:332, 03:334, 03:340, 03:346, 03:353, 03:357; Miscellaneous Chemical Studies: 03:442, 03:453.

ANALYTICAL CHEMISTRY

Analytical studies using chemical, nuclear, and spectroscopic techniques.

03:387 X-RAY EXCITED OPTICAL FLUORESCENCE SPECTROSCOPY (XEOFS). Fassel, V. A.; D'Silva, A. P.; DeKalb, E. (Ames Laboratory, Chemistry Division).

These investigations on the optical fluorescent emission of various solid materials and gases under x-ray irradiation are focused on the description of the spectra observed and their analytical applications. The success already achieved by the XEOFS technique for the ultratrace (part per billion level) determination of the lanthanides in various reactor materials suggests a multitude of further application studies. The analytical studies are complemented with explorations on the potentialities of various fluorescent host systems as radiographic phosphors, neutron detectors, and in-pile, fuel-burnup monitors. Selective energy-transfer processes are being utilized in analytical schemes for the part per billion quantitative determination of nitrogen impurity in highly purified noble gases and Hg in samples of environmental or biomedical interest.

PUBLICATIONS

D'Silva, A. P., and V. A. Fassel, Analytical Applications of X-Ray Excited Optical Fluorescence: Direct Determination of Rare Earth Nuclear Poisons in Uranium at the Part per Giga (1 in 10^9) Level, Anal. Chem., 43: 1406 (1971).
______, E. L. DeKalb, and V. A. Fassel, Quaternary Oxide Hosts for the X-Ray Excited Optical Fluorescence Detection of Rare Earths in Nuclear Materials at the Part per Giga Level, Anal. Chem., 42: 1846 (1970).
DeKalb, E. L., A. P. D'Silva, and V. A. Fassel, X-Ray Excited Optical Fluorescence Spectrometry: Scope of Application to Trace Rare Earth Determinations, Anal. Chem., 42: 1246 (1970).
Saranathan, T. R., V. A. Fassel, and E. L. DeKalb, Analytical Applications of X-Ray Excited Optical Fluorescent Spectra: Direct Determination of Fractional Parts per Million Amounts of Rare Earths in Thorium, Anal. Chem., 42: 325 (1970).

03:388 ANALYTICAL ATOMIC EMISSION AND ABSORPTION SPECTROSCOPY. Fassel, V. A.; Kniseley, R. N.; Winge, R. K.; Butler, C. (Ames Laboratory, Chemistry Division).

Detailed observations on the atomic and molecular absorption, emission, and fluorescence spectra of various electrical plasmas and flames in the optical and infrared regions are providing important insights on: (a) the relative concentrations of stable reactive species in the various zones of these hot gases; (b) mechanism of free atom formation processes from aerosol droplets or powdered samples introduced into plasmas or flames; (c) free atom depopulation processes; and (d) the significance of these observations on practical analytical applications of these devices. Mechanistic studies on solute vaporization interferences (interelement effects) in flames or plasmas are being conducted in an effort to understand how these interferences occur and to develop schemes for their elimination. These studies are laying the groundwork for applying plasmas and flames to the practical solution of singularly difficult analytical problems encountered in nuclear reactor technology and in the biological, environmental, and nutritional sciences.

PUBLICATIONS

Winge, R. K., V. A. Fassel, and R. N. Kniseley, Direct Nebulization of Metal Samples for Flame Atomic Emission and Absorption Spectroscopy, Appl. Spectrosc., 25: 636 (1971).
Fassel, V. A., R. W. Slack, and R. N. Kniseley, Flame Emission Spectrometric Determination of Aluminum, Cobalt, Chromium, Copper, Manganese, Niobium, and Vanadium in Low and High Alloy Steels, Anal. Chem., 43: 186 (1971).
______, J. O. Rasmuson, R. N. Kniseley, and T. G. Cowley, Relative Free-Atom Populations in Nitrous Oxide–Acetylene Flames Used in Analytical Spectroscopy, Spectrochim. Acta, Part B, 25: 559 (1970).
Reif, I., R. N. Kniseley, and V. A. Fassel, Effect of the Area Sensitivity of Photomultiplier Tubes on the Measurement of Integrated Spectral Line Intensities, Appl. Opt., 9: 2399 (1970).
Golightly, D. G., R. N. Kniseley, and V. A. Fassel, The Image Dissector Photomultiplier as a Detector in a Rapid Scanning Approach to Direct-Reading Analytical Emission Spectroscopy, Spectrochim. Acta, Part B, 25: 451 (1970).

03:389 ANALYTICAL SEPARATIONS. Fritz, J. S. (Ames Laboratory, Chemistry Division).

The chief objective of this research is to devise new and better methods for quantitative separation of metal ions present in analytical samples. The separation methods are intended to fit into a comprehensive scheme so that the components of virtually any sample can be separated on a routine rather than a custom basis.

Methods that have been worked out and that are currently being investigated are based on ion exchange and on column partition chromatography. In order to obtain rapid separations, two high-speed liquid chromatographs have been constructed. Automatic detection of eluted elements is accomplished spectrophotometrically using uv detection or by mixing a color-forming reagent with the column effluent. Future plans include improved automation of the separations and development of specific, chelating ion exchange resins for retention of certain metal ions.

PUBLICATIONS

Fritz, J. S., and W. G. Millen, Chromatographic Separation and Colorimetric Determination of Gold, Talanta, 18: 323 (1971).
Seymour, Mark D., John P. Sickafoose, and James S. Fritz, Application of Forced-Flow Liquid Chromatography to the Determination of Iron, Anal. Chem., 43: 1734 (1971).
______, Donald R. Beuerman, and John J. Richard, Chromatographic Separation of Copper with an Alpha-Hydroxyoxime, Talanta, 18: 1095-1102 (1971).
______, and Donald R. Beuerman, Chromatographic Separation of Molybdenum Using an Aliphatic Alpha-Hydroxy Oxime, Anal. Chem., 44: 692 (1972).
______, and Joseph J. Topping, Chromatographic Separation of Vanadium, Tungsten, and Molybdenum with a Liquid Anion-Exchanger, Talanta, 18: 865-872 (1971).

03:390 SPARK SOURCE MASS SPECTROMETRY. Svec, H. J.; Conzemius, R. J. (Ames Laboratory, Chemistry Division).

Considerable progress has been made with a pioneering development of an electrical detection system for the spark source mass spectrometer. The system is now supplemented with an auto-programmer that permits close interaction between the operator and a computer via time share facilities. The most recent addition to the system involves automatic and simultaneous control of the spark gap width and the ion illumination angle of the instrument. This makes possible a constant ion current and instrumental sensitivity. The effect is a dramatic improvement in the analytical precision attainable. The overall system has been tested with a highly purified sample of dysprosium metal. Isotopic abundance measurements on the five most abundant nuclides of Dy were made with uncertainties of 0.3 to 1.1%. The $^{160}Dy/^{158}Dy$ and $^{156}Dy/^{158}Dy$ ratios were determined with uncertainties of 0.4 and 0.9%, respectively. A further improvement in measuring precision is expected when development of a new collector that will obviate having to depend upon the total ion beam monitor as a reference is completed. This will eliminate effects due to fluctuations in the number of multiply charged ions upon the analysis. The final phase in this overall project concerns automatic control of the spark position relative to the instrument ion optics. Preliminary manual experiments indicate that this can be expected to lower the measuring uncertainties of $\leq 0.1\%$. It should then be feasible to use the spark source mass spectrometer with its broad capabilities for ionizing all materials to make isotopic abundance measurements that are as good as any made using surface or electron bombardment ionization.

PUBLICATION

Furgerson, L. B., R. J. Conzemius, and H. J. Svec, Application of Low-Cost Operational Amplifiers to Electrical Detection in Spark-Source Mass Spectrometry, Talanta, 17: 762-66 (1970).

03:391 DEVELOPMENT OF ACTIVATION ANALYSIS TECHNIQUES. Voigt, A. F.; O'Toole, J. J.; Clark, R. G.; Malaby, K. L. (Ames Laboratory, Chemistry Division).

Neutron activation analysis is potentially the most sensitive method for the determination of some elements and is a strong competitor with other methods for many more elements as well as an independent check of the methods. Multi-element analysis using solid state gamma spectrometry has many applications to technological problems related to energy production, to environmental research, to the solution of forensic and cultural problems, etc.

Development of these methods and their use in the determination of trace metals in the environs of a mining and smelting operation in Canada have provided data for a model of the distribution of metallic pollutants from localized sources. The distribution of toxic elements, such as mercury, arsenic, antimony, and selenium, as well as of less toxic metals, like chromium, cobalt, zinc, rare earths, and gold, in the area has been determined by the analysis of many samples of water, soil, plant materials, and human hair. The ecological significance of the release of these elements from the smelter and their subsequent deposition is being assessed.

Similar multi-element activation analysis is being applied to pot sherds from pre-Columbian Mexican cultures with the goal of learning more about the relations between cultures in various geographical areas during the Toltec period.

PUBLICATIONS

O'Toole, J. J., R. G. Clark, K. L. Malaby, and D. L. Trauger, Environmental Trace Element Survey at a Heavy Metals Refining Site, in Proceedings of the American Nuclear Society Topical Meeting on Nuclear Methods in Environmental Research, Columbia, Mo., August 23-24, 1971, J. Vogt (Ed.), University of Missouri Press, Columbia, Mo., 1972.

Becknell, D. E., and A. F. Voigt, Neutron Activation Analysis of Heavy Rare Earths, J. Radioanal. Chem., 8: 89 (1971).

Menapace, L. M., Sr., and A. F. Voight, Thermal Neutron Activation Analysis for Potassium, Holmium, and Lanthanum in Tungsten Bronzes, J. Radioanal. Chem., 6: 219 (1970).

Clark, R. G., and W. A. Stensland, Service Oxygen Analysis with 14 MeV Neutrons at Iowa State University, J. Radioanal. Chem., 4: 365 (1970).

Kato, T., and A. F. Voigt, The Production Rates of Rare Earth Nuclides by 70 MeV Bremsstrahlung for Photon Activation Analysis, J. Radioanal. Chem., 4: 325 (1970).

03:392 COPPER ARCHAEOLOGY. Friedman, A. M.; Lerner, J. L.; Fields, P. R.; Milsted, J.; (Olsen, E., Field Museum of Natural History). (Argonne National Laboratory, Chemistry Division).

Over the past years we have analyzed the impurities present in copper obtained from approximately 400 ore samples from all over the world. A statistical treatment of the distribution of these impurities indicates that by analysis for seven major impurities one can determine the type of ore from which a given copper sample came. This statistical treatment has been applied to artifacts from various areas and the results appear to be of archaeological interest in that the types of ores used have a correlation with the technical abilities of ancient societies. The analyses were first done by use of spectrographic and activation analytical techniques, but these have lately been supplanted by spark source mass spectrometry.

As a test of the method, some North American Indian artifacts were analyzed and shown to have a probability of >90% of having been made of native copper as would have been predicted.

Next, a survey of seven Moche (an ancient Peruvian society dating from ~500 B.C. to 1000 A.D.) artifacts showed that they had used ores of all types and even learned to make bronze alloys. Since this was a relatively isolated civilization, it appeared that a survey of Moche artifacts would shed some light on the metallurgical development of these people with time. We are now in the process of analyzing a series of dated Moche copper pieces and will continue these experiments.

PUBLICATIONS

Friedman, A. M., E. Olsen, and J. H. Bird, Moche Copper Analyses: Early New World Metal Technology, Amer. Antiq., 37: 254 (1972).

Schweizer, F., and A. M. Friedman, Comparison of Methods of Analysis of Silver and Gold in Silver Coins, Archaeometry, 14(1): 103-107 (1972).

03:393 NUCLEAR MEDICAL ISOTOPE RESEARCH. Friedman, A. M.; (I. Rayudu and E. Fordham, Presbyterian St. Lukes Hospital). (Argonne National Laboratory, Chemistry Division).

This project is the beginning of a study of the medical utility and production of isotopes for diagnostic medical testing. We are at present engaged in a study of the production of millicurie amounts of ^{52}Fe and are using the products of these irradiations for studies, in experimental animals, of the chemical behavior of Fe compounds. Our initial aim is to find suitable complexing agents to cause an enrichment of ^{52}Fe in bone marrow. We have been able to achieve enrichments of ~400 with respect to surrounding tissue. This will make it feasible to use these ^{52}Fe complexes to diagnose some diseases of the red-blood-cell-forming structure.

We intend to study the production and use of ^{204}Bi and ^{204}Pb during the coming year, since these isotopes are expected to be useful for studies of tumors and bone growth while their half-lives are short enough to minimize radiation damage to the patient. However, their medical utility will depend on the time it takes for their compounds to concentrate at the desired sites. For this reason we will be studying the effects of different complexing agents.

03:394 TRACE ELEMENTAL ANALYSIS BY CHARGED PARTICLE INDUCED X-RAY FLUORESCENCE. Hillman, M.; Gordon, B. M.; Kraner, H. V. (Brookhaven National Laboratory Department of Applied Science).

The technique of inducing x-ray fluorescence by heavy charged particles (e.g., protons or alphas) combined with detection of the x rays by solid state detectors has made possible simultaneous analysis of most trace elements at the subnanogram level. The present program points to the development of a system sufficiently automated so as to be capable of handling the requisite number of samples for broad surveys of elemental baselines in the environment.

Current studies are being devoted to development of sample handling and preparation for the large variety of sample types to which the technique will be applied. These different sample types are being provided by collaborators in different fields who have shown interest in applying the technique to their particular problems. The various calibration experiments necessary for making the technique quantitative are also being carried out. Related to this effort, the computer analysis of the obtained x-ray energy spectra into elemental abundances is actively being pursued.

The apparatus will move shortly to a more permanent radiation facility at the BNL RARAF accelerator, which presently produces 4-MeV protons. The program will then consist of tying the various techniques into one automated system capable of handling the multi-elemental analysis of a large number and large variety of samples, particularly those for the baseline studies that have been proposed.

PUBLICATION

Gordon, B. M., and H. W. Kraner, Trace Element Analysis by Charged Particle Induced Characteristic X-rays, in Trace Substances in Environmental Health, Chap. V, p. 419, University of Missouri, Columbia, Mo., 1972.

03:395 SULFUR TRIOXIDE, OXYGEN, PLATINUM ELECTRODE IN A FUSED SULFATE. Salzano, F. J.; Newman, L. (Brookhaven National Laboratory, Department of Applied Science).

There is presently interest in the behavior of sulfur oxides in ambient air. Sulfur trioxide is of special interest since it is a corrosive irritant and one of the end products resulting from the injection of SO_2 into the atmosphere. Although there are numerous methods for the continuous determination of SO_2 in ambient air, there is no method for SO_3 (or H_2SO_4). A study was undertaken to examine the O_2, SO_3, Pt/(Na, Li, K)$_2$SO$_4$ electrode as a possible means for continuous measurement of SO_3 in ambient air. The behavior of this electrode was studied at SO_3 concentrations in the parts-per-million range. The cell studied consisted of two similar electrodes isolated from each other by a solid cation-permeable membrane. One electrode was used as a reference through which passed an air or oxygen stream containing a fixed and known concentration of SO_2. Through the other electrode was passed a similar gas stream containing a variable concentration of SO_2. The SO_2 passed into each electrode through a platinum inlet tube that converted a fraction of the SO_2 in the gas stream to SO_3. The EMF vs concentration behavior of this cell was studied and found to exhibit Nernstian behavior. This work showed that the electrode has possible applications as a continuous monitor of ambient air for both SO_2 and SO_3. It is expected that sulfate is present in ambient air in a variety of forms such as $H_2SO_4 \cdot xH_2O$, $(NH_4)_2SO_4$, $(NH_4)HSO_4$, and as refractory sulfates; however, the relative proportions of these species present under various environmental conditions have not been established. Future work will be aimed at determining the distribution and nature of sulfate species, and applying the above technique and others in order to understand the behavior and distribution of sulfate species in ambient air.

03:396 APPLICATIONS OF NUCLEAR METHODS TO ART AND ARCHAEOLOGY. Sayre, E. V.; Harbottle, G. (Brookhaven National Laboratory, Chemistry Department).

The composition and structure of works of art and of archaeological artifacts are being studied by means of neutron activation, which is a nondestructive method for quantitative chemical analysis of objects, and which provides a unique measurement of some chemical impurities that may be present at trace levels. Among the materials studied are: pottery from a variety of ancient sources throughout the world together with clays from which they might have been formed; some minerals used in ancient cultures, e.g., turquoise and steatite; medieval glass; ancient silver and gold objects; and oil paintings.

The patterns of trace elements determined in the archaeological materials provide a new method of classifying and grouping them, and, as well, indications of the geographic sources of the objects, the materials and methods used to fabricate the objects, and sometimes the period during which the objects were made.

The chemical nature and the distribution of the pigments of an oil painting are determined by activating the entire painting and then placing x-ray film in contact with the active painting to obtain an autoradiographic image. The composition of the paintings in terms of the types and amounts of pigments used is obtained by analyzing the spectra of the induced gamma-ray activities. These observations help to characterize and identify the genuine works of particular artists.

It is planned to refine techniques for thermoluminescence and ^{14}C dating and to apply them to archaeological and art objects.

PUBLICATIONS

Harbottle, G., Neutron Activation Analysis of Potsherds from Knossos and Mycenae, Archaeometry, 12: 23 (1970).

Sayre, E. V., and L-H. Chan, High Resolution Gamma-Ray Spectroscopic Analysis of Fine Orange Pottery, in Science and Archaeology, R. H. Brill (Ed.), The MIT Press, Cambridge, Mass., Chap. 12, pp. 165-177, 1971.

Olin, J. S., and E. V. Sayre, Compositional Categories of English and American Pottery of the American Colonial Period, in Science and Archaeology, R. H. Brill (Ed.), The MIT Press, Cambridge, Mass., Chap. 14, pp. 196–209, 1971.

Cotter, M. J., and E. V. Sayre, Neutron Activation Analysis of Oil Paintings by Ralph A. Blakelock, in International Institute for Conservation-American Group, Bulletin 11, No. 2, p. 91, 1971.

Meyers, P., and E. V. Sayre, The Determination of Trace Elements in Ancient Silver Objects by Thermal Neutron Activation Analysis, in International Institute for Conservation-American Group, Bulletin 11, No. 2, p. 29, 1971.

03:397 APPLICATIONS OF NUCLEAR AND RADIOCHEMICAL TECHNIQUES IN CHEMICAL ANALYSIS. Finston, Harmon L. (Brooklyn College of the City University of New York, Chemistry Department).

The method for determining cross sections of radioactive nuclides has been developed and applied to ^{126}I, ^{58}Co, ^{124}Sb, ^{22}Na, and ^{127m}Te. Work on ^{57}Co, ^{54}Mn, and ^{88}Y is in progress and work on ^{92}Nb, ^{182}Ta, and ^{181}Hf will soon commence. The Westcott convention will be tested by irradiation under different thicknesses of cadmium. Special techniques in activation analysis being developed include work on mercury determination involving neutron activation and x-ray counting and the development of inelastic neutron scattering as a method of activation. A study of particulate matter in automobile exhaust using nuclear methods of analysis has been initiated. The study of mechanisms of synergistic solvent extraction is continuing. A procedure will be developed to synthesize tetraphenylarsonium chloride labeled with radioactive arsenic. The study of the use of chlorendic acid as an extractant for metal cations will be continued.

PUBLICATIONS

Kardonsky, S., H. L. Finston, and E. T. Williams, $^{40}Ar(n,\alpha)^{37}S$ Reaction at 14.4 MeV, Phys. Rev. C, 4: 840 (1971).

———, H. L. Finston, and E. T. Williams, Reactions of ^{20}Ne with 14.3-MeV Neutrons, Phys. Rev., C, 4: 846 (1971).

03:398 NEUTRON ACTIVATION ANALYSIS. Rowland, F. S. (University of California, Department of Chemistry, Irvine, California 92664).

The general purpose of this work has been to extend the applicability of neutron activation analysis. Instrumental neutron activation analysis has been applied to the determination of mercury in museum specimens of swordfish and tuna (in collaboration with V. P. Guinn and G. E. Miller). The single swordfish (caught 1946) and seven tuna (caught 1878 to 1909) showed mercury concentrations in the same range (<0.1 ppM) as that found concurrently in fresh specimens, suggesting that such levels of mercury are probably the natural state for these large fish.

Molecular site information, in addition to elemental abundance data, is being sought through a combination of neutron activation analysis with hot atom chemistry. In low-temperature (−196°C) irradiation, the ^{38}Cl atoms formed by the reaction $^{37}Cl(n,\gamma)^{38}Cl$ are much more likely to be found in an organic state after irradiation for initially organically bound chlorine than for initial Cl^- ions, all in aqueous solution. Current experiments are determining the possible utility of molecular neutron activation analysis for several chlorinated species.

PUBLICATION

Miller, G. E., P. Grant, R. Kishore, F. Steinkruger, F. S. Rowland, and V. P. Guinn, Mercury Levels in Museum Specimens of Tuna and Swordfish, Science, 175: 1121 (1972).

03:399 CHEMICAL ANALYSIS BY ION MICROPROBE MASS SPECTROMETRIC METHODS. McHugh, J. A.; Stevens, J. F. (Knolls Atomic Power Laboratory, Mass Spectrometry).

The production of secondary ions by bombardment of a solid with an energetic primary ion beam is the basis of a mass spectrometric method for surface and bulk solids analysis. The technique is relatively new in the field of micro-area analysis. It possesses a capability for rapid analysis and provides a high elemental detection efficiency for most elements, including the lightest. The objectives of this research are to explore application areas and to contribute to the understanding of methods for quantitation of secondary ion yield data.

A current study involves the elemental analysis of single micrometer-size airborne particulates. Airborne particulates represent many particle classes of varying chemical composition. In order to extract maximum information from a particle collection, it is necessary to obtain elemental compositions of individual particles. Our results indicate the ion microprobe is quite valuable in this area and with such results one may be able to more easily interpret, pinpoint, and eventually control sources of harmful particulate pollution.

The quantitative interpretation of secondary ion spectra is a complex problem with the relative elemental efficiencies depending quite strongly on the chemical makeup of the surface and the solid matrix. A study has been initiated to measure relative secondary ion efficiencies for a number of elements in known samples. This will be a continuing program aimed at developing a quantitative formulation (empirical, semi-empirical or theoretical) to reduce secondary ion yield data to elemental concentrations in a sample.

03:400 ^3He ACTIVATION ANALYSIS. Markowitz, Samuel S. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

The purpose of this research is to apply nuclear reactions induced by low-energy ^3He ions for chemical studies, including nondestructive trace concentration analysis and surface analysis. The scope includes the development of the method to those difficult elements, such as oxygen, carbon, fluorine—and more recently—chlorine, sulfur, potassium, and calcium. The concentration of various elements as a function of depth from the surface can also be measured. The use of ^3He activation analysis has been demonstrated in several laboratories around the world for studying the effects of trace concentrations of certain elements in super-pure material. Surface studies may be pursued by activation techniques, and by studies of direct nuclear reactions and in-beam counting of scattered particles and gamma radiation. Work is also in progress on the determination of the extent, if any, that low-Z fission of matrix elements can interfere with sensitive trace-impurity analysis. There is potential here for further application of this technique to biologically interesting media and to samples of environmental importance.

PUBLICATION

Lee, Diana M., James F. Lamb, and Samuel S. Markowitz, Rapid Non-Destructive Fluorine Analysis by ^{3}He Activation, Anal. Chem., 43: 542 (1971).

03:401 ENVIRONMENTAL CHEMISTRY. Newton, Amos S. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

As part of a recently formed environmental studies group, work is proceeding on studies involving environmental problems. As a start we are cooperating with Dr. R. W. Risebrough in the study of chlorinated hydrocarbons in marine systems, especially mussels. Work is progressing on an evaluation of experimental methods by gas–liquid chromatography and mass spectrometry.

A second study that is being started is an investigation of the physicochemical aspects of the mercury problem. This involves a study of the thermodynamic properties, especially bond energies, of organic mercury compounds. The mechanisms, kinetics, and equilibria involved in the conversion of inorganic mercury to organic mercury will also be investigated.

A recent study in this field was the evaluation of reverse flow gas chromatography as a method of concentrating a very dilute solution of mixed high-boiling components by injecting a large volume of the solution on a suitable column, eluting the solvent, and reversing the flow to elute the minor constituents as a single peak. These components can then be reinjected on a very sensitive gas–liquid chromatography column for separation and analysis with combined GLC and mass spectrometry. The characteristics of the reverse flow unified peak were determined as a function of the characteristics of the column, the time of reversal, and the characteristics of the individual trace components.

03:402 NUCLEAR METHODS OF ANALYSIS OF ENVIRONMENTAL SAMPLES. Gordon, G. E.; Viola, V. E. Jr.; Walters, W. B. (University of Maryland, Department of Chemistry, College Park, Md. 20742).

Instrumental nuclear methods of analysis involving both long-range incoming and outgoing radiations have considerable advantage over wet chemical or conventional instrumental methods which involve absorption or emission of short-range radiation (e.g., x rays, uv, or visible). With nuclear activation methods, one can use projectiles such as thermal neutrons or high-energy γ rays and observe γ rays from the products that are of such long range as to be little affected by the complex, poorly characterized matrices encountered in environmental samples.

Two years ago we demonstrated the measurement of about 24 minor and trace elements in urban atmospheric particulate material by the use of instrumental neutron activation analysis (INAA). We are attempting to extend the list of observable elements by use of improved Ge(Li) detectors and so far have been able to observe S, Rb, Zr, Ag, Cs, Gd, Nd, Tb, and Ta in most aerosol samples and, occasionally, Tm and Dy.

We are also investigating the applicability of instrumental photon activation analysis (IPAA) in which samples are irradiated with bremsstrahlung from the National Bureau of Standards Linac. Thus far we have found IPAA capable of analysis for Na, Cl, Ca, Ti, Cr, Ni, Zn, As, Br, Zr, Sb, I, Ce, and Pb, among which Ti, Ni, As, Ar, I, and Pb are difficult or impossible via INAA. The elements Ni, As, and Pb are of particular interest because of their known toxicities.

We are now seeking instrumental nuclear methods for other toxic species of very low abundance such as Be and Cd. Methods under consideration include charged-particle activation, observation of prompt γ rays following neutron capture or other nuclear reactions, and excitation of nuclear isomers with intense, low-energy γ radiation.

PUBLICATIONS

Gordon, G. E., Instrumental Activation Analysis of Atmospheric Pollutants and Pollution Source Materials, in Proceedings of the International Symposium on Identification and Measurement of Environmental Pollutants, Ottawa, June 1971, National Research Council of Canada, Ottawa, 1972, pp. 138–143.

———, W. H. Zoller, E. S. Gladney, and A. G. Jones, Trace Elements in the Urban Atmosphere, in Proceedings of the American Nuclear Society Topical Meeting on Nuclear Methods in Environmental Research, Columbia, Mo., August 23–24, 1971, J. Vogt (Ed.), University of Missouri Press, Columbia, Mo., 1972, pp. 30–37.

Zoller, W. H., and G. E. Gordon, Instrumental Neutron Activation Analysis of Atmospheric Pollutants Utilizing Ge(Li) Gamma-Ray Detectors, Anal. Chem., 42: 257 (1970).

03:403 INSTRUMENTATION AND SMALL COMPUTER SYSTEMS FOR ANALYTICAL CHEMISTRY. Fisher, D. J. (Oak Ridge National Laboratory, Analytical Chemistry Division).

Instrumentation is central to any analytical procedure; our aim is to develop methods that can meet the present and projected analytical requirements of the U. S. Energy Program. Automation through computer control of instrumental systems makes possible rapid and highly precise results for large numbers of samples at minimum cost.

Currently we are developing programs to assist in processing data from several of our automated systems. These include the GeMSAEC, the scanning electron microscope, polarographs, and coulometric analyzers. Least square procedures are being applied in flame photometric and density gradient analysis.

We have interfaced a PDP-8/E computer to a Perkin–Elmer Atomic Absorption Spectrophotometer for the determination of Na, K, Ca, Mg, and Mn. The sample load for these analyses arising from environmental sources is now ~5000/month. If feasible, we plan to attach this same computer to a Technicon AutoAnalyzer, so that automatic phosphate analysis (Mo-Blue method) can be performed.

The work on kinetic methods of chemical analysis using the GeMSAEC fast photometric analyzer is directed to determination of trace metals of environmental origin. A particular objective is the expansion of our initial studies of chemiluminescent reactions, using the GeMSAEC analyzer, in search for rapid methods for measuring contamination of natural waters.

Work on computer-controlled electroanalytical methods is continuing with emphasis on exhaustive electrolysis under controlled-potential conditions.

PUBLICATIONS

Kelley, M. T., ORCAL—A Conversational Calculating Language for the ND-812 Computer, Chem. Instrum., 3: 345 (1972).

———, and J. M. Jansen, Programming Concepts for the GeMSAEC Rapid Photometric Analyzer, Clin. Chem., 17: 701 (1971).

McCracken, J. E., J. C. Guyon, W. D. Shults, and H. C. Jones, Instrument for Coulometric Titrimetry with Feedback-Controlled Electrolysis Current, Chem. Instrum., 3:(3) (1972).

Coleman, R. L., J. A. Dean, W. D. Shults, and M. T. Kelley, Applications of the GeMSAEC Centrifugal Photometric Analyzer in Environmental Analysis: The Determination of Phosphate, Anal. Lett. 4: 169 (1971).

———, W. D. Shults, M. T. Kelley, and J. A. Dean, Environmental Applications of a Centrifugal Photometric Analyzer, Amer. Lab., 3: 26 (1971).

03:404 PHOTOELECTRON SPECTROSCOPY (ESCA) FOR SURFACE ANALYSIS. Hulett, L. D. (Oak Ridge National Laboratory, Analytical Chemistry Division).

Photoelectron spectroscopy is a very general and effective technique for identifying and measuring concentrations of elements and compounds adsorbed on the surface of solids. Our objective is to apply the technique as an analytical tool in solving problems in the U. S. Energy Program. In pollution studies we have found that surfaces of smoke particles and fly ash can be analyzed easily. Sulfur, in three different valence states, sulfate, sulfite, and sulfide, was found on coal smoke particles. For fly ash specimens taken from a steam plant equipped with a Catox device for SO_2 removal, we found that adsorbed sulfur was always present as sulfate.

In the Environmental Science Division of ORNL the transfer of elements on the surfaces of soil particles is of interest. For work of this type we have shown that small amounts of cadmium adsorbed on kaolinite can easily be detected. Next, we plan to start measurements of nitrates and amines from fertilizers adsorbed on soils. Our general plans for future work of this type are as follows: (1) Develop the ESCA technique as a general means of analyzing the surface of particulate matter. In the past, surface analysis has only been in the province of fundamental research. We hope to make it routine. (2) Develop means of gas analyses by adsorption of gases on solids, followed by examination of the solids by photoelectron spectroscopy. (3) Work in collaboration with other pollution studies groups that are interested in surface problems. In addition to the examples of soil studies given above, we also plan to be of help in SO_2 removal studies that involve adsorption on solid surfaces.

PUBLICATIONS

Hulett, L. D., T. A. Carlson, B. R. Fish, and J. L. Dutham, Studies of Sulfur Compounds Adsorbed on Smoke Particles and Other Solids by Photoelectron Spectroscopy, in Determination of Air Quality, Plenum Press, Inc., New York, New York, 1972.

———, and T. A. Carlson, Measurements of Chemical Shifts in the Photoelectron Spectra of Arsenic and Bromine Compounds, Appl. Spectrosc., 25: 23 (1971).

———, and T. A. Carlson, Analysis of Compounds of Biological Interest by Electron Spectroscopy, Clin. Chem., 16, 677 (1970).

03:405 ELECTROCHEMISTRY IN MOLTEN SALTS. Manning, D. L. (Oak Ridge National Laboratory, Analytical Chemistry Division).

Electrochemical measurements provide the best—and essentially only—method of analysis suitable for use in molten salts at high temperatures. The primary objective of this program is to develop fundamental data required for on-line techniques for chemical studies of molten salt systems. Various electrode assemblies are being used to study the behavior of components in molten salt systems; to determine selected elements, such as tritium and hydrogen; and to elucidate reaction mechanisms occurring between materials of construction such as Ti and Cr, and the molten salt itself. Voltammetry, chronopotentiometry, and chronoamperometry have all been used.

We are continuing to collect basic data and further characterize the electroactive species in the different molten fluoride solvents. We have been primarily concerned with the study of more stable electroactive species (uranium, corrosion products, etc.), which are more adaptable to on-line monitoring, but plan now to study the more unstable constituents, such as Mo, Nb, Tc, and Ru, particularly valence states and disproportionation reactions at low concentrations. Ring disc voltammetry and thin layer methods have been utilized to characterize unstable intermediates in aqueous solutions; efforts will be made to adapt these techniques to high-temperature cells. We plan to develop electro-optical methods for the study of unstable intermediates. In this approach, the unstable intermediate is electrically generated in situ and spectral data are obtained by scanning the electrode solution interface.

PUBLICATIONS

Bronstein, H. R., and D. L. Manning, Lanthanum Trifluoride as a Membrane in a Reference Electrode for Use in Certain Fluoride Melts, J. Electrochem. Soc., 119: 125 (1972).

Manning, D. L., and G. Mamantov, Determination of the Diffusion Coefficient of Nickel(II) in Molten $LiF-BeF_2-ZrF_4$ by Linear Sweep Voltammetry and Chronopotentiometry, High Temp. Sci., 6: 533 (1971).

Whiting, F. L., G. Mamantov, G. M. Begun, and J. P. Young, Raman Spectra of Solute Species in Molten Fluorides; O_2^-, CrO_4^{2-}, CO_3^{2-}, Inorg. Chim. Acta, 5: 260 (1971).

Jenkins, H. W., G. Mamantov, and D. L. Manning, Electrode Potentials of Several Redox Couples in Molten Fluorides, J. Electrochem. Soc., 117: 183 (1970).

03:406 NUCLEAR METHODS OF ANALYSIS. Ricci, E. (Oak Ridge National Laboratory, Analytical Chemistry Division).

Our present effort in nuclear methods of analysis aims at the investigation and exploitation of four different systems: (1) automated nondestructive neutron activation analysis at the HFIR; (2) gamma photon activation analysis at the Oak Ridge Electron Linear Accelerator (ORELA); (3) analysis aided by radioactive sources, e.g., neutron activation with ^{252}Cf or x-ray fluorescence with ^{147}Pm sources; and (4) charged particle activation analysis using physics machines.

Because of the high flux at HFIR, only a short irradiation time is required to achieve great sensitivity; by measuring the induced activity with a computer-coupled Ge(Li) detector system we can determine many elements nondestructively. Proton reaction analysis, charged particle reaction analysis, and x-ray excitation by proton, alpha, and ^3He particles at MeV energies also have a number of useful and sensitive applications, particularly in the low Z region of the periodic table.

We now have the HFIR lab in operation and are beginning to explore its special potential; our aim is multielement analysis using very small samples. We are studying impurities in fossil fuels, ash, materials of construction, sediments, water, and vegetation by mainly nondestructive techniques. We have developed a computer program to handle the γ spectra obtained from these irradiated samples using a Ge(Li) detector. This work is being complemented by similar studies using photon activation at the ORELA. Some special samples will continue to be surveyed by charged particle activation. Proton reaction analysis has been demonstrated as a useful tool for $^{13}C/^{12}C$ and $^{15}N/^{12}C$ ratios in biological experiments, and the technique is now being evaluated for other applications.

PUBLICATIONS

Ricci, E., Simple, Reliable Basic Equation for Proton-Reaction Analysis of Biological Materials, Nucl. Instrum. Methods, 94: 565 (1971).

———, Determination of ^{12}C, ^{13}C Isotopic Abundances and N/C Ratios in Biological Substances by Proton-Reaction Analysis, Anal. Chem., 43: 1866 (1971).

———, Chemical Stability of Biological Substances Subjected to Proton-Reaction Analysis, J. Radioanal. Chem., 9: 272 (1971).

———, Elementary Physics of Radioactivation and Radioisotopes, International Encyclopedia of Pharmacology and Therapeutics, Vol. 1, Chap. 2, Sec. 78, pp 31–62, Y. Cohen (Ed.), Pergamon Press, Inc., New York, 1971.

Bate, L. C., Loss of Mercury from Containers in Neutron Activation Analysis, Radiochem. Radioanal. Lett., 6: 139 (1971).

03:407 ANALYTICAL CHEMISTRY FOR TRANSURANIUM ELEMENTS. Stokely, J. R. (Oak Ridge National Laboratory, Analytical Chemistry Division).

The chemistry and nuclear properties of transuranium elements produced within the AEC's transuranium element program are studied at the Transuranium Research Laboratory at ORNL. Our program has as its objective a concomitant study of the analytical chemistry of the nuclides and analytical assistance in applying conventional techniques to solutions of these elements. The divalent oxidation states of transuranium elements have been studied; the most significant result is the discovery of a 2^+ state in californium, which opens the possibility of an oxidation–reduction technique for the determination of this element. Having demonstrated the first absolute chemical analysis of curium, thus making possible half-life determinations by specific activity measurements, we now plan to apply the technique to other trivalent actinides. The solution absorption spectrum of this element will be obtained and an electroanalytical method for determination of berkelium pursued.

Since low-level alpha counting is the preferred method of measuring many of these elements, we plan to emphasize handling, preparation, and concentration of alpha emitters. Alternate methods of detection, including the use of thermally stimulated exoelectron emission detectors, are also being studied.

PUBLICATIONS

McCracken, J. E., J. C. Guyon, and W. D. Shults, Coulometric Microdetermination of Neodymium Using Feedback-Controlled Electrolysis Current, Anal. Chem., 44: 305 (1972).

———, J. R. Stokley, R. D. Baybarz, C. E. Bemis, Jr., and R. Eby, Determination of the Half-Lives of ^{246}Cm and ^{248}Cm by Absolute Specific Activity Techniques, J. Inorg. Nucl. Chem., 33: 3251 (1971).

Stokley, J. R., R. D. Baybarz, and J. R. Peterson, The Formal Potential of the Bk(IV)–Bk(III) Couple in Several Media, J. Inorg. Nucl. Chem., 34: 392 (1972).

———, Controlled-Potential Coulometric Determination of Plutonium in the Presence of Iron, Anal. Chem., 43: 603 (1971).

Baybarz, R. D., J. R. Stokely, and J. R. Peterson, Absorption Spectra of Bk(III) and Bk(IV) in Several Media, J. Inorg. Nucl. Chem., 34: 739 (1972).

03:408 EFFECTS OF RADIATION ON ANALYTICAL METHODS. Zittel, H. E. (Oak Ridge National Laboratory, Analytical Chemistry Division).

The objectives of this program are twofold: (1) to study the effects of radiation—alpha, beta, and gamma—on analytical methods and devise ways to circumvent or eliminate those that are deleterious and (2) to utilize radiation as a positive analytical tool whenever possible. For the past year or so the latter has been emphasized.

Studies carried out on various organic dyes, commonly used as pH indicators, show that dyes as a group are easily degraded (decolorized) by gamma radiation. The concentration required to measure accurately the radiolytic degradation is very low (~10^{-6}–10^{-7} M) and the total gamma dosage necessary to produce a large decrease in absorbance (color) is quite small (10^2–10^3 rad). We noted that the presence of ions that react readily with the radiolytic water products protects the dye from radiolytic degradation. A preliminary study of the effects of Cu^{2+} on the radiolytic degradation of Methyl Orange was carried out. We find that the extent of protection is a function of Cu^{2+} concentration, and that by selecting the proper conditions less than 1 ppB copper can be measured accurately. No interference is shown by the presence of nonactive ions such as Al^{3+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, Ni^{2+}, and Ba^{2+}. Other active ions such as Fe^{3+} probably will interfere, but because of the relative ease and accuracy of delivering reagent, i.e., gamma radiation, at very low concentration, we feel that this unique usage of radiation may lend itself to analytical methods for ppB amounts of the active ions. While the method is by nature nonspecific, by the proper selection of conditions it should be possible to cause it to be no worse in this respect than any other redox method.

PUBLICATIONS

Zittel, H. E., Effects of Gamma Radiation on Colorimetric Determination of Iron, Anal. Chim. Acta, 58: 323 (1972).

______, Radiation and Thermal Stability of Spray Solutions, Nucl. Technol., 10: 436 (1971).

______, Effects of Radiation on Common Analytical Reagents, in Progress in Nuclear Energy, Analytical Chemistry, Series IX, Vol. 10, pp. 393-412, D. C. Stewart and H. A. Elion (Eds.), Pergamon Press, Oxford, England, 1970.

______, In-Field Behavior of Cumulative Effects on Certain Electrodes in a Gamma Field, Anal. Chem., 42(11): 1593-1596 (1970).

ALSO SEE Nuclear Spectroscopy: 03:4; Heavy Element Chemistry: 03:79; Chemical Spectroscopy: 03:246; Structural Chemistry: 03:377; Separations Chemistry: 03:419; Miscellaneous Chemical Studies: 03:442, 03:443, 03:444.

SEPARATIONS CHEMISTRY

Basic and applied studies of chemical separations.

03:409 SOLVENT EXTRACTION PHASE EQUILIBRIUM CHEMISTRY. Bautista, Renato G. (Ames Laboratory, Chemical Engineering Division).

The separation of a multicomponent mixture into each individual component by solvent extraction is conceptually an ideal separation process. However, the interaction between components in one phase, whether physical or chemical in nature, is complicated some more in the presence of a second phase, such as the organic phase in a solvent extraction process. A means of predicting the concentration of a component in one phase, given the concentration in the other phase, would be of value in optimizing the separation and concentration of the desired component.

The equilibrium data for the system samarium chloride–neodymium chloride–cerium chloride in equilibrium with 1M di-(2-ethylhexyl)phosphoric acid have been correlated empirically. The equilibrium single component nonlinear models predict the organic concentration as a function of the aqueous lanthanide concentration and acidity over a wide range. The binary system models predict the total organic concentration as a function of mole fraction of Sm in the aqueous phase and acidity, at total aqueous lanthanide concentrations of ~0.64M and 0.11M. The ternary system models predict the total organic concentration as a function of mole fraction of Ce and acidity, at three different mole fractions of Sm on a cerium-free basis (0.1, 0.15, and 0.9) and at a total aqueous concentration of ~0.6M. These models consist of a series of linear terms analogous to Raoult's Law for ideal solutions and a series of nonlinear terms predicting the deviation from ideality (interaction effects).

An attempt will be made to develop a correlation of the multicomponent phase equilibria based on thermodynamic activity coefficients. The determination of activity coefficients for single, binary, and ternary rare earth solutions will be made using specific ion electrodes and direct vapor pressure techniques.

PUBLICATIONS

Harada, Takeo, Renato G. Bautista, and Morton Smutz, Extraction of Yttrium in the System $Y(NO_3)_3-HNO_3-H_2O-$Di(2-Ethylhexyl)-Phosphoric Acid, Met. Trans., 2: 195-197 (1971).

Ioannou, Tom K., Renato G. Bautista, and Morton Smutz, Correlating Multicomponent Equilibrium Data for the Extraction of Lanthanides with Di(2-Ethylhexyl)Phosphoric Acid as the Solvent, in Proceedings of the International Solvent Extraction Conference, April 1971, The Hague, Netherlands, Society of Chemical Industry, England, Vol. II, pp. 957-965, 1971.

03:410 SOLVENT EQUILIBRIA AND EXTRACTOR DESIGN FOR SEPARATING THE RARE EARTHS BY SOLVENT EXTRACTION. Burkhart, Lawrence (Ames Laboratory, Chemical Engineering Division)

Effective design of rare earth extraction systems hinges upon the availability of good equilibrium data in a form that is readily available and can be used for both design and control. Equilibrium data for the distribution of the two-solute system $TmCl_3-YbCl_3$ between HCl (aqueous) and di(2-ethylhexyl)phosphoric acid have been correlated. At equilibrium, the distribution of solute in the organic phase is a function of total solute, mole fraction of ytterbium, and acidity in the aqueous phase. Using an assumed general functional relationship, expressions for the partial derivatives of each variable were computed and evaluated from experimental data. The same procedure is now yielding correlations for the three solute system, $TmCl_3-YbCl_3-LuCl_3$.

To check the usefulness of the correlations, they are verified by simulated column runs. The data are also used to study the dynamic response and control of a rare earth extraction column by using digital simulation techniques. A predictive control model now under study has shown that the addition of a feedforward loop adds materially to the effectiveness of the control. An approximate means of correcting for the transient portion of the feedforward loop is being determined.

PUBLICATIONS

Thomas, N. E., M. Smutz, and Lawrence Burkhart, Separation of Thulium and Ytterbium in Acidic Chloride Solution by Fractional Solvent Extraction, Ind. Eng. Chem., Fundam., 10: 435 (1971).

Erskine, William, R. C. Seemann, Lawrence Burkhart, Predictive Control of a Rare Earth Extraction Column, in Proceedings of the Symposium on Digital Similation of Continuous Processes, International Federation of Automatic Control, Vol. 1, pp. 1-8, 1971.

03:411 INVESTIGATION OF STABLE, LABILE RARE EARTH COMPLEXES AND THEIR APPLICATION IN CATION EXCHANGE SEPARATION OF THE LANTHANONS. Powell, Jack E. (Ames Laboratory, Chemistry Division).

The purpose of this investigation is the development of optimum techniques for isolation of components found in natural and fission-produced rare earth (Sc, Y, and La–Lu) mixtures. Countercurrent processes, such as ion exchange and solvent extraction, used in conjunction with complexing agents, have proved to be highly effective in resolving such mixtures, but the cost of some highly pure individual rare earths prohibits their extensive use in nuclear and other applications. In cation exchange separations, it has been found that polyaminopolycarboxylic acid anions such as EDTA (ethylenediamine-N,N,N',N -tetraacetate) and HEDTA (N'-hydroxyethylethylenediamine-N,N,N'-triacetate) provide adequate process separation factors, but that certain of their properties are disadvantageous economically. To cite several drawbacks: $EDTA^{4-}$ anion forms relatively insoluble $H_4(EDTA)$ and HLn(EDTA) species in pH ranges suitable for facile column operation; and HEDTA (whose protonated form $H_3(HEDTA)$ is more soluble than $H_4(EDTA)$) is selective only for the rare earths La–Sm and Ho–Lu.

Because it appears that lack of symmetry makes $H_3(HEDTA)$ more soluble than $H_4(EDTA)$, and because it seems that the –OH functional group of HEDTA is responsible for its lack of selectivity toward the lanthanons Sm–Ho, the immediate goal is to synthesize, characterize, and evaluate N'-alkyl-substituted ethylenediamine-N,N,N'-triacetate reagents, which are expected to possess the combined desirable qualities of EDTA and HEDTA but lack the undesirable traits of both.

03:412 METALS SEPARATIONS BY LIQUID–LIQUID EXTRACTION. Mason, G. W. and S. Lewey (Argonne National Laboratory, Chemistry Division).

The purpose of this program is to acquire the pertinent solvent extraction data necessary for devising separation systems that may be used in (1) providing more economical thorium and uranium fuel for the rapidly expanding reactor requirements, (2) processing spent fuel and accompanying waste in a manner that shows proper concern for our environment, and (3) isolation of the heavy elements including super-heavy elements.

The purification of thorium from rare earths should be markedly simplified by a process based on data being obtained using di-(2-ethylhexyl)-phosphoric acid in an interacting diluent. The separation factor between thorium and the most extractable rare earth exceeds 10^3.

Our recent mutual separation of U, Th, and Sc and separation of Am(VI) from trivalent actinides using sterically hindered phosphorus-based extractants indicates the feasibility of a similar approach for the development of other separations. The efficiency of extraction for a given element in the systems $X_2PO(OH)$ or $(XO)_2PO(OH)$, where X represents hydrocarbon groups, may be varied by factors exceeding 10^{10} as a function of steric hindrance in the extractant molecule and its acidity. Separation factors between pairs of elements may be varied by factors greater than 10^5. Future research should lead to important new or improved separation procedures.

Future research will include the preparation and study of phosphorus-based extractants in which sulfur is substituted for some or all of the oxygen. It is expected that these extractants will prove effective in extracting the transition elements and their super-heavy element analogs.

PUBLICATIONS

Peppard, D. F., G. W. Mason, A. F. Bollmeier, and S. Lewey, Extraction of Selected Metallic Cations by a Highly Hindered $(GO)_2PO(OH)$ Extractant in Two Different Diluents from an Aqueous Chloride Phase, J. Inorg. Nucl. Chem., 33: 845-856 (1971).

Lewey, S., G. W. Mason, and D. F. Peppard, Comparative Extraction of Selected M(III) Cations by $(2\text{-}C_2H_5 \cdot C_6H_{12}O)PO(OH)_2$ and $(2\text{-}C_2H_5 \cdot C_6H_{12})PO(OH)_2$, J. Inorg. Nucl. Chem., 33: 2531-2539 (1971).

A-12

03:413 ION EXCHANGE RESIN SYSTEMS. Diamond, Richard M. (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

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Our interest has been in the factors underlying ion exchange resin selectivity. For the usual strong base or acid resins we believe the difference in hydration of the exchanging ions in the two phases, the resin phase and the external solution, is the principal cause of selectivity. We recently studied six heterovalent anion exchanges to show that the selectivity order is the reverse of that expected from Coulombic interaction in the resin phase between the resin site and counter ion, but just what is expected on the hydration picture.

In addition, we have studied the behavior of several simple anion exchange systems in a number of mixed organic–aqueous media. The results seemed to bear out expectations, as well as leading to the practical prediction that such media would provide poorer separation factors for simple anion exchanges, although not necessarily for exchanges involving complex anions such as the halometallic complexes. In contrast, it is known that cation exchange in mixed organic–aqueous media may lead to better separations, and we plan to investigate this situation, suspecting that here ion pairing may play a larger role. Polyvalent cations will be used, as well as monovalent ones, to emphasize the effect of Coulombic interactions.

Another planned investigation is into the phenomenon observed long ago by Kraus and his colleagues that large anions, such as $AuCl_4^-$, are absorbed by strong acid cation exchange resins from moderately concentrated LiCl solutions even better than are monovalent cations. Again there is an asymmetry in resin behavior, as we do not observe a comparable effect with large cations and a strong base anion resin.

A-12

03:414 SEPARATION OF ^{234}U FROM ^{238}Pu BY RESIDUE ADSORPTION. Kirby, H. W. (Mound Laboratory, Nuclear Operations Department).

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The technique of residue adsorption, discovered at Mound Laboratory in 1959, has become a useful tool for the quantitative separation of trace elements. It is based on the principle that trace quantities of inorganic compounds that precipitate at the macroscopic level can be made to adsorb quantitatively on nonreactive surfaces if the microcrystals can be brought into close enough contact with the surfaces. A residue adsorption method is being developed for the analytical determination of trace ^{234}U in ^{238}Pu by alpha spectrometry and for determining the $^{232}U/^{234}U$ ratio in the same matrix. The method is based on the strong tendency of plutonium in all its oxidation states to hydrolyze in neutral or weakly acid aqueous solution under conditions which permit the dissolution and desorption of uranium.

The plutonium–uranium solution is evaporated to dryness on a platinum disc and the residue, after being converted in situ to a nitrate or fluoride, is hydrolyzed. The desorbed uranium is repeatedly deposited on a fresh surface, dried and desorbed again until a residue is obtained that is sufficiently pure to yield a satisfactory alpha spectrum of the uranium isotopes. Thus far the method has been applied successfully to mixtures in which the ^{234}U represented only 1.75% of the total alpha activity.

The objective of current work is to increase the efficiency of the process so that sources containing a much smaller fraction of uranium isotopes can be successfully analyzed.

03:415 SEPARATIONS PROCESS DEVELOPMENT. Hurst, F. J., B. Weaver and F. G. Seeley (Oak Ridge National Laboratory, Chemical Technology Division).

The AEC program has a continuing need for new processes to recover or separate materials not treated previously and more economical processes to replace existing processes. New separation reagents and/or systems of indicated utility in atomic energy processing are continually being suggested from sources such as the Separations Research Studies. It is the purpose of the Separations Process Development Program to develop such suggestions into complete processes through laboratory scale.

Current and planned studies include the development of solvent extraction processes for recovering uranium from wet-process phosphoric acid and lithium from salt brines and for separating and purifying plutonium from reactor wastes. High-pressure (small particle size) ion exchange has been shown to have a number of important potential advantages over conventional ion exchange. Tests of the use of high-pressure ion exchange in several separation systems are being made to determine whether this technique might broaden the range of application of ion exchange in separation processes.

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PUBLICATIONS

Hurst, Fred J., David J. Crouse, and Keith B. Brown, Recovery of Uranium from Wet-Process Phosphoric Acid, Ind. Eng. Chem., Process Design Develop., 11: 122 (January 1972).

Weaver, Boyd, and R. R. Shoun, Heavy Actinide Element Partitioning by Extraction with Monoacidic Phosphorus Esters—HEPEX, Ind. Eng. Chem., Process Design Develop., 10: 582 (1971).

Coleman, C. F., and B. Weaver, Selective Stripping of Plutonium from Organic Extracts, U. S. Patent No. 3,580,705, May 25, 1971.

03:416 FLUORIDE SALT SEPARATION TECHNOLOGY. McNeese, L. E., J. R. Hightower, Jr., M. J. Bell, H. O. Weeren, and B. A. Hannaford (Oak Ridge National Laboratory, Chemical Technology Division).

The purpose of this program is to establish a sound technological base for processes that separate components of fluoride salt mixtures; this work is applicable to the processing of fuel from a molten-salt breeder reactor. Separation techniques under study include fluorination, reductive extraction using molten bismuth, and oxide precipitation. The program is concerned with (1) developing equipment and information necessary for the design of fluorinators for removing uranium from molten salt, (2) correlating hydrodynamic and mass transfer data resulting from studies of countercurrent contact of salt and bismuth in packed columns, (3) developing data for designing equipment to selectively precipitate oxides from molten fluoride mixtures, and (4) developing special instrumentation for use with molten salt and bismuth such as salt–metal interface location detectors. A typical example of work in progress is the study of gas holdup and axial dispersion in the liquid phase in open bubble columns. Column diameters ranging from 1 to 6 in. and a range of values of surface tension, viscosity, and density of the liquid phase are used. The resulting correlation will be applicable to the design of bubble column gas–liquid contactors that are of industrial importance and to the design of continuous fluorinators.

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03:417 TRITIUM SEPARATION TECHNOLOGY. Watson, J. S., F. J. Smith, and R. C. Forrester (Oak Ridge National Laboratory, Chemical Technology Division).

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Increased awareness of the biological hazards of tritium imposes restraints on future nuclear reactors, and new, improved tritium-separating and -handling techniques are needed. These restraints will have an especially large impact on thermonuclear reactors because of the large quantities of tritium required and produced by breeding. The purpose of this program is to obtain basic engineering and chemical information relating to tritium-removal processes. The initial efforts are directed at removal from fluids proposed for the blanket and coolant of thermonuclear reactors, but the fundamental information obtained will also be applicable to other reactor concepts. The program is beginning with fundamental mass transfer and thermodynamic studies of tritium in liquid potassium and liquid lithium. Studies with lithium will concentrate on mass transfer of tritium to plane or cylindrical solid surfaces and thermodynamic properties at high temperatures (up to 1000°C). Results will be most applicable to recovery processes based upon permeation of tritium through metal windows. Studies with potassium will concentrate on lower temperatures. Mass transfer studies will include rates of sorption in packed beds and rates of precipitation in cold traps. Thermodynamic studies will include determination of solid-liquid equilibria and sorption isotherms with several sorbents of interest.

Eventually, tritium removal from helium, molten salts, or liquid metals of interest to reactor systems will be considered.

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03:418 SEPARATIONS CHEMISTRY RESEARCH—DESCRIPTIVE CHEMISTRY. Weaver, B., J. W. Roddy, W. J. McDowell, R. R. Shoun, A. D. Kelmers, D. O. Campbell. (Oak Ridge National Laboratory, Chemical Technology Division).

The purpose of the separations chemistry program is to establish new separation systems and to study their pertinent chemistry. The function of the descriptive chemical studies is to search out and evaluate new potentially useful separation methods and reagents and to determine applicable areas and degrees of utility in radiochemical and other separations. It also includes preparation and purification of selected materials and recording of their descriptive chemistry as a contribution to chemical knowledge per se. Current studies include examination of potential new agents for separations, search for chemical and physical bases for new separations or extension of existing methods, systematic surveys, and compilation and analysis for recall in abstracting bibliographies. Support will be provided as needed for process development. Methods and materials are studied in support of transplutonium research (including continuing development of liquid scintillation alpha counting) and of biochemical separations. The latter will include specifically the isolation and purification of "colony-stimulating factor," involved in the maturation of white blood cells and of high medical significance. Increasing attention will be given to pertinence to environmental problems, e.g., scintillation spectrometry in monitoring of actinide contaminations and metal hydrides in control of tritium.

PUBLICATIONS

Weaver, Boyd, and R. R. Shoun, Comparison of Some Monoacidic Organophosphorus Esters as Lanthanide—Actinide Extractors and Separators, J. Inorg. Nucl. Chem., 33: 1909 (1971).

McDowell, W. J., and H. D. Harmon, Unsymmetrical Dialkyl Sulfoxides as Extractants. I. Preparation and Extraction Surveys with Three Sulfoxides. II. Equilibria and Species in Iron(III) Extraction by Methyl-4,8-dimethylnonyl Sulfoxide, J. Inorg. Nucl. Chem., 33: 3107 (1971).

Seeley, F. G., and D. J. Crouse, Extraction of Metals from Nitrate and Sulfate Solutions by Amines, J. Chem. Eng. Data, 16: 393 (1971).

Sisson, D. H., V. A. Mode, and D. O. Campbell, High-Speed Separation of the Rare Earths by Ion Exchange, Part II, J. Chromatogr., 66: 129 (1972).

Egan, B. Z., J. E. Caton, and A. D. Kelmers, Separation of E. coli rRNAs by Reversed-Phase Chromatography, Biochemistry, 10: 1890 (1971).

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03:419 FUNDAMENTAL STUDIES OF SEPARATION PROCESSES. Rogers, L. B. (Purdue University, Department of Chemistry, West Lafayette, Indiana 47907).

The program is designed to extend the capabilities of chromatographic methods of separation, to use chromatography to study fundamental physical properties, and to optimize separation procedures of potentially wide utility. First, using natural abundances of isotopes, optimization of the $^{13}CO_2-^{12}CO_2$ separation on different column packings is being done with the goal of obtaining a nearly complete separation so as to broaden its potential use in biomedical studies. A comparison of the chromatographic separation behaviors of CH_3OH and CD_3OH with those predicted from classical vapor pressure measurements is also planned. Second, using a high-precision gas chromatograph, two different phenomena derived from diffusion-limited processes are being studied using changes in peak shape and retention volume. Third, further studies of ion exchange and steric exclusion (for molecular size and/or conformation), both at pressures up to 50,000 psi, are being made. Fourth, supercritical-fluid chromatography is being explored as a possible small-scale preparative approach for pure oligomers. Measurements of separation efficiency at column pressure will also be evaluated.

PUBLICATIONS

Lorenz, L. J., and L. B. Rogers, Specification of Gas Chromatographic Behavior Using Kovats Indices and Rohrschneider Constants, Anal. Chem., 43: 1593 (1971).

Bidlingmeyer, B. A., and L. B. Rogers, Steric-Exclusion Chromatography at Pressures Up to 3500 Kilograms per Square Centimeter, Anal. Chem., 43: 1882 (1971).

______, and L. B. Rogers, Investigation of Pressure-Induced Changes in the Chromatographic Selectivity of Methyl and Ethyl Orange on Silica Gel, Separ. Sci., 7: 131 (1972).

Maldacker, T. A., and L. B. Rogers, Effect of Loading on Separation Efficiency Using Steric Exclusion Chromatography, Separ. Sci., 6: 747 (1971).

Taylor, P. J., R. A. Culp, C. H. Lochmuller, L. B. Rogers, and E. M. Barrall, II, Effect of an Electron Field on Gas Chromatographic Retentions by Liquid Crystals, Separ. Sci., 6: 841 (1971).

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03:420 THE SEPARATION OF KRYPTON AND XENON FROM REACTOR ATMOSPHERES BY SELECTIVE PERMEATION. Stern, S. A., S. K. Sen, and A. K. Rao (Syracuse University, Department of Chemical Engineering and Materials Science, Syracuse, New York 13210).

The general objectives of this study are to develop an efficient process for removing rare gas fission products from nuclear reactor atmospheres by permeation through polymeric membranes. The study has been concerned, in particular, with the separation of krypton and xenon from mixtures with air by selective permeation through dry, asymmetric (Loeb-type) cellulosic membranes.

Permeability, diffusion, and solubility coefficients were first determined for Kr, Xe, Ar, N_2, O_2, and CO_2 in symmetric cellulose acetate and ethyl cellulose membranes as a base of reference. The transport of gases across these membranes was found to be controlled by activated diffusion, with solution equilibrium established at the membrane interfaces. A detailed mechanism of diffusion was proposed from an analysis of derived solution and diffusion parameters. Both types of membranes undergo second order transitions in the experimental temperature range (−5 to 85°C). The permeation of the above gases through asymmetric cellulose acetate and ethyl cellulose membranes is also controlled by activated diffusion, but marked structural differences exist between the symmetric membranes and the dense surface layer of the asymmetric membranes.

The absolute permeability of asymmetric ethyl cellulose membranes to gases is generally larger than that of similar cellulose acetate membranes, and of the same order as reported for silicone rubber. However, the separation factors for krypton and xenon relative to oxygen and nitrogen are less favorable for ethyl cellulose than for silicone rubber. As a result, future work will be directed towards the development of a permeator with hollow silicone rubber fibers as separation barriers; the performance of this permeator will then be studied under conditions of practical interest. Preliminary evaluations indicate that such a permeator could provide the basis for an economically competitive process for krypton and xenon separation.

A-12 1a U 2

03:421 DYNAMICS OF SOLVENT EXTRACTION SYSTEMS. Babb, A. L. and K. L. Garlid (University of Washington, Department of Nuclear Engineering, Seattle, Washington 98195).

This project is concerned with the improvement of separation processes used for liquid and gaseous waste streams from nuclear power and reprocessing plants.

Random single analysis of two detector signals proportional to the organic volume fraction at different locations in a pulsed solvent extraction column is currently being developed as a method for rapidly determining significant changes in the flow characteristics within the column. Cross-correlation and cross-spectral density functions are calculated and are sensitive indicators of operating conditions within such a column and provide early warning of incipient flooding or other inefficient modes of operation. This type of warning is important for processes that must be operated remotely. Data are now processed indirectly using an off-line digital computer, but in the near future the data will be analyzed directly.

Experimental separation of radioactive krypton and xenon from nonradioactive carrier gas is being conducted on a laboratory scale using thin silicone membranes that allow different compounds to permeate at different rates, thus providing separation capabilities. A new membrane support has been designed that should eliminate some of the problems of membrane rupture that have been encountered in the past. Permeabilities, allowable pressures, effects of radiation, and the overall feasibility of using permselective membranes to isolate and/or recover radioactive components on a large scale are being studied. Future studies will include the use of ultrathin membranes as they become available.

PUBLICATIONS

Babb, A. L., R. E. McKee, and N. R. Foster, Jr., Transient Holdup Behavior of a Pulsed Sieve Plate Solvent Extraction Column, Ind. Eng. Chem., Process Design Develop., 9(2): 272-278 (1970).

ALSO SEE Thermodynamics: 03:315, 03:316; High-Temperature and Inorganic Chemistry: 03:342, 03:358; Analytical Chemistry: 03:389, 03:397; Engineering Chemistry: 03:422, 03:423, 03:426, 03:427, 03:436, 03:437.

ENGINEERING CHEMISTRY

Basic nuclear and chemical engineering studies.

03:422 BENCH SCALE MIXER–SETTLER SOLVENT EXTRACTION STUDIES. Bautista, Renato G. (Ames Laboratory, Chemical Engineering Division).

The bench scale countercurrent solvent extraction of the rare earth chlorides in contact with the organic phase di(2-ethylhexyl) phosphoric acid is being carried out in a continuous, horizontal box-like and multistage mixer settler. The aqueous–organic phase interface in the settling chamber can be set by means of an interface control tube, thus making steady-state runs much easier to achieve. The operational stability of the mixer settler has been proved by the minimum time and problems encountered to return to normal operation after introducing intentional upsets of varying degree in the flow rates and interface positions.

A mathematical dynamic model of this mixer–settler is now available for simulation of startup to steady state. This model is based on the hydrodynamic information obtained for this chemical system, the physical dimensions of the apparatus, and the previously reported experimental data on the system's approach to steady state. The computer simulation is strongly influenced by the mass transfer mechanism. These findings should be of value in studies of all similar equipment, including opaque and liquid metal systems.

The operating characteristics of this equipment are presently being studied in detail to serve as a basis for scale-up. The effect of various parameters, such as power input to the impeller and other factors affecting the extraction rate of the rare earth di(2-ethylhexyl)phosphoric acid system, will be determined. Single mixer–settler units of increasing size will be used to develop scale-up parameters.

PUBLICATION

Casto, Martin G., Morton Smutz, and Renato G. Bautista, Separation of Lanthanum from a Rare Earth Chloride Mixture Using a Multistage Mixer–Settler, Trans., AIME, 250: 42–45(1971).

03:423 MASS TRANSFER AND FLUID FLOW PATTERNS IN DROPLETS. Burkhart, Lawrence. (Ames Laboratory, Chemical Engineering Division).

Mass transfer is particularly important during the early stages of extraction, and transport processes during droplet formation are being studied to determine how solute travels through the drop during this period. The fluid has a significant amount of internal motion and so bulk flow plays an important role. Profiles of forming liquid droplets have been determined and the necessary equations for simulating them developed on the computer. Studies of flow patterns inside these droplets have shown that abrupt changes in the internal fluid motion coincide with corresponding shifts in mass-transfer rates. Such changes have been correlated with fluid velocities and physical properties of the fluids. The correlation is being generalized in terms of dimensionless groups so that it can be incorporated into design procedures for perforated plate or spray-type equipment.

Study of flow patterns is being continued by use of a numerical solution of the Navier–Stokes equations to study flow patterns inside transparent droplets. These results show solute transport trajectories, generation of interfacial area, and droplet shapes during formation. When the results can be verified experimentally, then the same simulation program can also be used to study transport processes inside opaque liquid metal systems.

PUBLICATION

Halligan, J. E., and Lawrence Burkhart, The Asymptotic Curvature at Droplet Separation, J. Colloid Interface Sci., 37: 208 (1971).

03:424 CORROSION IN LIQUID METAL SYSTEMS. Burnet, George. (Ames Laboratory, Chemical Engineering Division).

A major barrier to many applications of liquid metals is the lack of suitable container materials. Advanced reactor concepts often include liquid metals as heat transfer fluids or fuel carriers. Corrosion tests are being conducted in isothermal spinner-type units and in convection loops at temperatures in the range of 300 to 800°C. Work has focused on the lead–bismuth eutectic and on pure bismuth. Container materials of low neutron capture cross section are of particular interest. Exploratory work has started on the use of tin and tin alloys as liquid metals.

03:425 LIQUID METAL WETTING AND SURFACE TENSION. Burnet, George. (Ames Laboratory, Chemical Engineering Division).

A variety of metal alloys and ceramic materials have been developed for high-temperature applications. Very little is known about the degree to which these materials are wetted by liquid metals, and surface tension data are very incomplete. Equipment, techniques, and computer programs have been developed for this study and are being adapted to several container material–liquid metal systems. Efforts are being made to develop generalized correlations between surface tension and thermodynamic properties.

PUBLICATIONS

Maze, R. C., and G. Burnet, Modifications of a Non-Linear Regression Technique Used to Calculate Surface Tension from Sessile Drops, Surface Sci., 24: 335-342 (1971).

———, and G. Burnet, Estimation of Non-Equilibrium Surface Tension, Surface Sci., 27: 411 (1971).

03:426 PURIFICATION OF LIQUID METALS BY ADSORPTION. Burnet, George. (Ames Laboratory, Chemical Engineering Division).

A number of advanced nuclear reactor concepts call for the removal of relatively small amounts of certain metals (e.g., fission products) from carrier metal streams such as those of bismuth or bismuth alloys. These separation problems are most often associated with the reprocessing of spent fuels. Exploratory work has shown that conventional adsorbents, such as activated carbon and silica gel, are capable of removing impurities from liquid bismuth. An experimental method has been developed for obtaining equilibrium data for the systems being studied.

03:427 RECOVERY OF METALS FROM FLY ASH. Burnet, George. (Ames Laboratory, Chemical Engineering Division).

Over 20 million tons of fly ash are produced each year in the United States; only 10% is put to some use. A typical fly ash contains about 25%, by weight, aluminum oxide and about 20%, by weight, iron oxide. Preliminary work is underway on the recovery of aluminum, iron, and possibly other metals from the ash, and also on uses of the residue. Hydrometallurgical processing shows promise of yielding high-purity aluminum oxide for use as a raw material for aluminum manufacture, and a high grade iron oxide that, upon pelletization, can be used as blast furnace feed.

03:428 MOLECULAR DISTRIBUTIONS FROM TORSION EFFUSION CELLS AND THEIR EFFECT ON EXPERIMENTAL THERMODYNAMIC PROPERTIES. Fitzgibbons, D. A.; Stevenson, F. D. (Ames Laboratory, Chemical Engineering Division).

Recent work at Los Alamos on molecular distributions from Knudsen effusion cells has demonstrated the limitations of assuming molecular equilibrium within such cells. The fact of nonequilibrium in the Knudsen cell makes suspect the equilibrium assumptions of the torsion effusion cell. Work is now in progress to extend the Monte Carlo work on gaseous transmission probabilities, recently done at the Ames Laboratory, to the recalculation of the effect of molecular distributions from a torsion effusion cell.

A preliminary report has been issued that details the calculations to be made. Since this is one of the principal methods of obtaining high-temperature thermodynamic data (vapor pressures, heats of vaporizations, etc.) an effort will be made to establish limiting internal cell geometries that would minimize the effect of such geometries on the torque produced by the effusing beam. Initial work is expected to take into account internal cell and sample geometries while future work is expected to account for the distribution of molecular velocities and the interaction effects of the molecules with the cell walls. It is hoped that, as a result of this work, more accurate thermodynamic data will result from torsion effusion measurements.

03:429 LIQUID METAL DIFFUSION STUDIES. Shuck, Frank O. (Ames Laboratory, Chemical Engineering Division).

Recent work has demonstrated the utility of resistivity composition measurement in liquid metal diffusion studies. Successful diffusion coefficient measurements have been completed for alloys of indium, bismuth, and lead in mercury utilizing a capillary reservoir cell equipped to monitor capillary composition by means of changes in electric resistivity. At present, this work is being extended in several directions. On the basis of the newly accumulated data available, an effort is being made to correlate available liquid metal diffusion data and provide improved prediction of liquid metal diffusion coefficients. The present low-temperature capillary–reservoir resistivity cell is being redesigned for operation at higher temperatures. This redesign will requtre a considerable amount of experimental testing of design and possible materials. A pilot study of isotopic separation of liquid metals by diffusion is also being undertaken. The object of the present study is to demonstrate the feasibility of separation of metal isotopes by liquid diffusion and provide information for possible design for such a separation process.

PUBLICATIONS

Wenger, J. C., and F. O. Shuck, Diffusion in Liquid Indium Tin Alloys at 300°, Met Trans., 2: 867 (1971).

Kaiser, R. H., and F. O. Shuck, Diaphragm Cell Measurement of Liquid Cadmium–Indium Diffusion Coefficients at 300°C, Met Trans., 1: 2336 (1970).

Buell, C. H., and F. O. Shuck, Diffusion in the Liquid Bismuth–Tin System, Met Trans., 1: 1875 (1970).

Nanda, A. K., and F. O. Shuck, Diffusion in $I_N - H_C$ Amalgams, Met Trans., 1: 353 (1970).

03:430 EXPERIMENTAL ERRORS IN KINETIC MODELING. Stevenson, F. D. (Ames Laboratory, Chemical Engineering Division).

The objective of this work is to establish statistically the effect of various experimental errors on the uncertainty of kinetic model parameters. How such experimental errors affect the convergence of sequentially designed experiments is also of concern. Recent work at the Ames Laboratory has shown that the statistical method of *Nonlinear Parameter Estimation coupled with the Sequential* Design of Experiments is an extremely effective and economical approach to modeling chemical reactions. Work in this area has shown the importance of modifying the experimental design after each new bit of information is obtained from experimentation. Pseudo-experiments will be carried out for several kinetic models by adding random error of a specified variance to calculated results in an effort to find how the different experimental errors in, say, temperature, reactant concentrations, etc., contribute to the uncertainty in the calculated rate constants and other kinetic parameters. These errors are then propagated into the subsequent design of experiments in an unknown way. Work in this area is expected to clarify this.

PUBLICATIONS

Graham, Robert J., and F. D. Stevenson, Kinetics of the Chlorination of Niobium Oxychloride by Phosgene in a Tube-flow Reactor. An Application of Sequential Experimental Design, Ind. Eng. Chem., Process Design Develop., 11: 160-164 (1972).

______, and F. D. Stevenson, Effects of Experimental Error on Parameter Estimation and Convergence of a Sequential Experimental Design, Ind. Eng. Chem., Process Design Develop., 11: 164-169 (1972).

Sater, Vernon E., and F. D. Stevenson, Ind. Eng. Chem., Process Design Develop., 11: 355-359 (1972).

03:431 NUCLEATION. Eberhart, J.; Blander, M. (Argonne National Laboratory, Chemical Engineering Division).

A study of homogeneous nucleation of vapor bubbles in superheated liquids was initiated because of the importance of this phenomenon in reactor safety; for example, the superheating of sodium coolant. Determinations were made of the homogeneous list of superheat for a large variety of pure liquids and several binary mixtures. The results were consistent with predictions of nucleation theory. A theoretical approach to predicting the limit of superheat is also being explored from the standpoint of classical thermodynamics. Nucleation studies of binary systems will continue, and measurements will be initiated to test the nucleation theory for heterogeneous bubble nucleation at a liquid–liquid interface.

03:432 CONTROLLED THERMONUCLEAR REACTOR CHEMISTRY. Maroni, V.; Veleckis, E.; Blander, M. (Argonne National Laboratory, Chemical Engineering Division).

Experimental studies were continued to obtain pressure–composition–temperature data for the Li–LiH, Li–LiD, and Li–LiT systems. This work is intended to fulfill the need for comprehensive thermodynamic information about these systems as they pertain to the anticipated use of liquid lithium in the blankets of future D–T fusion reactors. Thus far, three complete hydrogen pressure versus composition isotherms have been obtained at 705, 799, and 898°C; these data, which are far more precise than all previous measurements, have allowed the calculation of hydrogen pressures over very dilute hydride solutions of interest for thermonuclear reactors. Measurements will be made at other temperatures and with deuterium and tritium.

Estimates were made of the permeation rates of tritium near the core of a prototypical fusion reactor plant. Calculations revealed that it may be possible to operate a static lithium blanket in a D–T-fueled reactor and still achieve adequate recovery rates of tritium.

We plan further studies of the chemistry of lithium systems with possible contaminants.

03:433 METAL HYDRIDES. Wiswall, R. H. Jr.; Reilly, J. J. (Brookhaven National Laboratory, Dept. of Applied Science).

This study of the chemistry and physics of solid metal hydrides is oriented toward two of their practical applications: the storage of hydrogen for use as a fuel, and the separation of the hydrogen isotopes in processes involving exchange between hydride and gaseous hydrogen.

Many metals and alloys take up large quantities of hydrogen, which can later be recovered by raising the temperature or lowering the pressure. The volume of such a hydrogen reservoir is usually less than that of a tank of compressed gas. Furthermore, the expense of the compression process is avoided. For such an application, one desires a hydrogen–metal system with an adequate equilibrium pressure at ordinary temperatures, a low heat of dissociation, and high hydrogen content. Previous work in this program has resulted in the discovery of several systems that are satisfactory in the first two respects. A number of alloys remain to be tested with hydrogen, and it is hoped that future research will result in a system of practical interest.

The isotope separation application depends upon the fact that the stability of many metal hydrides differs markedly from that of the corresponding deuterides or tritides; dissociation pressures often vary by a factor of two or more. Such an effect can be utilized for a more or less complete resolution of an isotopic mixture, by means of a countercurrent multi-stage operation. Research is in progress both on the quantitative determination of isotope effects in new hydrogen–metal systems and on the engineering application of previously studied hydrides.

PUBLICATIONS

Reilly, J. J., A. Holtz, and R. H. Wiswall, Jr., A New Laboratory Gas Circulation Pump for Intermediate Pressures, Rev. Sci. Instrum., 42: 1485 (1971).

______, and R. H Wiswall, Jr., The Higher Hydrides of Vanadium and Niobium, Inorg. Chem., 9: 1678 (1970).

______, and R. H. Wiswall, Jr., Method of Storing Hydrogen, U. S. Patent No. 3,516,263, June 23, 1970.

03:434 HEAT TRANSFER AND TRANSPORT BY CONDENSING VAPORS. Bonilla, Charles F. (Columbia University, Liquid Metals Research Laboratory, Department of Chemical Engineering and Applied Chemistry, New York, New York 10027).

In the heat transfer and transport area of this program, the hydrodynamics of a thin falling liquid film in low turbulent flow, applicable to predicting heat transfer in vapor condensers, was studied by modeling with a light oil in a thick channel. Probably the most accurate measurements to date of velocity and turbulence distribution in laminar boundary sublayers were obtained. A final phase being completed is a study of the surface waves generated when the surface is unrestrained, as in a condenser with vapor space.

Finally, a study of heat transfer in pool boiling and condensing of elemental selenium was completed, and a similar study for $NO_2-N_2O_4$ is under way. These are providing information on vapor–liquid phase change in reacting or polymerizing materials, which will serve as a model for, and will aid in the understanding of, the alkali metals in these phase changes. Additional related studies on the condensing heat transfer, condensing condensation or accommodation factor, and thermal conductivity of mercury vapor up to the 500 to 1000 psia pressure range are commencing.

PUBLICATIONS

Erginez, H. S., and C. F. Bonilla, The Thermal Conductivity of Mercury Vapor, in Proceedings of the Fifth International Symposium on Thermophysical Properties, American Society of Mechanical Engineers, 1970, p. 64.

Navarro, L. J., J. Larrain, and C. F. Bonilla, The Thermal Conductivity of Liquids by the A.C.-Heated Hot Wire Method (Dowtherm A and E, Dow Corning 710, Isopar M, Liquid g and N_2O_4), in Proceedings of the Fifth International Symposium on Thermophysical Properties, American Society of Mechanical Engineers, 1970, p. 64.

03:435 CHEMISTRY MATERIALS IN NUCLEAR TECHNOLOGY. Olander, Donald R. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

This project is concerned with investigation of various chemical–materials problems that are pertinent to nuclear technology. Theoretical work includes analysis of the performance of the gas centrifuge method of separating uranium isotopes, the migration of constituents of uranium–plutonium oxide materials in the temperature gradient of operating fast reactor fuel elements, and the interaction of hydrogen with metals.

Current experimental programs involve molecular beam mass spectrometric studies of the surface reactions of various gases with pyrolytic graphite and of fluorine with uranium dioxide. The transport properties of high-temperature liquids, such as the viscosity of molten uranium dioxide and cesium and the diffusion of rare earths in molten uranium metal, are under investigation. Laser pulsing of solid compounds is studied in an attempt to understand very rapid vacuum vaporization processes. Homogeneous gas phase reactions induced by proton irradiation (e.g., $O_2 \rightarrow O_3$ and $CO_2 + H_2 \rightarrow H_2O + CO$) are studied using mass spectrometric sampling to permit detection of free radical intermediates.

PUBLICATIONS

Omberg, R. P., and D. R. Olander, Effect of Condensation in the Boundary Layer on Mass Transfer from a Rotating Disk. I. Theoretical, Phys. Fluids, 14: 1605 (1971).

____ _, and D. R. Olander, Effect of Condensation in the Boundary Layer on Mass Transfer from a Rotating Disk. II. Experimental, Phys. Fluids, 14: 1834 (1971).

Olander, D. R., Description of the Hydrogen–Metal Interaction by a Morse Potential Function, J. Phys. Chem. Solids, 32: 2499 (1971).

____ ., Technical Basis of the Gas Centrifuge, Advan. Nucl. Sci. Technol., 6: 105-174 (1972).

03:436 CHEMISTRY OF RADIOIODINE IN HIGH-RADIATION-LEVEL SEPARATION PROCESSES. Schmitt, J. M. (Oak Ridge National Laboratory, Chemical Technology Division).

The purpose of this program is to obtain a better understanding of the complex chemistry of iodine in chemical processing systems as a basis for providing effective containment of radioactive iodine in nuclear-fuel-processing plants. Study of reactions important in the use of aqueous solutions (e.g., mercuric nitrate–nitric acid, concentrated nitric acid) for scrubbing iodine from process off-gases currently is receiving emphasis. The rates of reaction of various iodine species with the scrub solution components and the distribution of these species between the aqueous and gas phases are being determined. The studies have shown the importance of small amounts of organic impurities, which are readily iodinated under some conditions, on the behavior of iodine in various process systems. Investigation will continue of the formation of organic iodides in both gas and aqueous phases as a guide to minimizing their effects of process performance. Iodine reactions in other systems are continually being examined in a search for new and more efficient iodine-trapping processes.

03:437 CHEMICAL ENGINEERING RESEARCH. Watson, J. S.; McNeese, L. E.; Lindauer, R. B. (Oak Ridge National Laboratory, Chemical Technology Division).

This program includes several studies generally pertinent to applied programs of the AEC; however, the studies are made in a more fundamental manner than that usually employed in applied programs. Two of these studies are summarized below.

Very small resin particles have proved to be beneficial in small-scale ion exchange separations, and the application of these materials to larger, engineering-scale systems is under study. It is likely that some existing processes can be made more economical and some marginal processes may become practical. Recent experimental efforts have included study of thorium nitrate anion exchange rates in small (10 to 50-μ) resins. This system closely resembles the plutonium anion exchange process, which is limited by slow diffusion rates in the resin particle. Plutonium anion exchange has had practical significance for concentration and purification of plutonium solutions. Recent accomplishments include experimental data and improved techniques for calculating the performance of columns of various sizes and with different size resins.

The hydrodynamics of countercurrent flow of fluids with high densities and a high density difference in packed columns are studied to obtain fundamental data for the design of solvent extraction systems using liquid metals and molten salts. Existing correlations based on solvent–water systems are inappropriate for high-density systems. Experimental data and correlations have been obtained with mercury–water and with mercury–glycerol solutions. Recent efforts have included a systematic study of the effects of density difference so generalized correlations can be developed which describe both high-density and conventional low-density systems. Measurements have been made with water and relatively dense organic liquids, carbon tetrachloride (density, 1.6 g/cm^3) and dibromomethane (density, 2.5 g/cm^3). Correlations for holdup, flooding rates, and pressure drop are developed and tested.

03:438 BASIC MATERIALS CHEMISTRY RELATED TO FUSION REACTOR SYSTEMS. Cantor, S.; Strehlow, R. A.; Weaver, C. F. (Oak Ridge National Laboratory, Reactor Chemistry Division).

This is a new project that investigates fundamental chemistry associated with selection and application of materials for controlled thermonuclear reactors. Three areas are under study:

(1) overall evaluation of lithium-bearing fused salt blanket coolants — measurement of the effects of strong magnetic fields on the corrosivity and fluid dynamics of turbulently flowing salts; circulation of the extent of neutronic transmutations, its chemical effects, and the redox buffers required to control the consequences of the transmutations;

(2) tritium permeation and control — measurement, at low pressures, of the steady-state permeation of metals by hydrogen isotopes; determination of the reduction in permeation caused by surface oxides which inhibit corrosion in chromium-containing alloys; and

(3) chemical behavior of structural refractory metals — niobium, molybdenum, vanadium, and tungsten; synthesis of the more stable lower valence fluorides of these metals; solubility and reactivity of these refractory metal compounds in fused fluoride blanket coolants, (LiF, Li_2BeF_4); priority will be given to the metals, compounds and solutions that are technologically relevant to the corrosion, buffering, and tritium containment aspects noted above.

03:439 FACILITY FOR STUDIES OF RADIATION AND CHEMICAL EFFECTS INDUCED BY FAST ION BOMBARDMENT. Axtmann, Robert C. (Princeton University, Department of Chemical Engineering, Princeton, New Jersey, 08540).

Recent advances in plasma physics research have led to optimism concerning the prospects for fusion power and make timely the initiation of work on aspects of fusion technology other than plasma physics itself. It has long been apparent that the materials problems in practical fusion devices will be extremely severe. This project involves construction of a testing facility for the characterization and understanding of the effects produced by the bombardment of reactor materials by fast ions that escape the plasma. Among the phenomena to be studied are sputtering, blistering, creation of surface and bulk defects, and the permeation of light isotopes through metals. The current year's effort will be devoted almost entirely to the design and construction of an apparatus that will accelerate protons, deuterons, tritons and/or helium ions, at energies up to 50 keV and with current densities equivalent to those expected in practical fusion devices. Samples of various candidate metals, such as niobium, molybdenum, vanadium, and stainless steel, will be bombarded to high fluences and then examined for changes in chemical, physical, and metallurgical properties. In addition, studies of the rate of gaseous transport through the metals will be made. In the case of tritium, for example, such rates may have importance in the assessment of the environmental effects of fusion devices.

PUBLICATIONS

Herber, R. H., and Y. Hazony, Experimental Aspects of Mössbauer Spectroscopy, in Physical Methods of Chemistry, Vol. I, Part IIID, A. Weissberger and B. W. Rossiter (Eds.), Chap. IV, pp. 215-306, John Wiley & Sons, New York, 1972.

Perkins, H. K., and Y. Hazony, Temperature-Dependent Crystal Field and Charge Density: Mössbauer Studies of FeF_2, $KFeF_3$, $FeCl_2$, and FeF_3, Phys. Rev., B 5: 7-18 (1972).

Hazony, Y., H_c – QS – IS Correlations in Octahedral Iron Compounds, in Mössbauer Effect Methodology, I. J. Gruverman (Ed.), Plenum Publishing Corporation, 7: 147-166, 1971.
Axtmann, R. C., Close Coupling Between Experiments and Computers, A.I.Ch.E. Workshop, Chemical Engineering Computing, Vol. I, pp. 11-16, 1972.

ALSO SEE Heavy Element Chemistry: 03:88; Radiation Chemistry: Other; 03:159; High-Temperature and Inorganic Chemistry: 03:329, 03:339, 03:350, 03:358, 03:359.

MISCELLANEOUS CHEMICAL STUDIES

Studies of electrochemistry and corrosion, geo- and cosmochemistry, solid state and surface chemistry, catalysis, colloids, organic chemistry, and chemical physics.

03:440 SURFACE CHEMISTRY. Hansen, Robert S. (Ames Laboratory, Chemistry Division).

This project is concerned with chemical reactions at surfaces, physical adsorption at interfaces, and mechanical properties of interfacial films.

The chemical reactions under study are catalytic decomposition reactions, particularly of hydrocarbons and ammonia, at ultraclean metal surfaces. Techniques used most extensively are field emission electron microscopy and flash filament desorption spectroscopy; low-energy electron diffraction (LEED) and Auger spectroscopy facilities have been added during the past year. The work seeks to interpret reactivity in terms of surface structures and to establish intermediate states in surface reactions. For example, the kinetics of decomposition of ammonia on the (100), (110), (111), and (211) faces are being established, correlated with LEED structure measurements on these surfaces, and the research supplemented by extended Hückel calculations of bonding models for H, N, NH, and NH_2 adsorbed on these faces.

Physical adsorption of organic nonelectrolytes at the mercury–electrolytic solution is measured as function of polarization and organic solute concentration by capillary electrometer and double layer capacity techniques. The work seeks to develop a model permitting a priori calculation of dependence of adsorption on molecular parameters (especially polarizability) and electric field.

Mechanical properties of interfaces are inferred from measurements of propagation characteristics of transverse and longitudinal waves, in an effort to develop models for relaxation processes, especially molecular reorientation processes, in monomolecular films.

PUBLICATIONS

Hansen, Robert S., and Nelson C. Gardner, A Field Emission Study of the Decomposition of Acetylene and Ethylene on Tungsten, J. Phys. Chem., 74: 3646 (1970).
_____, and Jamil Ahmad, Waves at Interfaces, in Progress in Surface and Membrane Science, Vol. 4, J. F. Danielli, M. D. Rosenberg, and D. A. Cadenhead (Eds.), Academic Press, Inc., New York, 1971, pp. 1-56.
Broadhead, D. E., R. S. Hansen, and J. Keller, Some Experimental Problems in Electrocapillarity, J. Colloid Interface Sci., 35(3): 506 (1971).
Mann, J. Adin, J. F. Baret, Frederick J. Dechow, and Robert S. Hansen, Interfacial Forces and the Brillouin Spectrum of the Interfacial Light-Scattering Power, J. Colloid Interface Sci., 37(1): 14 (1971).
Sheets, Ralph W., and Robert S. Hansen, Promoted Adsorption of Pyridine on Nickel, J. Phys. Chem., 76: 972 (1972).

03:441 DEVELOPMENT OF THE ON-LINE CHEMICAL LABORATORY COMPUTER FACILITY. Day, P., J. Hines and A. Zielen (Argonne National Laboratory, Chemistry Division).

The effective integrated use of the computer in the modern chemistry laboratory offers a continuing challenge. Our program of on-line data acquisition and control has been extended to 14 experimental installations utilizing our Sigma-5 computer. The program calls for a continuing development of the existing interfaced experiments and the addition of new interconnections to the practical limit of the computer facility.

For each installation, research and development consists of the deduction and testing of logical schemes, implemented in computer code and new hardware, that fall into three principal areas: (1) the enhancement of communication (more natural and sophisticated) between the user and the computer through interactive graphic display devices that provide on-line display and analysis of data under user control at his keyboard; (2) increasing the amount, speed of acquisition and analysis of data for highly interactive control of time-critical experiments; and (3) maximizing the efficient access of user's programs to new and existing system resources (random access secondary storage, text editing, etc.) in a manner that will never jeopardize the integrity of any system user's resources.

03:442 EXTRATERRESTRIAL MINERALOGY: METEORITES AND LUNAR SAMPLES. Fuchs, L. H., G. W. Reed, Jr., S. Jovanovic and M. Blander (Argonne National Laboratory, Chemistry Division).

The mineralogy and petrology of lunar samples is a continuing study conducted in conjunction with the trace element studies of the principal investigator, George Reed of this laboratory. The purpose is to characterize specific samples received from NASA with regards to their mineral contents, meteoritic components, and textural evidences indicative of metamorphism.

The mineralogy and mineral chemistry of selected meteorites is another principal interest. Just completed is a study of the Murchison meteorite, a rare Type-2 carbonaceous chondrite. This study is probably the most extensive one ever conducted on a meteorite of this class. The mineral chemistry is especially important in view of the discovery by others of over a dozen amino acids in the low-temperature matrix of the meteorite. The Allende meteorite, a Type-3 carbonaceous chondrite, is under study. Specifically, we are concerned with the numerous calcium- and aluminum-rich mineral assemblages, which many believe to be high-temperature condensates from a solar nebula. The mineral contents and chemistry of individual inclusions will be related to the thermodynamics of condensation processes of M. Blander and others. This work is partially supported by NASA under a grant to M. Blander of this laboratory who is the principal investigator.

The recent acquisition of an ion microprobe by the laboratory will facilitate the study of the distribution and concentrations of trace elements in specific mineral sites. This field of study is basic to the origin and thermal history of extraterrestrial and terrestrial matter.

PUBLICATIONS

Reed, G. W., S. Jovanovic, and L. H. Fuchs, Fluorine and Other Trace Elements in Lunar Plagioclase Concentrates, Earth Planet. Sci. Lett., 11: 354-358 (1971).
Fuchs, L. H., Orthopyroxene and Orthopyroxene-Bearing Rock Fragments Rich in K, REE, and P in Apollo 14 Soil Sample 14163, Earth Planet. Sci. Lett., 12: 170-174 (1971).
_____, Occurrence of Wollastonite, Rhonite, and Andradite in the Allende Meteorite, Amer. Mineral., 56: 2053-2068 (1971).
Keil, M., and L. H. Fuchs, Hibonite, $Ca_2(Al,Ti)_{24}O_{38}$, from the Leoville and Allende Chondritic Meteorites, Earth Planet. Sci. Lett., 12: 184-190 (1971).

03:443 NUCLEAR, PHYSICAL, AND CHEMICAL PROCESSES DETERMINING THE CONCENTRATIONS AND DISTRIBUTIONS OF TRACE ELEMENTS IN SOLAR SYSTEM MATTER. Reed, G. W., S. Jovanovic and L. Fuchs (Argonne National Laboratory, Chemistry Division).

Our studies are directed toward understanding the geo- and cosmochemistry and physics of solar system matter by measuring the abundance and distribution of trace elements. We use primarily the extremely sensitive technique of activation analyses. Our most recent efforts have been directed toward investigating samples returned from the moon. Some of the elements being measured are relatively volatile and the results are of use in describing the thermal conditions in the surface of the moon. Other measurements are yielding data that help delineate the evolution of the moon and its relation to other solar system matter.

Similar investigations of meteorites and the earth are a part of our program. In the case of the earth, our studies are designed to contribute to determining the natural balance, distribution, and mobility of trace elements as a prerequisite for understanding the impact and redistributions imposed by human activity.

PUBLICATIONS

Reed, G. W., J. A. Goleb, and S. Jovanovic, Surface-Related Mercury in Lunar Samples, Science, 172: 258-261 (1971).
_____, Fluorine (9), Chlorine (17), Bromine (35), Iodine (53), and Mercury (80), in Elemental Abundances in Meteoritic Matter,

B. Mason (Ed.), Gordon and Breach, Science Publishers, Inc., New York, pp. 103-107, 143-148, 279-284, 401-406, and 487-491, 1971.

———, S. Jovanovic and L. H. Fuchs, Fluorine and Other Trace Elements in Lunar Plagioclase Concentrates, Earth Planet. Sci. Lett., 11: 354-358 (1971).

———, and S. Jovanovic, The Halogens and Other Trace Elements in Apollo 12 Samples and the Implications of Halides, Platinum Metals, and Mercury on Surfaces, in Proceedings of the Second Lunar Science Conference, The MIT Press, Cambridge, Mass., Vol. 2, pp. 1261-1276, 1971.

Turkevich, A., G. W. Reed, Jr., H. R. Heydegger, and J. Collister, Activation Analysis Determination of Uranium and ^{204}Pb in Apollo 11 Lunar Fines, in Proceedings of the Second Lunar Science Conference, The MIT Press, Cambridge, Mass., Vol. 2, pp. 1565-1570, 1971.

03:444 ORIGIN OF ORGANIC MATTER IN EARLY SOLAR SYSTEM. Studier, M. H. (R. Hayatsu and E. Anders, University of Chicago). (Argonne National Laboratory, Chemistry Division).

Meteorites of the rare class called carbonaceous chondrites contain appreciable quantities of organic matter. These meteorites are the oldest that have been observed, and, therefore, give the earliest clues concerning the evolution of our solar system. Some scientists have attributed the organic matter in meteorites to an extraterrestrial biological source because many of the compounds found are normally of biogenic origin. However, we have shown this postulate to be unnecessary by synthesizing essentially all of the compounds found to be indigenous to meteorites by merely heating mixtures of carbon monoxide, hydrogen, and ammonia in the presence of an iron meteorite catalyst. Indeed these studies have pointed out how such organic molecules might have become available as precursors to the formation of living organisms. Compounds synthesized from the simple gases, CO, H_2, and NH_3 include aromatic and aliphatic hydrocarbons, nitriles, amino acids, nitrogen bases, and porphyrin-like pigments. Included are eight compounds recently identified in interstellar space by astronomers using microwave spectrometry. Work on the probable origins of interstellar molecules and of the high-molecular-weight organic polymers found in meteorites is continuing.

This work was made possible by the development of powerful analytical techniques involving time-of-flight mass spectrometry and various forms of chromatography.

PUBLICATIONS

Hayatsu, R., M. H. Studier, and E. Anders, Origin of Organic Matter in Early Solar System. IV. Amino Acids: Confirmation of Catalytic Synthesis by Mass Spectrometry, Geochim. Cosmochim. Acta, 35: 939-951 (1971).

———, M. H. Studier, S. Matsuoka and E. Anders, Origin of Organic Matter in Early Solar System. VI. Catalytic Synthesis of Nitriles, Nitrogen Bases and Porphyrin-Like Pigments, Geochim. Cosmochim. Acta, 36: 555-571 (1972).

Studier, M. H., R. Hayatsu, and E. Anders, Origin of Organic Matter in Early Solar System. V. Further Studies of Meteoritic Hydrocarbons and a Discussion of Their Origin, Geochim. Cosmochim. Acta, 36: 189-215 (1972).

03:445 ELECTROCHEMICAL RESEARCH. Feldberg, S. (Brookhaven National Laboratory, Department of Applied Science).

The objectives of the present work are twofold: (1) Development of a general approach to membrane theory which will allow one to easily test a variety of models for membrane transport—biomembranes in particular. The theory incorporates the fundamental forces acting on ions and molecules in a membrane—diffusion, migration, flow, and frictional forces that exist between any two species moving relative to each other. Using computer simulation approach, a variety of problems which have either not been solved or whose solutions are unwieldy appear to yield readily to the approach. (2) Development of a collaborative program with Professor W. Nastuk, Department of Physiology, Columbia University, in order to investigate the effects of acetylcholine and related quaternary ammonium ions on the activation of skeletal frog muscle. With Professor David Mohilner, Department of Chemistry, Colorado State University, we are undertaking a study of the adsorption properties of a variety of physiologically effective quaternary ammonium ions on mercury as a function of the electropotential of the mercury surface. If the mechanism of physiological activity involves adsorption on membrane sites, there may be a correlation.

PUBLICATIONS

Feldberg, Stephen W., Nuances of the ECE Mechanism. III. Effects of Homogeneous Redox Equilibrium in Cyclic Voltammetry, J. Phys. Chem., 75: 2377 (1971).

Jeftic, Ljubomir, and Stephen Feldberg, Chromium(II) Catalyzed Aquation of Hexacyanochromate(III) to Pentacyanomonohydroxychromate(III), J. Phys. Chem., 75: 2381 (1971).

03:446 LOCALIZED CORROSION. Isaacs, H. S. (Brookhaven National Laboratory, Department of Applied Science).

A limitation to the use of stainless steels in aqueous environments results from localized forms of corrosion including stress corrosion cracking, crevice corrosion, or pitting. These forms of corrosion are all basically crevices and the factors differentiating their growth are being investigated. In all cases species from the steel and the environment are known to concentrate in the crevices. Investigation has shown that the growth of a specific crevice depends nonlinearly on the diffusion of the species, and the formation of a resistive film on the dissolving steel surface. In pits the concentration gradients are usually symmetrical giving rise to hemispherical pits while in crevice corrosion the concentration gradients are influenced by diffusion and convection, which give rise to the standard growth pattern within crevices. In the case of stress corrosion cracking, rupture of the resistive film within the pit leads to the development of transgranular stress corrosion cracks along slip lines. Future work is directed to the analysis of the species that form the resistive films within the crevices.

03:447 FLUORINATION OF ORGANIC MOLECULES. MacKenzie, D. R. (Brookhaven National Laboratory, Department of Applied Sciences).

Direct substitution of fluorine into organic molecules is notoriously difficult, and only within the last three years have useful methods been discovered. We have worked on one of these methods, involving the use of xenon difluoride (XeF_2) as fluorinating agent, to develop procedures for introducing F atoms into the aromatic ring of benzene and its derivatives. These procedures involved reaction in the vapor phase at temperatures considerably above ambient in order to keep the reactants in the vapor state. In attempting to extend the procedures to the pyridine ring system, the method was found suitable for volatile pyridine derivatives but not for pyridine itself. For the latter it was necessary to restrict the temperature to ambient or below, which required working in the liquid phase. Under these conditions, reasonable yields of the isomeric monofluoropyridines were formed, including the hitherto unreported 4-fluoropyridine.

Working in the liquid phase is also necessary for relatively nonvolatile compounds, such as most biologically active materials. A number of these compounds are desired for medical research when substituted with ^{18}F as a tracer, and a method of substituting fluorine directly and rapidly into such molecules would be of very great value. We are currently attempting this using XeF_2 with Δ9-tetrahydrocannabinol, the active ingredient of marijuana. Another fluorination method we are working on, photochemical fluorination with CF_3OF, could also have application to this and other compounds of biological interest.

03:448 NUCLEAR CHEMISTRY AND GEOCHEMISTRY RESEARCH. Kohman, Truman P. and Karol, Paul J. (Carnegie-Mellon University, Department of Chemistry, Mellon Institute of Science, Pittsburgh, Pennsylvania 15213).

The research objectives of this program are the elucidation of nuclear phenomena in nature, the application of nuclear techniques to the study of natural phenomena, and the determination of nuclear properties of geochemical and cosmochemical interest.

Measurements of the contents and isotopic composition of lead in chondrite meteorites are yielding precise determinations of their ages. This powerful dating tool is being applied to other classes of meteorites.

A search is being made for cases of extinct natural radioactivity with nonvolatile decay products, which would permit high-resolution dating of different, possibly earlier, events in the early solar system than those recorded by ^{129}I, and ^{244}Pu. Precise thallium isotope measurements, which have shown no 14-My ^{205}Pb in chondrites at the time of their formation, are being extended to achondrites and iron meteorites, which may be somewhat older. Effects of 80-My ^{146}Sm on the isotopic composition of neodymium will also be sought.

Correlations between the lead and thallium contents of chondrites and lead isotope data are yielding condensation temperatures and other information on their formation process. Studies have been initiated on the contents of Li, Be, and B, and the isotopic composition of Li, to obtain additional information on the chemical and possibly nuclear processes in the early solar system.

Theoretical evaluations of the time dependence of heavy element nucleosynthesis in the galaxy prior to and including the formation of the solar system, based on ratios of primary and extinct radionuclides in meteorites, are being extended to stable heavy elements and to the present time by using astrophysical data on the metal contents of dated globular and galactic star clusters. Improvements in the models will be attempted by considering other astronomical data.

The yields of a number of radionuclides in the high-energy proton bombardment of argon are being measured for the interpretation of the levels of the same nuclides in air, rain, and snow as a result of cosmic ray interactions with the atmosphere, in terms of various transport and precipitation processes.

Precise measurements of the $^{234}U/^{238}U$ alpha activity ratio in the uranium in young and old tektites are being made, in an attempt to determine whether significant amounts of soil or other weathered siliceous materials with low $^{234}U/^{238}U$ ratios were incorporated into them.

The Moessbauer spectra of iron in coals is being investigated in order to determine the chemical form of the nonpyrite iron present, by comparison with the Moessbauer spectra of various minerals. The technique is being extended to study the structural relationships between the related minerals.

Natural radioactivity of ^{48}Ca is being sought by the active daughter extraction of 1.82-day ^{48}Sc. Since low-level beta counting techniques have given negative results, the more sensitive sum-coincidence gamma–gamma system is being applied.

PUBLICATIONS

Kohman, T. P., Least-Squares Fitting of Data with Large Errors, J. Chem. Educ., 47: 657 (1970).

Huey, J. M., H. Ihochi, L. P. Black, R. G. Ostic, and T. P. Kohman, Lead Isotopes and Volatile Transfer in the Lunar Soil, in Proceedings of the Second Lunar Science Conference, The MIT Press, Cambridge, Mass., Vol. 2, pp. 1547-1564, 1971.

03:449 STUDIES ON COLLOIDAL PARTICLES: SCAVENGING OF AEROSOL PARTICLES BY A FALLING MACROSCOPIC PARTICLE.

Kerker, Milton (Clarkson College of Technology, Department of Chemistry, Potsdam, New York 13676).

The scavenging of atmospheric aerosol by rain cleanses the atmosphere and thereby enhances visibility, but it also results in radioactive fallout. In order to analyze the process by which a raindrop scavenges aerosol particles, it is necessary to characterize the fluid flow around the falling droplet and then to estimate the trajectory of the aerosol particle upon which fluid, inertial, thermal, diffusiophoretic, thermophoretic, and electrical forces may act. The result is expressed as the collection efficiency which is that fraction of aerosol particles contained in the track of a drop that is actually captured. The problem is formidable and a satisfactory theory has not yet been developed.

We have been carrying out an experimental study of this problem. This has presented a number of difficulties that have only recently been overcome. The formation in the laboratory and particle size analysis of submicron aerosols is a formidable feat. Furthermore, the amount of aerosol collected by a drop is so small that extremely sensitive experimental techniques must be used.

An experimental study of the collection efficiency of water droplets (0.71- to 2.54-mm. radius) freely falling through a silver chloride aerosol consisting of submicron spheres has been carried out at Clarkson College of Technology. Collection efficiencies measured were extremely low, dropping off sharply from a value of 3.1×10^{-1} for a 2.54-mm. droplet to a minimum of 6.3×10^{-6} for a 0.94-mm. droplet, and then appearing to rise again for smaller droplets. The collection efficiency varied inversely with particle size in this size range (from 0.2- to 0.7-nm radius), indicating that the mechanism of collection of these particles involves Brownian motion rather than inertial impaction as is the case for larger particles. These values of the collection efficiency are too small to account for appreciable fallout of such submicron particles by rain scavenging. It is particles of this size that contain a major part of the atmospheric radioactivity. However, further experiments presently under way will explore the effect of a longer time of free fall, which would more closely approximate conditions in nature and of electrical charge in order to explore this question more fully. In addition to providing an understanding of atmospheric scavenging, these data may also lead to a basic understanding of the phenomenon involved in the suppression of dust in industrial and mining environments by water sprays.

PUBLICATION

Hampl, V., M. Kerker, D. D. Cooke, and E. Matijević, Scavenging of Aerosol Particles by a Falling Water Droplet, J. Atmos. Sci., 28: 1211-1221 (1971).

03:450 INVESTIGATION OF SECONDARY ELECTRON YIELDS INDUCED BY ION IMPACTS ON THIN-FILM OXIDE SURFACES.

Dietz, L. A., J. C. Sheffield (Knolls Atomic Power Laboratory, Mass Spectrometry).

When an ion with keV energy strikes a surface under high vacuum it causes ejection of charged and neutral atomic species, including electrons and sometimes photons. Surprisingly little data are available about ion-induced secondary electron yields from thin oxide films, although the theory of secondary electron yield from metallic surfaces is well established. Amorphous films of aluminum oxide up to a few hundred Angstroms in thickness have an important use as ion-to-electron conversion dynodes in electron multipliers used for counting single ions. A knowledge of the statistical frequency distribution of secondary electrons ejected per ion impact allows one to place an upper limit on detection efficiency and to estimate measurement bias in the detection process.

A spectrometer for studying the secondary electron yield properties of a surface has been developed. The secondary electrons produced by ion impact are accelerated and focused onto the surface of a silicon solid state detector. Deconvolution of the resulting energy spectrum leads to precise estimates of secondary electron yields for monatomic or polyatomic ions of different mass, atomic number, velocity, and angle of entry into a given target surface. We plan to investigate many different target materials to determine the effect of atomic stopping power and chemical form of a surface on its secondary electron yield.

03:451 ELECTROCHEMISTRY, SOLID–FLUID PHASE BOUNDARIES.

Müller, R. H. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

The behavior of metal surfaces in contact with liquid and gaseous media is being investigated by electrochemical and optical techniques for the purpose of predicting the performance of materials in new environments and of extending the present range of operation of electrochemical reactors.

Series of generalized interference colors have been computed for the optical interference in transparent films on an arbitrary supporting medium. In addition to the usually considered phase change due to the optical path in the film, these color series also consider the phase change due to reflection at both film surfaces. As a test of the colorimetric computations, the thickness of films, derived from interference colors, is now being compared to thickness determinations that do not depend on the optical properties of the interfaces.

Ellipsometry has been used in two studies of surface layers on platinum substrates: chemisorption of carbon monoxide and electrolytic film formation. In the study of chemisorption of carbon monoxide, good qualitative correlation was found between ellipsometric and Auger electron spectroscopic measurements. Ellipsometric measurements of a H_2SO_4 film could be interpreted in terms of a dielectric film, while data of KOH films suggested absorption characteristics of the film that may be due to the inclusion of foreign particles. Construction of an automatic ellipsometer for the observation of transient anodic surface layers is in progress.

Electrolytic mass transfer boundary layers, responsible for the limited output of electrochemical reactors, have been characterized by optical interferometry. Errors in the observed boundary layer thickness, interfacial concentration, and concentration gradient due to light deflection have been computed for typical experimental conditions. These computations are now being compared to experiments by use of well-defined concentration fields resulting from diffusion and ionic migration. (Work directed jointly with Prof. C. W. Tobias)

PUBLICATIONS

Landolt, D., R. H. Muller, and C. W. Tobias, Crystallographic Factors in High-Rate Dissolution of Copper, J. Electrochem. Soc., 118: 36-40 (1971).

———, R. H. Muller, and C. W. Tobias, Anode Potentials in High-Rate Dissolution of Copper, J. Electrochem., 118: 40-46 (1971).

———, R. H. Muller, and C. W. Tobias, Transport Processes in ECM, in Fundamentals of Electrochemical Machining, C. L. Faust (Ed.), Electrochemical Society, 1971, p. 200.

Cooper, J., R. H. Muller, and C. W. Tobias, Periodic Phenomena in Copper Dissolution at Constant Current, in Fundamentals of Electrochemical Machining, C. L. Faust (Ed.), Electrochemical Society, 1971, p. 300.

03:452 ELECTROCHEMICAL SYSTEMS. Newman, John (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

This project deals with various problems of fluid flow and electrochemical transport processes. Mass transfer to a plane below a rotating disk at high Schmidt numbers is being studied experimentally. The corrosion of rotating iron and copper disks is being investigated theoretically. A device for concentrating electropositive cations using porous, fixed, flow-through, carbon electrodes is being studied experimentally. Mass transfer rates are being calculated for a system of two concentric cylinders, the inner one of which rotates. The transient response of potential to an interruption in current is being calculated for a rotating disk electrode. Diffusion coefficients of aqueous KOH solutions are being measured for concentrations to 1.2M.

Activity coefficients will be included in a calculation of limiting currents for copper deposition from solutions of copper sulfate and sulfuric acid. The effect of ionic migration on limiting currents should be estimated for turbulent flow situations. The current distribution on a rotating spherical electrode will be treated below the limiting current. Activity coefficients of mixed electrolyte solutions can be predicted on the basis of data for the binary systems. The accuracy of this scheme will be tested. Measurements will be initiated on the kinetics of dissolution of $Cd(OH)_2$.

PUBLICATIONS

Dunning, John S., Douglas N. Bennion, and John Newman, Analysis of Porous Electrodes with Sparingly Soluble Reactants, J. Electrochem. Soc., 118: 1251-1256 (1971).

Hsueh, L., and J. Newman, Concentration Profile at the Limiting Current in a Stagnant Diffusion Cell, Electrochim. Acta, 16: 479-485 (1971).

— —, and John Newman, The Role of Bisulfate Ions in Ionic Migration Effects, Ind. Eng. Chem., Fundam., 10: 615-620 (1971).

Selman, Jan Robert, and John Newman, High Sc Limit of Free Convection at a Vertical Plate with Uniform Flux Condition, J. Heat Transfer, 93: 465-466 (1971).

Smyrl, William H., and John Newman, Limiting Current on a Rotating Disk with Radial Diffusion, J. Electrochem. Soc., 118: 1079-1081 (1971).

03:453 SOLID STATE AND SURFACE REACTION STUDIES. Somorjai, G. A. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

Our research program is centered on studies of surface reactions and investigations of the structure of surfaces. The program may be divided into two parts (1) studies of the structure, chemical composition, and oxidation state of surfaces and of adsorbed gases using low-energy electron diffraction, and Auger electron spectroscopy and (2) investigations of chemical surface reactions or crystal surfaces by jointly using several techniques: molecular beam scattering, Auger electron spectroscopy, low-energy electron diffraction, and mass spectrometry.

In the first part we are studying the surface structure of adsorbed organic (aromatic) molecules on the (111) and (100) crystal faces of platinum by low-energy electron diffraction. Investigations of the surface structures of vanadium and iron crystals and the structures of adsorbed gases on these materials are in progress. The chemical compositions and oxidation states of various vanadium oxides and halides are being studied by Auger electron spectroscopy. The surface composition of indium–lead and silver–palladium alloys are being studied and are found to be different from their composition in the bulk.

In the second part of our research program catalytic surface reactions are studied on single crystal surfaces to explore the relationship between chemical reactivity and the atomic structure and composition of surfaces. The conversion of n-heptane to toluene has been found to be sensitive to the surface structure of platinum. The dehydrogenation of cyclohexane to benzene and the oxidation of ammonia are being studied using platinum crystal surfaces. The role of atomic steps at the surface in catalyzing many surface reactions has been uncovered. The ammonia synthesis is being studied on iron surfaces and catalytic oxidation reactions are studied using vanadium oxide surfaces. Molecular-beam-scattering studies from single crystal surfaces are being carried out to uncover the mechanism of energy transfer between the gas and the surface in surface chemical reactions such as in the dissociation of nitrogen oxides and during surface reactions of diatomic molecules (O_2, H_2, N_2, and CO).

PUBLICATIONS

Lang, B., R. W. Joyner, and G. A. Somorjai, Surface Sci., 30: 440 (1972).

— —, R. W. Joyner, and G. A. Somorjai, Surface Sci., 30: 454 (1972).

Somorjai, G. A., Principles of Surface Chemistry, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1972.

West, L. A., and G. A. Somorjai, J. Chem. Phys., 54: 2864 (1971).

Davy, J. Gordon, and G. A. Somorjai, J. Chem. Phys., 55: 3624 (1971).

03:454 TRANSPORT PROCESSES IN ELECTROCHEMICAL SYSTEMS. ELECTROLYTIC PROCESSES IN NONAQUEOUS SOLVENTS. Tobias, Charles W. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

The role of charge and mass transport in electrolysis and galvanic cell processes is subjected to quantitative evaluation. The objective is to provide the foundation for major improvements in existing technology and to open up possibilities for the implementation of new processes.

Current and planned work includes theoretical and experimental work on the distribution of limiting currents along planar electrodes in channel flow up to Re = 100,000, in 0.02- to 1-cm separation. Concentration fields in laminar boundary layers along extended surfaces are being analyzed by means of Laser–Mach–Zehnder Interferometry. Effects of electrolyte composition, flow, macro- and microgeometry on the nature of high-rate dissolution of metallic substrates are being studied, with particular emphasis on the elucidation of the role of anodic oxide layers. A parallel effort is directed toward the definition of optimal conditions for the shaping of refractory metal carbides, borides, etc., and of high-strength alloys by high-speed anodic dissolution.

Electrode reactions requiring high potentials—such as the reduction of alkali metals—are carried out in suitable organic ionizing media. The propylene carbonate family of solvents shows particular promise: chemical reversibility of reduction–oxidation, as well as favorable kinetic parameters obtained for alkali metals indicate that reduction of certain of the transition metals may be feasible. Thermodynamic and kinetic studies on the alkali series are currently being completed; indications are that practical processes for the recovery of these metals from their chlorides may be possible at ambient temperatures. Exploratory work on Group III, IV, V–VIb metals is now receiving renewed emphasis.

PUBLICATIONS

Landolt, D., R. H. Muller, and C. W. Tobias, Crystallographic Factors in High-Rate Anodic Dissolution of Copper, J. Electrochem. Soc., 118: 36-40 (1971).

— —, R. H. Muller, and C. W. Tobias, Anode Potentials in High-Rate Dissolution of Copper, J. Electrochem., 118: 40-46 (1971).

— —, R. H. Muller, and C. W. Tobias, Transport Processes in ECM, in Fundamentals of Electrochemical Machining, C. L. Faust (Ed.), Electrochemical Society, 1971, p. 200.

Cooper, J., R. H. Muller, and C. W. Tobias, Periodic Phenomena in Copper Dissolution at Constant Current, in Fundamentals of Electrochemical Machining, C. L. Faust (Ed.), Electrochemical Society, 1971, p. 300.

03:455 SURFACE AND INTERFACE PROPERTIES IN HETEROGENEOUS SYSTEMS. Campbell, D. O., I. L. Thomas, J. P. McBride. (Oak Ridge National Laboratory, Chemical Technology Division).

This program seeks fundamental information on properties and reactions of solid–liquid and solid–gas interfaces. One current study is of the production of specific isotopes (e.g., of lanthanides or actinides) by (n,γ) reactions within molecular sieves, so that recoil moves product atoms to more accessible sites and permits selective elution. A second line of study is of the mechanisms of retention and release of volatile materials in metal oxides, and irradiation effects in solids containing sorbed or occluded volatile substances. A third line of study is of the generation and properties of colloids. A theoretical (computer) model of the interactions of similar colloidal particles has been extended to deal with different sizes and surface charges, and is being extended further to include the effects of external electric fields on the electrical double-layer barrier, and also to cover aerosols. The models will be tested against electrophoretic and other experimental measurements. Important contributions are expected to the technology of mixed concentrated sols, both for ceramic fuels and for nonnuclear applications.

Increasing attention is to be given to aspects of surfaces, particularly colloidal, that can be important in environmental problems, e.g., in investigations of the seemingly nonionic residues of radiostrontium, etc., in waste streams.

PUBLICATIONS

Thomas, I. L., and K. H. McCorkle, Theory of Oriented Flocculation, J. Colloid Interface Sci., 36: 110 (1971).

——, Method for Exchanging Counterions in Actinide Sols, U. S. Patent No. 3,629,138, Dec. 21, 1971.

Campbell, D. O., Isotopic Enrichment of Neutron Capture Product by Elution from a Faujasite Zeolite, Inorg. Nucl. Chem. Lett., 6: 103 (1970).

Smith, F. J., and N. A. Krohn, Electrophoretic Behavior of Thoria in Nitric Acid, J. Colloid Interface Sci., 37: 179 (1971).

03:456 ORGANIC COMPOUNDS IN NUCLEAR TECHNOLOGY.

Baldwin, W. H. and C. E. Higgins (Oak Ridge National Laboratory, Chemistry Division).

The continuing purpose of this program is the application of the materials and techniques of organic chemistry to chemical research and to nuclear and other technology.

Considerable effort is directed to support of the Transuranium Research Program, largely through preparation and study of organo-actinide compounds, including cyclopentadienides and adducts with cyclohexyl isocyanide. The stabilization of heptavalent neptunium in a (nonorganic) complex compound is covered elsewhere.

Because p-sexiphenyl is a scintillator that is needed for some research in the Health Physics Division, we are investigating new synthetic methods for it that may give a product that is more easily purified to the required degree.

The Chemical Technology Division requires a coolant for fuel-element-shipping casks that can withstand heat, radiation, and metallic sodium (residues from the reactor coolant). We have previously investigated biphenyl and diphenyl ether for thermal and radiation decomposition and are now exploring the effects of sodium on the stability of these materials.

PUBLICATION

Danford, M. D., J. H. Burns, C. E. Higgins, J. R. Stokely, Jr., and W. H. Baldwin, Preparation and Properties of Some Rare Earth and Americium Chelates, Inorg. Chem., 9: 1953 (1970).

03:457 ATOMIC COLLISIONS OF HEAVY IONS IN SOLIDS AND GASES.

Datz, S. (C. D. Moak, Physics Division, B. R. Appleton, and T. S. Noggle, Solid State Division). (Oak Ridge National Laboratory, Chemistry Division).

Collisions of multi-MeV heavy ions in gaseous and solid media are being studied in collaboration with members of the Solid State and Physics Divisions.

A remarkable specificity with target atoms for the creation of L subshell vacancies in 15- to 60-MeV I ions was observed; the ratio of $2p_{3/2}$ to $2p_{1/2}$ vacancies varied by a factor of 7 depending upon the collision partner ($Z_2 = 6$ to 82) and showed two maxima across the periodic table. A theory involving curve crossing of quasimolecular orbitals including fine structure predicts that only $2p_{1/2}$ electrons can be promoted by interaction of inner-shell atomic orbitals and should be strongly dependent on the collision partner. However, the qualitative behavior with Z_2 and the high cross section ($\sim 10^{-18}$ cm^2) for ionization of $2p_{1/2}$ or 2s is not yet explained.

Application was made to the states of ions as they penetrate matter. We observed that the L ionization cross section of the 150-MeV iodine was 10 times larger in a solid medium than in a gaseous medium (i.e., Se vs Kr, Br_2). This could be explained by the steady state population of M shell vacancies, which depends upon the collision frequency in the medium, these vacancies being necessary for quasimolecular promotion of iodine L shell electrons.

Interatomic potentials from high-energy heavy-ion channeling were further refined to give information at internuclear distances comparable to those of chemical bonds.

PUBLICATIONS

Datz, S., C. D. Moak, B. R. Appleton, and T. A. Carlson, Differentiation in L Subshell Vacancy Production in Iodine Ions by Atomic Collisions at 15–60 MeV, Phys. Rev. Lett., 27: 363 (1971).

——, F. W. Martin, C. D. Moak, B. R. Appleton, and L. B. Bridwell, Charge-Changing Collisions of Channeled Oxygen Ions in Gold, Radiat. Eff., 12: 163 (1972).

——, C. D. Moak, H. O. Lutz, L. C. Northcliffe, and L. B. Bridwell, Charge States of 15- to 140-MeV Bromine Ions and 15- to 162-MeV Iodine Ions in Solid and Gaseous Media, At. Data, 2: 273 (1971).

Lutz, H. O., J. Stein, S. Datz, and C. D. Moak, Collisional X-Ray Excitation in Solid and Gaseous Targets by Heavy Ion Bombardment, Phys. Rev. Lett., 28: 8 (1972).

Appleton, B. R., S. Datz, C. D. Moak, and M. T. Robinson, Energy Loss Spectra of Channeled Iodine and Oxygen Ions in Gold, Phys. Rev., B, 4: 1452 (1971).

03:458 ELECTROCHEMICAL KINETICS AND CORROSION.

Posey, F. A., E. J. Kelly, R. E. Meyer. (Oak Ridge National Laboratory, Chemistry Division).

The program of this group is concerned with fundamental physicochemical studies on the kinetics of interfacial and mass transport processes, with principal emphasis on the study of corrosion reactions of metals and of a variety of electrode systems having application to electrolytic treatment or electroanalysis of solutions. A potentiostatic perturbation technique for determination of the specific conductance of electrolytes has been successfully applied to aqueous electrolytes and molten salts. The method, inherently superior to AC-bridge methods, should be applicable to solid state electrolytes as well, and confirmatory measurements are planned. In a continuing investigation of titanium corrosion, the effect of pH on potentiostatic current–time transients in the microsecond time domain is being examined. Such measurements should allow determination of specific surface intermediates, which undergo oxidation during each step of the overall corrosion reaction sequence. Electroanalysis with porous electrodes has been shown to be a versatile and simple technique, and variants of the method are being investigated. In many cases, it is possible to carry out simultaneous separations and analyses. Present studies are concerned with analysis of two or more solution components and with effects of some of the more common interfering species present in municipal and industrial waters or process streams.

PUBLICATIONS

Meyer, R. E., M. C. Banta, P. M. Lantz, and F. A. Posey, Chronopotentiometry and Voltammetry of the Ag–AgCl Electrode in Flowing Streams. I. Experimental, J. Electroanal. Chem., 30: 345-358 (1971).

——, M. C. Banta, P. M. Lantz, and F. A. Posey, Rapid Batch and Continuous Electroanalysis for the Chloride Ion, Desalination, 9: 333-350 (1971).

Posey, F. A., and R. E. Meyer, Chronopotentiometry and Voltammetry of the Ag–AgCl Electrode in Flowing Streams. II. Theoretical, J. Electroanal. Chem., 30: 359-373 (1971).

03:459 MECHANISMS OF CORROSION OF METALS AND ALLOYS.

Bacarella, A. L. (Oak Ridge National Laboratory, Reactor Chemistry Division).

The primary purpose of this program is a determination of basic mechanisms of corrosion of metals and alloys. Our present studies are concerned with the corrosion of copper and copper–nickel alloys in NaCl solutions, at pH's ranging from 0 to 9, and temperatures from 25 to 200°C. Since copper–nickel alloys are used in saline environments and have potential usefulness in geothermal brines, an understanding of the corrosion mechanisms, particularly at high temperatures, is essential. Electrochemical studies have shown that anodic polarization curves for pure copper have Tafel slopes (dE/d log i) equal to 2.3 RT/F and that the reaction rate is limited by mass transport of $CuCl_2^-$ from the copper surface to the bulk solution. On the other hand, nickel does not form stable complexes with chloride ions and its anodic dissolution is activation-controlled; polarization curves have slopes of 2/3 (2.3 RT/F). It is therefore probable that the dissolution mechanism of copper–nickel alloys will be either activation- or diffusion-controlled depending on alloy composition, pH, chloride ion concentration, and temperature. Presently the anodic dissolution of copper–nickel alloys is being studied as a function of these variables.

03:460 DIFFUSION OF STRONGLY ADSORBED SPECIES IN POROUS MEDIA.

de Nordwall, H. J. (Oak Ridge National Laboratory, Reactor Chemistry Division).

This program seeks to describe the transport of strongly adsorbed vapors through porous media as functions of temperature, medium structure, and the interaction of medium and vapor. At the two extremes of vapor–solid interaction the process will resemble a grain boundary or surface diffusion process and transport of an unadsorbed gas, both relatively well understood.

Following an evaluation of current theoretical approaches, to be started in July 1973, an experimental program will be mounted using various graphites (including pyrolytic carbons) as media because of their interest to nuclear technology. At first, emphasis will be on measuring diffusion coefficients for cesium over very wide temperature ranges at concentrations low enough for Henry's Law to apply to discover whether predicted variations in the activation energy describing the overall transport process apply. This will be followed by later work at higher concentrations and with different species in the series iodine, xenon, cesium, barium, and cerium, which have widely varying affinities for carbon.

03:461 SURFACE CHEMISTRY. Holmes, H. F., E. L. Fuller, Jr., and P. A. Agron (Oak Ridge National Laboratory, Reactor Chemistry Division).

A definitive elucidation of the surface chemistry of important refractory oxides is the main objective of this program. Primary interest is the interaction of the surfaces of these oxides with the habitually present water (as vapor and liquid). Active projects directed toward this objective include gravimetric adsorption studies of zirconium oxide surfaces (using water, nitrogen, and argon as sorbates); calorimetric measurements of the heat of immersion of zirconium oxide in water at 25°C; calorimetric measurements of the heat of immersion of thorium oxide in water at temperatures up to, and including, 200°C; calorimetric measurements of the net differential heat of adsorption of water on sol–gel thorium oxide at 25 and 150°C; and infrared spectroscopic studies of water adsorbed on zirconium oxide surfaces. Although not all of these projects will be completed within the next year, definite plans have been formulated for the following projects in the immediate future: gravimetric studies of the adsorption of carbon dioxide on thorium oxide; an infrared spectroscopic study of the adsorption of water and carbon dioxide on thorium oxide; calorimetric measurements of the heat of immersion of zirconium oxide in water at temperatures up to, and including, 200°C; and calorimetric measurements of the net differential heat of adsorption of water on zirconium oxide.

PUBLICATIONS

Gammage, R. B., E. L. Fuller, Jr., and H. F. Holmes, Adsorption on Porous Thorium Oxide Modified by Water, J. Colloid Interface Sci., 38: 91 (1972).

Holmes, H. F., E. L. Fuller, Jr., and R. B. Gammage, Heats of Immersion in the Zirconium Oxide–Water System, J. Phys. Chem., 76: 1497 (1972).

Fuller, E. L., Jr., H. F. Holmes, R. B. Gammage, and K. Becker, Interaction of Gases with Lunar Materials: Preliminary Results, in Proceedings of the Second Lunar Science Conference, The MIT Press, Cambridge, Mass., Vol. 3, p. 2009, 1971.

03:462 MOLECULAR DYNAMICS. Malinauskas, A. P. and B. K. Annis (Oak Ridge National Laboratory, Reactor Chemistry Division).

The molecular dynamics program seeks in a broad sense to understand and describe phenomena associated with the macroscopic transport of matter and energy in gases in terms of mechanisms on the molecular level. Because these mechanisms can be profoundly altered by the presence of boundary surfaces, the studies necessarily likewise encompass investigations of the behavior of gases at solid or liquid interfaces.

Current attention is about equally divided between two main areas, one a primarily experimental program of research involving investigations of inelastic gas molecule collisions using data obtained from thermal transpiration measurements, and a second which is concerned with providing a generalized theoretical framework for the description of aerosol transport through an extension of the dusty gas model.

The thermal transpiration studies presently being pursued concern binary gas mixtures in the pressure transition region between free molecule and hydrodynamic flow, and with pure gases in the near-hydrodynamic limit. Both investigations have been undertaken to establish the adequacy of theory in describing the thermal transpiration phenomenon as applied to these two separate sets of conditions. An investigation of the feasibility of supplementing the inelastic collision data obtained from the thermal transpiration measurements with the data derived from light-scattering experiments has also been undertaken.

PUBLICATIONS

Annis, B. K., A. P. Malinauskas, and E. A. Mason, Theory of Drag on Neutral or Charged Aerosol Particles, Aerosol Sci., 3: 55 (1972).

— —, Stress Induced Diffusion in Monatomic Gases and Gas Suspensions, Phys. Fluids, 14: 269 (1971).

— —, and A. P. Malinauskas, Temperature Dependence of Rotational Collision Numbers from Thermal Transpiration, J. Chem. Phys., 54: 4763 (1971).

Malinauskas, A. P., and E. A. Mason, Heats of Transport of Ideal Gases and Gas Mixtures, Trans. Faraday Soc., 67: 2243 (1971).

______, J. W. Gooch, Jr., B. K. Annis, and R. E. Fuson, Rotational Collision Numbers of N_2, O_2, CO, and CO_2 from Thermal Transpiration Measurements, J. Chem. Phys., 53: 1317 (1970).

03:463 RESEARCH IN THE FIELD OF CATALYSIS. Turkevich, John (Princeton University, Department of Chemistry, Princeton, N. J. 08540).

The primary objective is the conversion of nuclear energy into chemical energy through the use of heterogeneous catalysts. Nuclear radiation, present in large quanta, is to be broken up into smaller quanta in the solid support of the catalyst. In turn, these quanta will produce electrons, holes, hydrogen atoms, active ions, and radicals that will transport the energy to active centers on the surface where the catalytic reaction is to take place. Silica of uniform pore size has been selected as the support. Either organometallic molecules, e.g., ferrocene, or small metallic particles of uniform size are chosen as the catalytically active agent. Hydrogen atoms in the support show promise as vehicles of energy transfer.

Two subsidiary objectives are also present in this research. First, attempts will be made to store nuclear energy in solids or on surfaces in the form of hydrogen atoms. Secondly, synthesis of small particles of uniform size will be pursued. It is postulated that the smaller the size, the greater the catalytic activity and presumably the greater the stability. Furthermore, since radioactive metallic particles are used in cancer therapy and diagnosis, any advances in producing uniform particles of controlled size may increase their effectiveness in medicine.

PUBLICATIONS

Turkevich, John, Yoshio Ono, and Javier Soria, Further Electron Spin Resonance Studies of Cu(II) in Linde Y Zeolite, J. Catal., 25: 44–54 (1972).

— —, Javier Soria, and Michel Che, Localization of Energy in Organic Molecules as Revealed by Dynamic Nuclear Polarization of Diphenylpicrylhydrazyl in Polystyrene, J. Chem. Phys., 56: 1463 (1972).

— —, and Yoshio Ono, Catalytic Activity and the Nature of Active Centers in Zeolites, Advan. Chem. Ser., No. 102, pp. 315–326, American Chemical Society, 1971.

— —, and Gwan Kim, Palladium: Preparation and Catalytic Properties of Particles of Uniform Size, Science, 169: 873 (1970).

Clarkson, R. B., and J. Turkevich, The Adsorption of Oxygen on Porous Vycor Glass by an EPR Technique, J. Colloid Interface Sci., 38: 165 (1972).

03:464 HIGH-ENERGY NUCLEAR INTERACTIONS WITH MATTER AND NUCLEAR PROCESSES IN NATURE. Schaeffer, Oliver A. (State University of New York at Stony Brook, Department of Earth and Space Sciences, Stony Brook, N. Y. 11790).

The main thrust of the research has been the study of accelerator- and cosmic-ray-proton-induced nuclear reactions especially those producing rare gas nuclides and long-lived radioactive nuclides. High-energy-proton production of stable and radioactive rare gases is being investigated from vanadium, barium, uranium, and iron targets. The results on the spallation of vanadium with protons have indicated that the Monte Carlo cascade calculations and experimental relative cross sections do not agree as well as previously supposed.

The production of ^{36}Cl and ^{14}C by cosmic rays is being studied. A new method for counting ^{36}Cl in the gas phase as methyl chloride has been successfully developed and is being applied to measurement of the ^{36}Cl proton production cross section from iron and nickel targets as well as a study of the depth variation of the cosmic-ray-produced ^{36}Cl in the El Taco meteorite. Cosmic-ray-produced ^{14}C found in tree rings is under investigation. It is planned to extend the previous study (which showed a short period variation in ^{14}C production during 1940 to 1970) to the period 1740 to 1770, before the industrial revolution.

Use of a laser beam to selectively vaporize small areas of samples enables the measurement of the rare gases. Work is in progress to detect helium isotopes in the various phases of meteorites to elucidate diffusional losses of cosmic-ray-produced tritium or ^{3}He during the lifetimes of certain meteoroids.

PUBLICATIONS

Kirsten, T., and O. A. Schaeffer, High Energy Interactions in Space, in Elementary Particle Research in Science and Technology, L. C. Yuan (Ed.), Academic Press, Inc., New York, 1971.

Baxter, M., and J. Funkhouser, Rare Gases in the Lost City and Suchy Dul Meteorites, J. Geophys. Res., 76: 4056–4060 (1971).

Hudis, J., T. Kirsten, R. W. Stoenner, and O. A. Schaeffer, Yields of Stable and Radioactive Rare-Gas Isotopes Formed by 3- and 29-GeV Proton Bombardment of Cu, Ag, Au and U, Phys. Rev., C, 1: 2019–2030 (1970).

Turekian, K. K., D. P. Kharkar, J. G. Funkhouser, and O. A. Schaeffer, An Evaluation of the Uranium–Helium Method of the Dating of Fossil Bones, Earth Planet. Sci. Lett., 7: 420-424 (1970).

03:465 IONIZATION PHENOMENA. Watson, R. L. (Texas A and M University, Cyclotron Institute, College Station, Texas 77843).

Investigations of inner shell ionization produced by heavy charged particle bombardment are currently being conducted. A major emphasis of this program is being directed toward the study of simultaneous K- plus L-shell ionization produced in fast collisions with deuterons, alpha particles, and carbon ions. In particular, a detailed examination of the K_β to K_α x-ray intensity ratios for x-ray emission produced in a wide range of elements by these incident projectiles is being carried out. By observing the variation of the K_β to K_α intensity ratio as a function of target thickness, the probability per K vacancy for simultaneous L-shell vacancy production can be estimated.

Another aspect of the program includes the measurement of K x-ray production cross sections for a variety of heavy ions up to and including Ar. Previous measurements with alpha particles and deuterons led to the discovery of significant deviations from the projectile Z dependence expected on the basis of the plane-wave Born approximation. The primary purpose of the present cross section measurements is to extend the Z dependence investigations to higher projectile atomic numbers.

In addition, a study of double K-shell ionization resulting from heavy ion–atom collisions is currently underway. These experiments involve the detection of K x-ray–K x-ray coincidences using two Si(Li) x-ray spectrometers. A high-resolution Bragg crystal spectrometer is presently under construction for the purpose of observing the hypersatellite peaks in the x-ray spectra arising from the radiative deexcitation of atoms having two initial K-shell vacancies.

PUBLICATIONS

Lewis, C. W., R. L. Watson, and J. B. Natowitz, Projectile Z Dependence of K X-Ray Emission Induced by Alpha Particles and Deuterons, Phys. Rev., A 5: 1773 (1972).

———, J. B. Natowitz, and R. L. Watson, Precise Test of the Z^2 Dependence of X-Ray Emission Induced by α Particles and Deuterons, Phys. Rev. Lett., 26: 481 (1971).

Watson, R. L., and T. K. Li, Energy Shifts Observed in Ni K X-Rays Produced by Fission Fragment Collisions, Phys. Rev., A 4: 132 (1971).

———, J. R. Sjurseth, and R. W. Howard, An Investigation of the Analytical Capabilities of X-Ray Emission Induced by High Energy Alpha Particles, Nucl. Instrum. Methods, 93: 69 (1971).

———, C. W. Lewis, and J. B. Natowitz, X-Ray Emission Induced by 30 to 80 MeV Alpha Particles, Nucl. Phys., A, 154: 561 (1970).

ALSO SEE Nuclear Spectroscopy: 03:2; Nuclear Reactions: 03:34, 03:36; Heavy Element Chemistry: 03:88; Radiation Chemistry: Gaseous; 03:119; Radiation Chemistry: Other; 03:166; Thermodynamics: 03:305, 03:320, 03:325; High-Temperature and Inorganic Chemistry: 03:347, 03:355; Structural Chemistry: 03:381; Analytical Chemistry: 03:404; Separations Chemistry: 03:420; Engineering Chemistry: 03:431, 03:438.

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