RESEARCH AND DEVELOPMENT IN PROGRESS
SUMMARIES OF THE USAEC BASIC RESEARCH PROGRAM IN CHEMISTRY

JANUARY 1973
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BASIC RESEARCH PROGRAM
IN CHEMISTRY

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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
Nuclear Spectroscopy

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


We are studying nuclear energy levels and transitions via electron, gamma, beta, and alpha spectroscopy; nucleus–atom–environment interactions and atomic properties and transitions. The following nuclear decay scheme analyses are underway: (data complete, reduction process will soon be started: $^{211}$Bi, $^{239}$Pa, $^{242}$Ra, $^{235}$Th, $^{239}$Pu, $^{241}$Am, $^{242}$Cf, $^{256}$Fm, and $^{19}$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 transuranic elements. We intend to remeasure some K 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 $^{146}$Pr) will be measured in $^{207}$Bi, $^{242}$Sm, $^{242}$Ra–$^{24}$Y, and $^{84}$Ni to complete our survey of this phenomenon (the study of the $^{146}$Prm spectrum has been completed). We are studying fast (10$^{-12}$-sec) ion recharging times on insulting oxide films on metals to determine the recharging mechanism. We will re-measure 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 $^{152}$Sm, $^{152}$Er, $^{99}$As, and $^{99}$Mo.

Publications


The University of Arkansas' 400-kV Cockroft–Walton Linear Accelerator is being extensively used for the production of new isotopes and isomers. Decay schemes of the newly identified radionucleides, as well as those that were not too well established previously, are being investigated using coincidence counting techniques. The cross sections for ($n$,p), ($n$,x1), ($n$,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 $^{241}$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 $^{241}$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


A study of the level densities and nuclear deformation is nearing completion in our laboratory. There is evidence for the existence of several new isotopes and isomers with half-lives ranging from milliseconds to seconds. Interesting effects have been observed, e.g., different rotational bands with different nuclear deformation and with different spins. An improved method for normalization of the level model energies to the liquid drop model is being developed.

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


The half-lives of most radionuclides up to about 5 to 10 years in general known with at least fair accuracy, but for many longer-lived radionuclides, e.g., $^{34}$Si, $^{191}$Ir, $^{199}$Ir, half-lives are poorly known, or unknown. Two of these, $^{85}$Sr and $^{199}$Ag, are of particular interest for dating and environmental studies.

High-precision methods for measuring long half-lives can be used to study the effects of chemical binding upon the half-life of a radionuclide. 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. The apparatus has also performed well in chemical–effects measurements. The instrument will be employed in a long-term program of measurements of the number of radioisotopes prepared at BKU 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.; Robinson, 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 or nuclear reactions, and with x-ray photodetection and Mössbauer spectroscopy.

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

PUBLICATIONS


03:6 ELECTRON EJECTION IN RADIOACTIVE DECAY

Robinison, W. (Brookhaven National Laboratory. Chemistry Department).

The act of nuclear transformation by radioactive decay or other processes constitutes a perturbation of the atomic electron, with consequent electron ejection from the atom. The probabilities of ejection of deep-shell electrons may 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 Brookha-ven and elsewhere for more than two decades, during which time a considerable amount of reasonably accurate data has been accumulated. Interest in the problem has continued 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 values 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


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 to determine the electric field gradients axes in the crystal and the quantitative estimation of the important exchange interactions between adjacent Fe spins, and to determine 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(NH3)62+ is under investigation, and exhibits strikingly magnetic hyperfine structure and a very low Debye temperature.

PUBLICATIONS


03:8 NUCLEAR SPECTROSCOPY. Bronner, D. 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 structure is less 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 involving 16Er, 17Er, and 18Er are currently being carried out. In most cases y-ray singles and coincidence spectra and conversion electron spectra are measured. Lifetimes of isomeric states are also under investigation.

PUBLICATIONS


03:9 AN EXPERIMENTAL STUDY OF NUCLEAR MODELS. I. DECAY SCHEMES AND NUCLEAR REACTIONS. II. MOONIC 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 the study of different types of nuclei. The first type is that of shell model nuclei. Studies will be performed on 89Sr, 90La, a series of Ce isotopes, 151Tb, 152Tb, and 153Tb. The second type is that of nuclei that lie in a transition region between spherical and well-deformed regions. A series of Ce nuclei, 152Eu, 153Eu, and 154Eu, 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 (p,2p) reaction. A new program using the facilities of LAMPF will be initiated in collaboration with LALS scientists. This program involves a study of nuclear structure using mononic x rays.

PUBLICATIONS


The use of ion beams heavier than the 4He or 16Ar 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 with mass number above 239U and in vibrations of the nuclear shell such as 181Pt. In the case of 239U 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^-8 to 10^-2 second range will be improved over what we have already achieved using 32Ar 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.


During the past 10 years heavy ion reactions induced by 1H, 2H, 3H, 4He, and other ions up to 22Ne have been used to produce new isotopes of the elements from Z = 76 to protactinium (Z = 96). 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 100 high spin levels have been characterized including many with half-lives in the millisecond time ranges. When using heavy ion 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 nuclei 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 above 100.

PUBLICATIONS


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 nuclear states in terms 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 should be useful in evaluating the synthesis of super-heavy elements by means of heavy-ion reactions. It is in fact possible to calculate the survival ratio of super-heavy 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


These studies involve experimental attempts to characterize the fission process. The stability of nuclei with respect to fission upon the nuclear deformation; this has an immediate application to the synthesis of super-heavy elements by means of heavy-ion reactions. It is in fact possible to calculate the survival ratio of super-heavy nuclei with respect to fission. These studies involve experimental attempts to characterize the fission process. The stability of nuclei with respect to fission upon the nuclear deformation; this has an immediate application to the synthesis of super-heavy elements by means of heavy-ion reactions. It is in fact possible to calculate the survival ratio of super-heavy 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


The availability of very heavy ions (Z > 80) 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 near future. The first is the nuclear Josephson effect, which is the predicted very large probability for transferring a pair of nucleons in the superfluid theory of heavy nuclei. The analogy is to the Josephson junction. 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 nuclei 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 above 100.

PUBLICATIONS


Our current program involves the study of radioactive decay of elements for which Z > 80 in order to determine the energies, intensities, and coincidence relationships of the emitted beta and gamma rays. Studies are also in progress to determine the half-lives, masses, and alpha-decay branching for highly neutron-deficient, uncharacterized isotopes of U, Pa, and Am. 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 nuclei 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 13Te to further characterize the 6-ns isomer located at 1797 keV in 131Te. Recent studies on the decay of 13Tin suggest this isomer may have spin and parity E^+g^+.

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 nuclei (A > 180) that have been previously un-
observed, as well as semi-theoretical calculations of the properties of unknown nuclides. The calculations have recently been extended to the nuclei hypothesized to exist in the region near $Z = 114$ and $N = 184$.

**PUBLICATIONS**


**03:16 A GENERAL NUCLEAR CHEMISTRY RESEARCH PROGRAM COMBINING CONVENTIONAL NUCLEAR SPECTROSCOPIC TECHNIQUES WITH ON-LINE SPECTROSCOPY AND NUCLEAR REACTIONS.** McHarris, Wm. C. and Berenthal, 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 nuclear system. The experimental techniques employed are primarily y-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 y-ray spectroscopic studies of nuclei near the $Z = 50$ and $N = 82$ closed shells; in-beam $(a,xn)$ and $(H,xn)$ spectroscopy of nuclei near the edge of the rare earth region of deformation; investigations of the structure of odd-odd nuclei by $(p,xn)$ studies of nuclei near and within the 20- and 26-nucleon shells; study of the radioactive decays of even-even neutron-deficient Pb isotopes; $(p,d)$, $(p,t)$, $\alpha$, and $\alpha$ direct reaction charged particle spectroscopy; study of anomalous EC/EC 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 $\beta^-$ 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 monitoring of environmental pollutants.

**PUBLICATIONS**


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 nuclei is of considerable interest. Several new prasendium and neodymium isotopes in the transition region have been identified and the level structures of these nuclei have been studied. The lower levels in the even-even isotopes $^{134}$Ce, populated by the decay of $^{134}$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-odd neutron and odd proton nuclei. We have found the low-level spin sequence of $^{134}$Pr, populated by $^{134}$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, $^{139}$Pr is of particular interest, because it is expected to populate a level structure analogous to that of $^{134}$Ce.

**PUBLICATIONS**


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

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

In the Coulomb excitation area we will continue to complete elaborate studies of the longer-lived and more abundant activities: $^{23}$Th, $^{235}$U, $^{238}$U, $^{239}$Pu, and $^{248}$Cm. Correlation of these results with the measured Coulomb excitation excitation probabilities should yield accurate hexadecapole moments.

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

By using the Doppler shift-plunger method, we will make accurate E2 lifetimes for several salient targets such as $^{238}$U, $^{239}$Pu, and $^{248}$Cm. Correlation of these results with the measured Coulomb excitation excitation probabilities should yield accurate hexadecapole moments.

Although we will utilize ORIC as the prime source of heavy ions below (Coulomb excitation) and above the barrier (reaction $\gamma$-ray spectroscopy) a host of new information on nuclear collective states can be obtained.

In the region of medium-weight, even-even, spherical nuclei we continue to examine the applicability of a vibrational treatment. Experiments on $^{233}$U 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**


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

This research program is concerned with experimentally deter-
mining the properties of light- and medium-mass nuclei using the Princeton University sector-focus cyclotron. Of special interest is the location and the properties of excited nuclear states with high angular momentum. Current nuclear models predict one limiting category of such 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 circuits. Multiparameter data are accumulated in a Sigma 2 computer. An electromagnetic isotope separator of radius 150 centimeters is used both to produce non-uniformly rare samples of short-lived radioisotopes and to implant radioisotopes in ferromagnetic media for perturbed gamma–gama gamma angular correlation studies. Presently, the electromagnetic isotope separator is being modified 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 spectrometer in the next year, we intend to supplement our studies of nuclei for high spin stability with high particle spectroscopy involving pick-up reactions such as (p,t) or (t,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 processes occurring during the capture of negative muons 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


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 transition mass range A = 150 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 nuclear level. 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 nuclear decay and beta decay by neutron-transfer reactions and radioactive decay spectroscopy, (b) an investigation of the Os level structure from the decays of 152Pd and 152Ir; (c) investigations of the level spectra of neutron-deficient, even–even Os nuclei in- in-beam experiments and by 200Sb and by radioactive decay; (d) characterization of a newly discovered 12- isomer of 151Au; (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


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 studying collective states in transitional nuclei, we have studied the low-lying structure of neutron-deficient nuclei with neutron numbers 84, 86, and 88. Both the in-beam x̃ny method and radioactive decay have been used to determine energy, spin, and parity of levels in 163, 164, 165, 166, and 167Gd. In the decay studies the odd-odd parent nuclei 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-transparent device of Watson will be used to obtain in-beam conversion-electron spectra from (x̃,x̃ny) 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


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 the principal goal is the understanding of nuclei with Z or N > 45, 46, or 47 in which the g, 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 y-decay properties of nuclear levels by selective excitation via in-beam nuclear reactions such as (p, x̃), (p, x̃), and (x̃, x̃), 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 y-ray, yγ, or py coincidence angular correlation techniques, and (c) measurements of internal conversion coefficients.

Extensive use of high-resolution Si(Li) particle and electron and Ge(Li) y-ray detectors is made in singles or in multiparameter coincidence arrangements. The structures of 42Ca, 43Ca, 44Ca, 45Ca, 46Ca, 47Ca, and 48Ca, together with 49Ti and 50Ti are currently being investigated.

PUBLICATIONS


03:26 
YALE HEAVY ION ACCELERATOR IN-HOUSE RESEARCH. Rasmussen, J. O. and Rezanka, F. (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 labora-

tories 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 the DECAMPERU computer. 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 in coincidence with reactions of (heavy ion, x̃) 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 99 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 a 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 an outside user of the Berkeley Super HI, we plan to carry out reaction experiments aimed at elucidating the nuclear shape effects, both static and dynamic, in collisions of heavy nuclei.

PUBLICATIONS


03:327 
HIGH ENERGY NUCLEAR CHEMISTRY. Steinberg, E. P.; Kaufman, S. B.; and Wilkins, D. B. (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 nuclear) reactions. Radiochemical and on-line counting techniques are employed and aliquot 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 conducting 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

NUCLEAR REACTIONS
Studies of nuclear structure by detection and analysis of collision processes between nuclei.
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 124Cf, (2) the 124Cp, 228Zn and 224Cp, 226Zn reactions from 1.5 to 11.5 GeV, and (3) the 28Mg(p, 2p) 26Na reaction from 3.0 to 11.5 GeV, (4) the 28Si(p, 2p, 3p) and (5) the 28Si(p, n) 28Si reaction from 15 to 11.5 GeV, and (5) the spallation reaction for the 124Cp, 228mn 228U reaction at 7.6 GeV are being prepared for publication. 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 fission nuclei. Further development of this idea is being actively pursued.

The origin of the so-called fragmentation products (A \approx 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 radioactive studies of fission-fragmentation. ditiuiosaeobandbmauig ilso but direct measurements of short-lived rare earth a emitters are also in progress since the measured yield of a given mass is 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 3 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 by 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.

Spectroscopy and radiochemical detection methods for radio-elevated solar neutrinos, particularly the Li 2(v, e-)Be system, are under intensive investigation.

PUBLICATIONS


03:30 FORMATION CROSS SECTIONS OF HIGH-ENERGY FISSION AND SPALLATION PRODUCTS. Friedlander, G., Chu, Y. Y., Cumming, J. B., Huds, 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 products are among the basic data needed for understanding of high-energy nuclear reactions, and a program of measurements of such cross sections has been in progress at NAL 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 emitters are also in progress since the measured yield of a given mass chain may have to be corrected for feeding or depletion by decay.

Measurements of spallation cross sections in a Cu target irradiated with 3.9-GeV 4N 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


03.31 COMPUTER SIMULATIONS OF HIGH- AND LOW-ENERGY NUCLEAR REACTIONS. Harp, G. D., Friedlander, G., Miller, J. M., and Miller, J. M., 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 (3,5) 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, p 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

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 4He are being extended to include irradiations by 3.9- and 2.1-GeV 16O ions. It is planned to do similar experiments with 200-GeV protons from NAL.

PUBLICATIONS

03.33 STUDIES OF HIGH-ENERGY NUCLEAR REACTIONS WITH COUNTER TECHNIQUES. Remsberg, I. P., Brookhaven National Laboratory, Chemistry Department.

The primary objective of this work is the characterization and elucidation of the 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. Particle telescopes are employed to determine the kinematic energy and 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

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 5- 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, 2p), (p, D), (p, 4He), etc., 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 nuclear 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

03.36 NUCLEAR CHEMISTRY RESEARCH. Sugarman, Nathan; and Turkovich, Richard (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 extraterrestrial 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, and fragment regions. The results 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 sequence of bombardments 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


03:37 THE MECHANISMS OF NUCLEAR REACTIONS


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 transformed from the incident to the target nucleus. It is anticipated that these studies will occupy us for the near future.

PUBLICATIONS


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 $^{132}$Te) at very acute angles (~20°) with respect to the fission axis 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 stringent 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 ions. Further studies are now underway to determine the proton-induced fission of $^{237}$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-heavy mass region and beyond.

PUBLICATIONS


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 86-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($^{7}$He, $^{11}$He)$^{4}$C and $^{16}$O($^{14}$He, $^{8}$He)$^{8}$Be have been used to study neutron-deficient nuclei and reactions like $^{58}$Mg($^{12}$C, $^{15}$C)$^{77}$P 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 and nuclear structure; furthermore, some of these studies permit fundamental investigations of the beta-decay process itself and its interaction with nuclear symmetry principles.

PUBLICATIONS


03:40 NUCLEAR REACTIONS WITH POLARIZED PROTONS AND NEUTRONS. Consett, 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 surpasses, 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 $^3$He scattering between 15 and 45 MeV. These measurements establish $^3$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.

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

PUBLICATIONS

HEAVY ION NUCLEAR REACTIONS. Harvey, B. G., and Hendrie, D. L. (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, 4He, and 4He ions) in the energy range of hundreds of MeV, and by carefully controlling the target nuclei, 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 that measure their total energy, rate-of-energy loss, and time-of-flight. 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.

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 heavy targets will be bombarded at the SuperHILAC and at CERN by radioactive beams. In addition to investigations stimulated by radiochemical separation and measurement techniques with the purpose of identifying and measurement of the yield of radioactive products with half-lives of a few minutes or less. 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-nuclear formation, cluster-transfer, spallation, and fission.

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

The continuing programme 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 $A^{-1}$ (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 relevant to the comparison of these models 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 actual cases when suitable data is available, this model is applied 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-Dirac formalism. 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 high-energy 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.

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PUBLICATIONS


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 nuclear and charged 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 include highly excited nuclei 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

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


03:45 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, the nature of the compound nucleus to form because the centrifugal force is too great. Even with impact parameters corresponding to some what smaller amounts of angular momentum which 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- and out-of-beam from a target of 209Bi irradiated by 70MeV 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 polarization of the incident beam, we can attempt 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 separate out fraction of the cross section due 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 Morettto, 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; 6) influence of angular momentum on fission probabilities—involved also in heavy ion reaction studies; 6) fission fragment angular distributions (from aligned nuclei) provides information on the configuration states involved when nuclei undergo fission and may also give information about the pairing gap at the saddle point; and 7) studies of nuclear viscosity and inertias as available from fission phenomena (also involved in heavy-ion reaction studies).

PUBLICATIONS


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. The key to an 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 with the system being still unstable toward fission; and 4) compound nucleus formation. It is the aim of this project to understand the general dynamic features of the phenomena under study and to attempt 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 electromagnetic 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 those 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 FISSION 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).

This project is concerned with the study of the energization of nuclear fission by heavy-ion reactions. By means of the use of energy-jet 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 4He ions. These studies include (1) total reaction cross section and elastic scattering measurements, from which nucleon-nucleon reaction parameters are derived; (2) fission fragment angular correlation measurements, which permit the separation of compound nucleus from direct processes; and (3) fragment angular distributions, fission measurements, and 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 (Me, xn) and (Me, xn) reactions, where x is in the range 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 nuclear fragment y 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 fission induced by charged particles from the cyclotron; and (2) by observing fission products collected in foils placed against a 252Cf source, we will measure ranges for various mass chains to search for fine structure of kinetic energy release previously suggested in the vicinity of the double-closed-shell products of mass A ~ 132.

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

PUBLICATIONS


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 that interesting features seem to be associated with the deformability of the fragments. We are measuring prompt neutron emission in the fission of 209Bi 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 new way which has been shown to be reasonably applicable. We plan to measure the average total kinetic energy of fragments from the fission of...
NUCLEAR REACTIONS

$^{249}$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 super-heavy elements would again be lower.

PUBLICATIONS


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 nuclear reactions that are of importance to an atomic energy program. These rates are of importance in fission reactors and in fission devices, so that the energies covered range from thermal to thermonuclear. Although heavy element and fission product nuclei are of special interest to this program, the emphasis is on the use of light and medium elements. The program is designed to study reactions of interest as a function of energy but requires much larger samples. In cases where 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


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 in 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 experiment 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.

In addition, we 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.

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 spectrometer attached to the reaction target. Some of these recoils are being used to produce mono- and carbon ions recoiling from extremely thin targets. In this way the primary radiation of Ions is being sought as it arises from nuclear 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: charge exchange, recoil shakeoff, and a kind of non-adiabatic coulomb disruption of the electron cloud by the incident and emitted particles.

PUBLICATIONS


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 $^{93}$U to $^{49}$Ca. The very low fission cross sections of the compound nucleus are sharply enriched with energy, 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 element, the ternary fission cross sections are observed to increase in the microfission range. If the 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 $^{16}$O ions. A fraction of the ternary products recoils out of the target and are trapped on collecting foils, and then radiochemically separated and counted. The bombarding ions are being carried out at various angles with respect to the target. The experiment is in an attempt to look at angular correlations and fission anisotropy as well as to discriminate between spallation and ternary fission.

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 differentiated.

PUBLICATIONS


Dewanjee, M. K., and Preiss, I. L., Decay of Samarium Isotopes: to develop a model based on a Thomas-Fermi approach whereby specific shape in the residual nucleus. Many other areas of nuclear reaction models; and indeed other determine whether a specific reaction mechanism may favor a of these phenomena. Such models will be very useful in treating ability of isomerism due to a change in nuclear shape presents an important problem. Our main thrust has been in the develop- and to ascertain whether.

Mass regions to determine the magnitude of deformation for Se, The question of the equilibration process in nuclear reactions, while that of $^{154}$Pm indicates a deformation 30% larger than EQUILIBRATION MODELS. Blann, M. (University of Rochester, Troy, New York 12181).

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

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

03:56 NUCLEAR STRUCTURE STUDIES. Preiss, Norbert T. (Purdue University, Department of Chemistry, Lafayette, Indiana 47907).

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 photoneutron reactions of $^{58}$Ni between 40 and 100 MeV exhibit a characteristic 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 $^{188}$Au, $^{190}$Au, $^{192}$Au, and $^{193}$Pm. The isomerism in the case of Au suggests that a nucleus, while that of $^{193}$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 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 when specific reaction mechanisms 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: $^{151}$Sm, $^{153}$Sm, $^{155}$Sm, and $^{157}$Sm, J. Inorg. Nucl. Chem., 34: 1105 (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 majority of nuclear reactions in the region of highly overlapping levels. Of immediate interest is the study of (a) (α,n) 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 a number of different 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
PUBLICATIONS


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).

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

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

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

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


ALSO SEE Nuclear Spectroscopy: 03:9, 03:11, 03:15, 03:16, 03:23, 03:26; Heavy Element Chemistry: 03:68, 03:79, 03:72, 03:74, 03:77, 03:81, 03:84, 03:89, 03:90, 03:95, 03:97, 03:99; Hol 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.

03:05 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$_4$:H$_2$O are being investigated at low temperature and high resolution. Er$^{3+}$ 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 U$^{3+}$ 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 systems are in progress and we will extend into 1973 and 1974: Cm$^{3+}$ (aq), BaCm, CfCm, SmCf, crystal matrixes, SkBr$_2$. 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 electron configuration interaction for a heavy ion, Pa$^{5+}$ (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 some of these determined parametrically lends strong support to the mode of approach we have taken. Further calculations in the actinide range are planned.

PUBLICATIONS


03:66 THEORETICAL STUDIES OF NUCLEAR STRUCTURE IN THE HEAVY ELEMENTS. Chairman, R. R. (Argonne National Laboratory, Chemistry Division.)

The purpose of this research program is to develop a good theoretical description of deformed nuclei, 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 nuclear 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


Braid, T. H., Chasan, R. R., Erskine, J. R., and Friedman, A. M., (d,p) and (d,t) Studies of the Actinides. II. $^{252}$Cm, $^{262}$Cm, $^{262}$Cm, and $^{262}$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 $^{7}$Pb.Fm. This nuclide decays predominantly (99%) by electron capture. Because of the expected high spin $^{7}$Fm for the $^{7}$Fm ground state, electron capture decay selectively populates the high-spin states in $^{7}$Fm. We have identified the $^{7}$Fm(514) and $^{7}$Fm(624) proton states in $^{7}$Fm. 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 $^{7}$Fm is being investigated with the help of an alpha magnetic spectrometer and a high-resolution gamma detector. We have already identified the $^{7}$Fm(622) and $^{7}$Fm(734) single-neutron states in $^{7}$Fm.

We recently completed the decay scheme of $^{36}$Am and identified several electric monopole (E0) transitions in $^{36}$Pu. With the aid of this information several 0$^+$ and 1$^-$ states in $^{36}$Pu were identified. The 0$^+$ states are of special interest to nuclear physicists because so far they are not well understood. These 0$^+$ states are also populated in (p,$\alpha$) reactions on actinide targets. No plan has yet been made to investigate the decay scheme of other low-spin odd-odd nuclides (like 2.1-h $^{36}$Es) and measure the rotational constants and B(E2)/B(E1) ratios for the 0$^+$ bands. This information will aid us in a better understanding of nuclear structure.
Dunlap, B. D., Shenoy, G. K., Kalvius, G. M., Cohen, D., and Bloomquist, C. A. A. (Argonne National Laboratory, Chemistry Division.)

This program, in which cross sections, excitation functions, the products of nuclear reactions, and fission are studied, is also included at producing elements 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 films 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 $^{239}$Cf, $^{240}$Cm, and $^{241}$Cf with $^4$He and $^3$He are in progress. We have started the measurement of electron binding energies in Am. Alpha groups associated with $^{250}$Fm decay will be investigated. Major emphasis in 1975-76 will be given to heavy-ion reactions such as stripping, transfer reactions, compound nucleus formation, and fission using the Berkeley SuperHILAC. 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


CHEMISTRY OF THE HEAVIER ACTINIDES. Fields, P. R.; Fried, S.; Carnall, W. T.; Cohen, D.; Barness, 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 transuranic 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 and Cf and make it possible to deduce general trends in electronic structure in the transuranic 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 fluoride or Cl and I are also under investigation. Solution absorption spectra of Bk and Cl are being studied in acid and basic, particularly in carbonate, solutions, in conjunction with an investigation of oxida-tion-reduction reactions.

PUBLICATIONS


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 neutrons that could be used to do this are not 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 high-energy neutrons. However, the available 28-GeV protons, secondary products as heavy as 241Cl were observed to be produced. The effective cross sections for producing heavier elements are unfortunately so low as to prove impractical using existing cyclotron 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. R.; Erskine, J. R., 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 energy loss and momentum effects. The objective of such measurements is to understand the importance of relevant parameters in the reaction process. A more practical objective is to provide information required for the elucidation of the fission reaction mechanism for heavy elements. These studies include the distributions of mass, nuclear charge, and kinetic energy of the fission fragments; and angular by an outer-sphere mechanism. Such reactions are significant for the development of optical spectroscopy and is now being used to study the behavior of actinide nuclei.

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 Division.)

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. This apparatus is sensitive to radioactivity and can cope with large quantities of radioactive material needed for the development of new detection methods. The apparatus is sensitive to radioactivity and can cope with large quantities of radioactive material needed for the development of new detection methods.

PUBLICATIONS


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 actinide elements provides important information about 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

\[ \text{Ru(NH}_3\text{)}^2+ + \text{Ni(III)} = \text{Ru(NH}_3\text{)}^+ + \text{Ni(II)} \]

and the kinetic study of the reaction

\[ 2\text{Pd(VII)} + \text{Fe(II)} = 2\text{Pd(IV)} + \text{Fe(III)} \]

The reactions (1) and (2) are the first studies of a reduction reaction with the neptunium ion 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 of the neptunium ion with a reductant via an outer-sphere path. Comparison with such kinetic parameters obtained in the well-documented Fe(II) oxidation should contribute to a theoretical understanding of the process.
Small traces of $^{244}$Pu may occur in natural material, either as residual amounts of primordial $^{244}$Pu (half-life $8.3 \times 10^7$ years) or 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 $2 \times 10^3$ atoms of $^{244}$Pu using the KAP three-stage (tunable 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

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 integrated into the development of models of 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$_x$[II], U$^+$, Np$^+$, and Pu$^+$ 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 bonding predominating in these complexes. Syngetic 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 90, the 5f electrons become more localized. With the present availability of milligram quantities of the heavy actinides through Cf has been initiated. X-ray crystallographic studies and magnetic susceptibility measurements from 2 to 300°K will be made on these specimens. It is hoped this information will provide a better understanding of the bonding properties of the actinide metals.

PUBLICATIONS

03:79 MASS SPECTROMETRIC SEARCH FOR $^{244}$Pu IN NATURE.

Mewherter, J. L.; and Rourke, F. M. (Knolls Atomic Power Laboratory.)
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 this apparatus is to separate the 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 elements with production cross-sections of heavy-ion reactions.

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 $^{100}$Ge with $^{208}$Pb), 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 the arrival time and $y$-position of the event within a couple of nanoseconds, and an approximate value of its $dE/dx$ 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 field 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 rigidity. 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.** Ghiorgo, A.; Nurima, 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 most stable 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 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 Berkeley 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 HEAVIER 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 eigenvalues of the density matrix are very large on collective excited states should be populated with greater probability than in transfer reactions involving light nuclei that have been most intensively studied in the past. It might be thought that quantum mechanical 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 effective. However, these effects are of no importance 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 region melts 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.

**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 $^{250}$Fm is used will be continued. Measurements of the prompt radiations, c.k.s., neutrons, $\gamma$ 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 $\gamma$ 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 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 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., $\alpha$ particles, are emitted. Such data will 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 correlations can be discovered by studying these phenomena, it may also 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, $\gamma$, emitted per fission event.

**PUBLICATIONS**


**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-ion beams will be available at the Super-HILAC. 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. 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 "splitback" 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 evaporations 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 charged particles. These processes can also be described as a function of excitation energy and angular momentum, and they provide valuable data concerning the static and dynamic properties of nuclear matter.
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 investigations on electronic, magnetic, and optical properties, and the effects of radiation damage and ion implantation on these materials.

PUBLICATIONS


03:89 NUCLEAR STRUCTURE STUDIES IN THE HEAVY ELEMENT REGION. 


03:89 NUCLEAR STRUCTURE STUDIES IN THE HEAVY ELEMENT REGION. 


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 various complex reactions are being measured for the ions $^{12}$C, $^{13}$N, $^{16}$O, and $^{23}$Ne. The excitation functions, energies, and angular distributions of the light-ion products (i.e., $^4$He, $^7$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 $^{252}$Cf nuclei produced in the reactions $^{244}$U($^4$He,5n) and $^{252}$Pu($^4$He,2n) are being determined by alpha counting of collected recoils.

These studies will be extended to other heavy element targets, e.g., $^{238}$Pu and $^{241}$Am, and to more complex projectiles (Ne to Ar). For this, improvements in the ORIC ion source will be necessary, so that heavier ion beams will have sufficient energy to penetrate the Coulomb barrier.

03:91 SEARCH FOR SUPER-HEAVY ELEMENTS BY NEUTRON MULTIPLICITY COUNTING. Halperin, J., Stoughton, H. W. and Schoech, R. E. (Oak Ridge National Laboratory, Chemistry Division.) An unexpected stability has recently been predicted for nuclei 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 $f$ is calculated to be very high ($f \approx 10$), we have assembled a neutron multiplicity counter to search for such nuclei. The counter accepts samples of about $50$ kg and has a sensitivity of about 1 spontaneous fission (of $f \approx 10$) 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 $\gamma$ 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 available to provide heavy-ion beams of adequate energy and intensity to test the possibility of synthesizing such super-heavy nuclei.

PUBLICATIONS


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. Thus leading to a large class of actinide compounds, that enter into the calculation of binding energies from first principles, and the second is the behavior of the 5f electrons with chemical bonding.

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


03:93 PHYSICAL CHEMISTRY OF THE ACTINIDE ELEMENTS. Nugent, L. J. (K. L. Vander Sluis, Physics Division). In the actinide region, it is impossible to observe 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 element (californium dibromide and americium diclode), 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


03:94 SOLID STATE AND SOLUTION CHEMISTRY OF THE TRANSURANIUM ELEMENTS. Peterson, J. R. (Consultant from University of Tennessee), Burns, J. B., 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 molten 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 1960's. We have worked out a crystal-growing technique to obtain single crystals of compounds such as LiCo$_4$NpH$_8$Np$_2$O$_4$OH$_2$·2H$_2$O which we have studied by x-ray diffraction to contain the square planar NpO$_4$ ion. This suggests that NpO$_4$(OH)$_2$ may occur in strongly alkaline solution, and we are planning to examine its structure spectroscopically. We also plan to see whether fluoride can be substituted for oxygen while maintaining the neptunium in the VII state.
PUBLICATIONS


03.05 SEARCH FOR NEW TRANSURANIUM ELEMENTS AND ISOTOPES. Silva, R. J.; Bemis, C. E. Jr.; Dittmer, P. F.; Etcholler, F.; 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 predictions 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 “G310 reaction. Because of the half-lives (milliseconds) 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 measurements of 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 (202,203No), is being applied to element-106 (206,207No). 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 nuclei 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 255No (T 1/2 54 minutes).

PUBLICATIONS


03.06 CHEMICAL STUDIES OF ACCELERATOR-PRODUCED ELEMENTS IN THE ACTINIDE, TRANSACTINIDE, AND SUPER-HEAVY 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 in the calculations 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 to begin to be studying the heaviest elements available, namely those in the range of 202 through 105. These elements are important in themselves because they are now seen at 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 in now nearing completion for the first aqueous chemical separation of element-105 (T 1/2 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 290. Since element-103 has its predicted beta half-life, these experiments are looking at a point where the chemistry should change drastically with a change of one in atomic number.

PUBLICATIONS


03.07 STUDIES OF LOW-ENERGY-INDUCED NUCLEAR FISSION. Loveland, Walter D. (Oregon State University, Chemistry Division). (Oak Ridge National Laboratory, Chemistry Division.)

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 system mass dissociation.

(b) Measurements of the neutron angular momentum in 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 dependence 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 252Cf (n, f). Isomer ratio measurements and fragment γ-ray angular correlations are used to study fragment angular momentum. Current studies of the fissile energy balance involve measurement of γ-ray-energy release in 252Cf (n, f). Research on unusual aspects of fission such as short-range 4- and 5-fission fission being carried out as well as studies of the nuclear structure of fragments near A = 132.

PUBLICATIONS


03.08 "SPECTROSCOPIC STUDIES OF ACTINIDE IONS IN CRYSTALLINE SOLIDS". Gruber, John B. (Washington State University, Department of Chemistry.)

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-ions 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 give unique 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 flashlamp techniques.

PUBLICATIONS

RADIATION CHEMISTRY: AQUEOUS


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 ~10⁻⁹ sec) spontaneously fissioning products of heavy-ion reactions. Heavy targets (²⁵²⁴B₁, ²³⁵¹U) will be bombarded with heavy ions (²⁵²⁴B₁, ²³⁵¹U, ²³⁵³U) 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 inorganic gas atoms will escape into an evacuated space lined with plastic and/or mica windows, 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 deuterium oxide track detectors, which are used 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 Hydrogen Atom, and the Radicals so formed lead to the products

\[
\begin{align*}
A + BH & \rightarrow AH + BH^- \quad \text{or} \quad B + BH_2 \\
A + BH & \rightarrow AH + BH^- + HBB + HBB + HAAH, \text{etc.}
\end{align*}
\]

We have shown that mercaptans can act alone or as the mercaptanyl 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.

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 Millor, J.: (Argonne National Laboratory, Chemistry Division).

The primary processes taking place in irradiated water and the reactions of hydrated electrons (e₁), H atoms, and OH radicals are being investigated by pulse radiation techniques. The pulse length of our new high-current, L-Band (1300 MHz) Linac has been increased from about 1 x 10⁻¹² sec to near 50 x 10⁻¹² sec by the recent installation of a new prebuncher. This single 50-picosecond pulse delivers a dose of 5 to 3 kilorads. Reactions of 50-picosecond 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(e₁) is presently reported as ranging from 3.4 to 5.0. The absolute value of G(e₁) as well as the decay rate of e₁ at subnanosecond time intervals will provide information regarding "spur" size and e₁ distribution. Our pulse radiolysis studies will also be used to study pre-hydration reactions of e₁.

Studied involving subexcitation electron, e₁, OH-, and H₂O₂ reactions with scavengers at high concentrations, such as those in living cells, are under investigation. Other pulse radiolysis studies utilizing standard spectrophotometric and conductometric techniques, and γ irradiation will continue on aqueous oxygen and methanol solutions. The excitation of BH⁺[N⁺]₃, Ru(bipyridyl)³⁺, and electron tunnelling in aqueous glasses and other inorganic and organic ions are also being studied along with enzymatic reactions of tritiated water and chemiluminescent reactions of e₁.

PUBLICATIONS


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 photolysis- 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

\[
\begin{align*}
A + BH & \rightarrow AH + BH^- \quad \text{or} \quad B + BH_2 \\
A + BH & \rightarrow AH + BH^- + HBB + HBB + HAAH, \text{etc.}
\end{align*}
\]

We have shown that mercaptans may act alone or as the mercaptanyl 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

\[
\begin{align*}
\text{CH}_3\text{C} &= \text{O-CH}_3 \\
\text{H} &= \text{HO}^- \\
\text{CH}_3\text{C} &= \text{O-CH}_3
\end{align*}
\]

reductive cleavage. Extension of this to polymersic 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 mercaptan solutions. 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.
The thymine has been replaced by bromouracil are very similar to developed to examine the reaction kinetics of radical intermediates. The results obtained for a solution of DNA in which all uracil. It is known from molecular studies that electron transfer on bromouracil causes dissociation of radicals react rapidly with DNA to form radicals. The subsequent reactions of these DNA radicals are being explored. Two of the main initial stable product then is CNO, though more complicated products can be formed such as CNO2 and CNO3. The free lactate radical is found to bring about conversion of the reduced form NADH to NAD+ in the presence of molecular oxygen.

**PUBLICATION**


**03.102 RADIATION CHEMISTRY OF CYANIDE ION.** Allen, A. O. and Bielski, E. 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 addition 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 y rays in the absence of oxygen yields a variety of products: NH2, CO2, CN-, CNO-, CH2O, HCO-, 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 NO2 converts the solvated electrons to OH radicals and simplifies the chemistry; the main initial stable product then is CN-, though more complicated products can be built 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).

Enzymatic 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) system, after the substrate (H2O2) was formed during 10-μsec pulse. A new transient absorbing light at 370 μm was discovered by this technique. Subsequently this transient was also seen in flow experiments when H2O2 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 acid 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 (NADH). The free lactate radical is found to bring about conversion of the reduced form NADH to NAD+ in the presence of molecular oxygen.

**PUBLICATION**


**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 reduction. The electron on bromouracil causes disassociation 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 Chava, 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 pulse radiolysis experiments are being carried out where profitable. Direct observation of the radical intermediates is precluded as it has been possible with SO2, PO1, HPO2, and several other radicals that can be formed both from radiolytically produced OH and photolytically produced radicals. When such direct observation is not possible, radical trapping with CH3NO2 is used to convert the radicals (H) to a more readily observed form (CH3N2O2). A large number of radicals, including the interesting (210) formed from NO2, have been studied in this way. Other studies include those of the peroxy radicals formed from transition metal–H20 complexes and the reactions of CN and HCN in irradiated solutions. Extensions of these studies are in progress.

**PUBLICATIONS**


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 identities for those studying related systems by other means such as pulse radiolysis. Examples are the reactions of e0 with H nitrites to form RC=NR and with oleic 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 been used to provide evidence for structural studies by means of 13C hyperfine splittings both in enriched compounds and at the natural abundance level.

**PUBLICATIONS**


**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 rates of radioactive 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 experiments 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**


---. 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 radiation chemistry of systems 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 these systems and have led to the determination of amino acids and peptides with $\epsilon_0^+$ (causing deamination), with H and OH (resulting in H abstraction from CH$_2$), and with O$^-$ (abstracting H from NH$_2$ also). Pyrimidine bases have been found to add OH or add radiation to either position 5 or 6. The initial adducts undergo consequent changes, which in the latter cases 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- or chloro- and chloro- and chloro-uracils 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 pyrimidine derivatives, including NAD$^+$, are currently being studied by ESR.

---. 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 usec and longer has been introduced with a PDP-8/B computer 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 ES$^+$ 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-bromouracils 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 Scanning 2000 channel sample and hold unit. Many different types of systems are being examined with emphasis being placed on studies involving the nature and radiation kinetics of intermediates produced by -OH and $\epsilon_0^+$- reactions.

---. RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS OF ORGANIC HALIDES. Schuler, R. H. (Carnegie-Mellon University, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213). Reaction of selective electron spin resonance 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 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 $\epsilon_0^+$ to produce a Cl$^-$ ion within microseconds and that CF$_3$Cl undergoes a similar reaction followed by hydrolysis of the CF$_2$ radical on a time scale longer than milliseconds. Reaction of $\epsilon_0^+$ with CF$_3$COOH initially produces the radical -CF$_2$COOH 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.
RADIATION CHEMISTRY: AQUEOUS

PUBLICATIONS


Farhataziz, and E. M. Hansen, Diffusion-Controlled Reactions of Amino Acids and Peptides, 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 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 quantitatively measurable on the submicromolar level. For example, studies of the radiolysis of 10⁻⁷ M solutions of p-bromophenol can be readily carried out at dose levels of ~100 rad. It has been shown that in this system reaction of the hydrated electron 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 reaction-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.

A 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 labeled organonitrogen 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


Farhataziz, and E. M. Hansen, Diffusion-Controlled Reactions of Amino Acids and Peptides, Radiation Research Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213.


The objective of this work is to test the dry electron model for the radiolysis of water by observations at times >10⁻⁶ s to support the hypothesis that this process is applicable to times >10⁻⁶ s. The primary species are considered to be H₂O⁺, H₂O₂, and OH, which are then reacted further. Alcoholic systems are rather analogous. High concentrations of anions are used to transfer an electron to H₂O⁻ before hydration, and this forms a source of hydrated electron, eaq., which is then supported by experimental evidence as follows. The yield of Cl⁻ in 1M NaCl is increased at 5 × 10⁻⁶ s in solutions to which N₂O has been added. We interpret this as indicating a reaction of Cl⁻, which has H₂O as precursor, and the observed yield is G ≈ 1. At concentrations of N₂O, hydration of Br⁻ is found at 10⁻⁴ s, indicating that the organonitrogen compounds are formed in very small yields. Since the spurious reaction is decreased in the alkane, it can be taken as an indication of the increase in spurious size brought about by the efficient positive hole migration in the solid state. This hypothesis will be investigated more fully. Further effort is required to substantiate the existence of H₂O⁺.

PUBLICATIONS


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 obtained 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 of an electron in water and provide evidence for compressibility of the cavity. A similar study of H atom reactions in water that 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 solution.

PUBLICATIONS


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 polyacrylamide, 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 hydrogen, oxygen or hydrocarbon radicals. In the high intensities of exciting light available in these laser photolysis studies, a significant photoinitiation 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 ions 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 spurs (the region of concentrated energy deposition) when 60Co 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 reaction 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 \( G_{\text{OH}} \) and \( G_{\text{SO}} \). \( G_{\text{OH}} \) is proportional to the electron fraction of water. The high values for \( G_{\text{NO}} \) and \( G_{\text{SO}} \) 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 \( G_{\text{NO}} \), \( G_{\text{CO}} \), \( G_{\text{OH}} \), and \( G_{\text{SO}} \); as a function of nitric acid concentration. Concomitant studies in the photochemistry 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


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 ex-plosion 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 rate of reaction on aerosol formations in \( \text{SO}_2 \) and organically polluted atmospheres is now under study. The chemical factors will be investigated by studying the effect of the primary pollutants (\( \text{SO}_2 \), \( \text{NO}_x \), \( \text{NO}_y \), \( \text{CO} \), \( \text{CH}_4 \), 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.
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
each of the stable ions. The principle advantage of this method is
that it allows the measurement of absorption changes as small as
one part in 10^6 and requires a much smaller number of pulses.

PUBLICATIONS

03:121 ELECTRON REACTIONS IN THE GAS PHASE. Foss-
senden, R. W. (Carnegie-Mellon University, Radiation Research
Laboratories, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213).
A microionization 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 gen-
erally found for halides. The wide range of attachment rates is
reflected by the rate constants for CF_3 (10^10) and cyclo-C_4F_4
(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 perfluoropropane which show a tran-
sition from three- to two-body behavior as a function of added
buffer gas.

PUBLICATIONS

Warnam, John M., Krishan M. Bansal, and Richard W. Fessenden,
On the Pressure Dependence of Electron Attachment to O_2,
Fessenden, Richard W., and Krishan M. Bansal, Direct Observation
of Electron Disappearance in Pulse Irradiated Fluorocarbon

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 forma-
tion of the observed stable products in the radiolysis of simple
cellular systems. An additional goal is the investigation of the
relationship between the decomposition mechanism of chemical
species generated by gamma ray 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 (es-
pecially perfluorocarbon) 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
ethene and hexafluorohrane, and the rare-gas-sensitized decom-
position of perfluorocarbons, using He and Ar metastable atoms
generated in a glow discharge. Further studies are concerned
with the gamma radiolysis of gaseous perfluorocyclobutane, 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 under-
take studies of the vacuum ultraviolet photochemistry of fluoro-
carbons and of fluorocarbon-hydrocarbon mixtures in the near
future.

PUBLICATIONS

Marcotte, R. E., and R. J. Hanrahan, Fast Flow Microwave Dis-
charge Studies of the System CF_3-CCL_3, J. Fluorine Chem.,
1: 57 (1972).
Donovan, James, and Robert J. Hanrahan, The Radiation Chem-
Buchanan, J. W., and R. J. Hanrahan, A Comparative Study of the
Gas Phase Radiation Chemistry of Phosphine and Ammonia,

03:123 THE RADIOLYSIS OF WATER IN A WIDE-RANGE
RADIOLYSIS SOURCE. Melton, Charles E. (University of,
Georgia, Chemistry Department, Athens, Georgia 30601).
Despite the fact that much chemical information has been obtained
by the interaction of ionizing radiation with a system. The present research
program was initiated to obtain detailed experimental and theo-
retical results that would provide a basis for understanding these
radiation-induced changes. The experimental technique for study-
ing 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 in creating homogeneous 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 inter-
molecular distance of 1.2 Å. Future studies will involve the
subsequent reactions of OH^-H_2O with H_2O to form OH^-H_2O
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 de-
terminate the effect on the negative ion complexes.

The second stage of future work will involve a study of the
charge neutralization reactions of the type H_2O^- + e^- products.

PUBLICATIONS

Melton, Charles E., Radiolysis of Water Vapor in a Wide Range
Radiolysis Source of a Mass Spectrometer. 1. Individual and
Total Cross Sections for the Production of Positive Ions, Neg-
ative Ions, and Free Radicals by Electrons. J. Phys. Chem.,
_____, Molecular Theory of Energy Conversion and of Initiation
_____, and George A. Neece, Rate Constants and Cross Sections
W. Massay, and B. N. Abels. The Isotopic Abundance
_____, and George A. Neece, Rate Constants and Cross Sections
for the Production of H_2O from O^- and H^- in Water. J. Amer.

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
77204).
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. How-
ever, the physical conditions within the heavy ion track are
poorly understood, and effective concentrations of reactive inter-
mediates 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 homogeneous 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 temperature in microseconds before after the collision. The investi-
gations where the difference in activation energies is known. An impor-
tant aspect of the investigation is the variation of gas density; at
very low densities the system should simulate a conventional,
low-dose-rate environment. Furthermore, 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 it
is proving to be a good guide to further analysis.

PUBLICATION

Meisels, G. G., C. T. Chen, B. G. Gieszner, and R. H. Emmel,
Energy Deposition Functions in Mass Spectrometry, J.
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 the rate of reactions. A detailed study of 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 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 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^{-14} sec; in alcohols only an upper limit of 1% could 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 under 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


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 the radiolysis of organic compounds. Ion chemistry in gases 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 6.0, 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 the product distribution by 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 Chemistry Building, Washington, D. C. 20234.


The objective is to study ionizing radiation 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

Firestone, R. F., and L. M. Dorfman, Pulse Radiolysis of Gases, which are present for chloro-, bromo-, and fluoro-substituted.

Bibler, N. E., and R. F. Firestone, Exchange Mechanism and have shown that the ELDOR spectrum of oriented radicals is

PUBLICATIONS determine the complete radical decay scheme as a function of

for reactions of D and II atoms with DOD, HOH, TOD, and TOH presence of chlorine and bromine nuclei as substituents in the

precursors of HD in HOH-D2 and
to date indicates that hydrogen atoms are the only immediate tions it has been possible to obtain evidence for cluster formation

mechanism for hydrogen atom and molecule formation. Evidence for trapped radical-lattice interactions. Through

of particular interest. radiated single crystals of various bromo, chloro, and fluoro

alcohol molecules. The solvated electron spectrum is unaffected lattice in determining the type and yield of radicals produced by

the absorption spectrum and decay time of solvated electrons. Chemistry, University, Alabama:5486).

molecular absorption spectra have been recorded.

petition between radiative decay and collisional steps. Crude solutions), polymers, glasses, and crystals.

molecule-forming mechanism is complicated and involves com- of condensed phases including liquids (except water and aqueous

nisms of decay of excited rare gas atoms and formation of ex-

Electrons are selectively solvated by microscopic domains of It is the objective of this research to examine the role of a host


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 fol-

low the intermediates by absorption spectroscopy, although, as in the case of HO, we sometimes use emission. Because our accelerat

(Phoenix) provides pulses of very high intensity, we can work with gasses, and devote most of our effort to such small molecules as O2 or NO. We are now studying the mechanisms of O2 formation, including sensitization by N2, Ar, and He and inhibition by H20, NH3, and SF6.

We also employ flash photolysis which sometimes offers simpler conditions for the study of an intermediate. Thus, we are looking at reactions of O2(D) and O2(A) produced by flash photolysis of O2.

An important goal in our work is the accurate measurement of rate constants of important elementary reactions, and pulse tech-
niques often can provide the desired reactant in a system simple enough for a quantitative study. We have recently done this for the H0 radical in the reactions HO2 + H2O = HO2 + O2 and HO2 + OH = H2O + O2.

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


03:130 KINETICS OF IONIZING-RADIATION-INDUCED REAC-

TIONS. 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 alkaline solutions and of the beta-ray-induced decomposi-

tion of water vapor.

Objectives of the rare gas studies include elucidation of mech-
nisms of decay of excited rare gas atoms and formation of the near infrared absorption spectra of these molecules. The mol-

ecule-forming mechanism is complicated and involves com-

petition between radiative decay and collisional steps. Crude mole-

cular absorption spectra have been recorded.

Objectives of the work with liquid alkane–alcohol solutions in-
clude determination of effects of solvent–solvent interactions on the absorption spectrum and decay time of solvated electrons.

Electrons are selectively solvated by microscopical domains of alcohol molecules. The solvated electron spectrum is unaffected by the presence of soleroat at ethanol concentrations above a few mole percent. Effects of solvent character and of solvent–solvent 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 H2+D2 and DOD+H2 and that Gp = G0H = 13.1 mole/100 eV. Rate constants and Arrhenius parameters for reactions of D and H atoms with DOD, HOH, TOH, and THF have been determined recently.

PUBLICATIONS


Bishop, W. P., and R. F. Firestone, The Radiolysis of Liquid n-


03:131 THE RADIATION CHEMISTRY AND MASS SPECTROM-
ETRY 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 understand-

ing 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 reac-
tions making up the overall conversion. (3) is mechanistic understand-

ing 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 pertinent to silanes, germanes, and their alkyl derivatives.

High-pressure mass spectrometry and tandem mass spectrom-
eter studies of the ionic reactions occurring in SiH4, SiH2H2, SiH3H2, GeH4, and in their mixtures with CH4, NO, H2O, N2, CH3H2, and CH3H6 are planned for the immediate future. Mass spec-

trometric studies of the reactions of SiH4, SiH2H2, and CH3SiH2 free radicals with themselves and with NO, H2O, CO, CO2, and un-

saturated hydrocarbons. Partially deuterated silane and germa-

ne have recently been done this for the HO radical in the reactions HO2 + H2O = HO2 + O2 and HO2 + OH = H2O + O2.

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


—, and F. W. Lampe, Thermochemistry of Simple Alkyl-


Kamaratos, E., and F. W. Lampe, A Mass-Spectrometric Study of the Mercury–Photosensitized Reactions of Silane and Methyl-


ALSO SEE Radiation Chemistry: Other: 03:140, 03:162; Hol Atom Chemistry: 03:207; Chemical Spectroscopy: 03:247; Engine-

ering 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. Ir-

cradiated single crystals of silanes, germanes, and fluoro derivatives of acetamide and acetic acid have been used as models for trapped radical–lattice interactions. Through ESR investigations 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, 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**


**03:123** 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-ethylenediaminecobalt(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 CoII. 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 nitric oxide explosive above 229°K 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 compound as C_{24}H_{44}N_{4}O; 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 reaction 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 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 intercalating a small amount of hydrogen 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 low temperatures 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**


**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 charges 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 $N_e$, the energy of the excess electron state, relative to the free electron in vacuo, $V_e$ is close to zero for alkali and approximately $-0.6$ eV for the symmetrical molecules neopentane and tetranebutylsilane. 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 $V_e$ 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 photoinjection 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


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 at 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


03.138 RADIATION CHEMISTRY AND PHOTOCHIMISTRY 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 hydro-porous media or on metal films. At present, effects of ultraviolet light (uv) and gamma rays are being compared, the particular system used being CHBr adsorbed on porous Vycor glass and irradiated at liquid nitrogen temperature. The uv energy is absorbed by the glass and not by the CHBr. The yield of free CH radicals, determined by electron spin resonance spectroscopy, varies with CHBr 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 excitations produced by uv do not travel as far through the glass as the separated electric charges or Wannier excitons produced by the gamma rays.

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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 free hydrocarbon ions may be produced on a very short time scale (<10^-10 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.

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03.140 RADIATION-INDUCED EFFECTS IN ORGANIC SYSTEMS. Johnson, 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; (2) the mobility of electrons in irradiated organic materials; (3) reactions of molecular ions at metal electrodes; (4) reactions of molecular ions at metal electrodes, 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.

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03.141 RADIATION CHEMISTRY OF MONOSUBSTITUTED AROMATIC COMPOUNDS. Knight, James A. (Georgia institute of Technology, Nuclear and Biological Sciences Division, Atlanta, Georgia 30322).

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

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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 benzyl nitrite is being investigated. Products identified from benzyl nitrite are hydrogen, hydrogen cyanide, the isomeric dicarbonylenes, the isomeric cyanobiphenyls, and the isomeric dicyanobiphenyls. Irradiations of pure benzyl nitrite and of benzyl nitrite 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.

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03:142 MECHANISM OF THE DECOMPOSITION OF INORGANIC OXYANIONS. Johnson, Everett R., William Holtschier, Arnold Francis, and Richard Rossamuller. (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 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(16O)/G(18O) 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 effects studies as a function of temperature and pressure are in progress.

Mechanism 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 18O and the resulting product examined by Raman spectra to determine whether 18O has been incorporated into the salt. The results to date indicate that an exchange reaction can be realized in the nitrates, chlorates, and perchlorates.

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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 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 graft 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 intraspor termination.

LET studies on polymers and single crystals of alkane are in progress. Our principal interest is parallel radical formation. Measurements of radiation-induced conductivity in vinyl monomers and alkans are in progress to determine the yields and drift mobilities of charge carriers and to determine recombination kinetics of the ions.

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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 present in this way and the EPS parameters (g tensors and nuclear hyperfine splitting tensors) are being determined. The first aspect of the results has been to predict the results of radiation damage in molecular crystals. Time and temperature variations of the EPS spectra are aids in revealing the motions and reactions of the paramagnetic species.

Organic materials being studied include carboxylic acids, amidines, halocarbon derivatives, and organometallic compounds. Inorganic materials include hydrazinium salts and a variety of sulfo complexes. Particularly these lead to excess-electron radicals. An effort to observe triplet states of some new carbones has been started and EPS studies of radiation damage in sugars is contemplated. A major objective has been to obtain nuclear hyperfine splitting for carbon 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.

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03:145 INVESTIGATION OF GAMMA-RAY-INDUCED POLYMERIZATION OF THE CARBORANES. Klingen, Theodore J. (University of Missouri, Department of Chemistry, University, Missouri, 65201).

This research involves the radiation-induced polymerization of organo-substituted derivatives of 1,3,6-carborane-1,3,6-carborane-1,3 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 radiation-induced 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 eze.
The investigation of other phases of the overall problem will include the study of the copolymerization of 1-vinyl-o-carbonate under the influence of radiation with compounds such as styrene. Also the screening of other substituted carbonates, such as bromomethyl-o-carbonate, o-carbonarodiacetic acid, and 3-hydroxyethyl-o-carbonate, 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.

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03:146 DETERMINATION OF RANGE OF LOW-ENERGY ELECTRONS IN ORGANIC MATERIALS. Berry, W. B., and Y. G. 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 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 such as phonons 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 0.2 or 3 nanometers apart. 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.

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03:147 ELECTRONIC STRUCTURE OF IRRADIATED ORGANIC LIQUIDS AND GLASSES. Fumabashi, Kokihi. (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.).

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03:148 THE RANGE AND ENERGY DEGRADATION SPEC- TRUM 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 0–100 eV energy.

The device, from top to bottom, consists of dielectric $D_1$ (10$^3$ to 10$^4$ nm), 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 $I_2$ and $I_2$ will be measured at each thickness $t_i$ of $D_i$, over a range of incident electron energies $e_V$. At each $V_i$ the collector voltage $V$ will be swept from the saturation current at $V_i > 0$ to $V_i = 0$. 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 surfaces of disordered metal films. A prototype device using SiO as dielectric and $t_1 = 10^{-12}$ Å slow electrons traverse $D_1$ and enter $D_2$ with $<2$ eV (the practical limit for $V_i$ at that thickness). If ohmic injection can be achieved, the characteristic energy-loss spectrum will be measured 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., N. 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 10–20 eV electrons, but on the average three low-lying states of alkali halides appear below the optical excitation 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 ~316°K are planned. Studies on CdS and other semiconductors will correlate with other solid state investigations at Notre Dame.

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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.)

Neononsec and subnanosecond pulse radiolyses are being used for study and the concentration dependence of the optical absorption spectrum of the electron in various polar liquids and their mixtures with alkanes. Such study should enhance understanding of the mechanism of formation and...
nature of solvated electrons. Absorption spectra have now been determined for the solvated electron \( \left( e^- \right) \) at 30°C in 22 alcohols and dimethyloxyethane and cyclohexane. In each case, the spectrum was present immediately within a 5-ns pulse and was unchanged in position and shape at longer times. The preliminary results suggest the following conclusion: (1) binding energies of alcohols and dimethyloxyethane are smaller than those of cyclohexane.

The triplet/singlet ratio averaged over spur size distributions 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. In those solvents, 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. Benzene-alcohol solutions both triplet and singlet excited states, the triplet state contribution again increasing with increasing solute concentration.

The triplet/singlet ratio averaged over spur size distributions in alkane solvents. Compounds chosen for such a purpose will include low-energy electrons is similar to the treatment for zero electron mobility is independent of the applied field up to rather high electric field strongly suggests a diffusive mechanism for electron transport in such systems.

An external electric field increases the escape probability of the electron, which has also been observed. Formally, the Onsager theory should be applicable for the evaluation of the enhancement factor but the analysis is too complicated. Our object in this direction will be the attempt to form chelates of the electron 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 low-energy electrons is similar to the treatment for zero electron mobility is independent of the applied field up to rather high electric field strongly suggests a diffusive mechanism for electron transport in such systems.

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 temperatures, triplet states can be present also in the macroscopic 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. Benzene-alcohol solutions both triplet and singlet excited states, the triplet state contribution again increasing with increasing solute concentration.

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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 Frenzy's radical (the nitrosodisulfonate radical anion) as well as other radicals formed by irradiating a host crystal of potassium hydroxylamine triulfonate. For the first time the spectrum of Frenzy'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 NO3 and NO2 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.

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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 benzene, and crosslinks. The dependence of the rate of monomolecular scission of organic high polymers are being analyzed to correlate the changes in monomolecular decay with the increase in chain length. A parallel study on amines has been started. Decomposition 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.

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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 melt 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 spectroscopic information concerning the 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 14N, 15N, 13C, 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


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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 stability and radiation sensitivity of these materials. The materials studied are simple base polymers typical of commercial plastics and elastomers. Precursors of chemical reactions, 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 polyurea 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 unstrained groups disappeared at a high rate, crosslink yields will be measured to account for the apparent change in unsaturation. The crosslink densities are important since they determine the elasticity of these rubber polymers.

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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 reactions 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 reaction 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 types have been irradiated by 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 aliphatic hydrocarbons. With the potentialities of using radiation in the processing of coal thus indicated, the program will be complete.

**PUBLICATIONS**


**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 ion-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 seems 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 are on 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 to date have shown that these simple compounds produce reactive fluorine-containing intermediates that may be suitable for synthesizing organic fluoruro 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.

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**03:163** RESEARCH CONCERNING IONIC AND FREE RADICAL REACTIONS IN RADIATION CHEMISTRY. Williams, T. Francon, (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 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 acetone, methanol, alkyl halides, sulfuric acid, 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 others; and (6) pulse radiolysis studies on nitriles.

**PUBLICATIONS**


**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 this relaxation mechanism may be involved in organic materials 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. (d) The quasi-free electron state in glassy matrices is being studied experimentally and theoretically. Models that 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. Double modulation photoreaction 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


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 warming reveals migration and neutralization of different populations of charge carriers at different temperatures. Thermal luminescence 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 heating 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 work is being planned to aid in understanding: (1) the dependence 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 on the glass transition temperature on this peak; (2) exothermal peaks attributed to anion–cation neutralization in hydrocarbon glasses; (3) the exothermal 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 these bleached samples are being determined by several laboratories. The present project seeks to learn more about the conditions controlling such energy changes and to determine the nature of the reactions that can initiate, reactions of sorbed radicals with molecules added after irradiation, and saturation of reaction sites as a function of dose and temperature. In particular, we find that alkyl chlorides, ethylene, and methane are all activated to produce sorbed radicals, observable by ESIR at 77°K. Admission of O2 to the radicals converts them to peroxy radicals. C2H5 admitted to sorbed CH3 produces C2H4, 2H2, and CH4 by addition followed by abstraction from surface silanol groups. Yields as a function of dose and temperature suggest a pre-existing 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, 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–C 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 geminate 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 C2H5 and of H2 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 ultra violet absorption spectra of trapped radicals; and photochemical reactions of radicals.

PUBLICATIONS


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 and to determine the inhomogeneous thermal dynamics 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 rephotobleached; 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 optical-bonding thresholds of photobleaching 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) the dependence 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


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 are not limited to aromatic compounds, but 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 in the photochemistry of benzene in hydroxyl solvents—water, alcohols, and acetic acid. Ultraviolet irradiation of such systems yields a variety of isomeric bicyclo[3.1.0]hexenyldene derivatives, at least some of which appear to have their origin in benzene, a primary photoproduct. The present studies, aimed at delineating the mechanisms of the photochemical processes, include product identification and determination of product ratios, studies on the dark reactions of benzene, examination on the chemical behavior of the various isolated products, and the use of isotopically labeled benzene to investigate rearrangements that occur prior to product formation. The reactions that occur upon ultraviolet excitation of benzene in the presence of electron donors 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 pyrrole was facilitated by the finding that in aqueous sodium borohydride it was reduced, and stabilized, before undergoing tautomer rearrangements to give rearrangements that occur prior to product formation. The reactions that occur upon ultraviolet excitation of benzene in the presence of electron donors 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.

PUBLICATIONS


Spectroscopic investigations on chlorophylls of varied isotopic composition revealed 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 $^1H$ 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


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, followed by charge destruction and quenching, $k_2$, or by hydrogen addition to the radical cation, $k_1$. Quenching rates are effectively given by $k_2$. Quantum yields of photoreduction depend on the relative values of $k_2$ and $k_1$: Scheme A

$$\text{Ar}_2\text{C} = \text{O}(\text{T}) + \text{R} \text{R}'\text{NCHR} \rightarrow k_2 \rightarrow \text{Ar}_2\text{C} = \text{O}(\text{Ar} \text{C} = \text{O}) + \text{R} \text{R}'\text{NCHR}$$

$$\text{Ar}_2\text{C} = \text{O}(\text{Sp}) + \text{R} \text{R}'\text{NCHR} \rightarrow \text{ArCOH} + \text{R} \text{R}'\text{NCHR}$$

(a) In photoreaction of fluoromine with p-substituted dimethylamines, a linear plot of log $k_2$ vs $R$ 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, $\text{Ar} \text{R} = \text{CH}_2 \text{CH}_2 \text{H}_2$, while quantum yields rise, $R = \text{CH}_2 \text{CH}_2 \text{H}_2$, with large alkyl groups lead to low $k_2$. Mono-N-alkylanilines resemble anilines and are not photoreducible agents but quenchers, indicating that reversible N—H transfer may be important.

(b) We have proposed, eq. 1, that interaction of triplet excited carbonyl $\log k_2 \sim \Delta G_{CT} \sim -\Delta H_{CE} = E(\text{Ar} \text{C} = \text{O}) / 1.06 + C$ (1)

compounds with electron donors, $k_2$, may be described in terms of triplet energy, $\Delta H_{CE}$, and reduction potential of carbonyl compound, $E(\text{Ar} \text{C} = \text{O})$, and ionization potential of donor. For a common acceptor log $k_2 \sim 1.0 P_D$, and this is being explored for varied donors, amines, alcohols, olefins, thiocompounds, etc. For a common donor log $k_2 = -1.0 P_D + E(\text{Ar} \text{C} = \text{O})$, and this is being explored for carbonyl compounds of varying excited state configurations.

PUBLICATIONS


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
of methylene by molecular 02 has been studied with both CHT and statistical, quantum mechanical, and kinetic points of view. The triplet is quite unreactive. The oxidation of triplet level. The spectroscopic analysis is correlated theoretically from hydrocarbons and halocarbons. and time-lapse spectrometry to detect and identify key inter-

TBr, and no trace remains to indicate dissociation had occurred. T atoms that do not react while "hot" react with yield measurements, absolute yields cannot be determined—the CHEMISTRY. Filipescu, Nicolae. (George Washington Uni-

fluorides. (e.g., DT + CD3 or CD3T + D from T +

wavelength of light leads directly to different initial energies for 1971, pp. 251-263. Ebisuzaki, Y., and M. Nicol, Raman Spectrum of Hexagonal ZnS

needed to break the T-Br bond (3.81 eV) appears as kinetic energy, Second International Conference on Organic Scintillators and

molecule into the two atoms and any excess energy above that Phenanthrene in Polymethylmethacrylate, in Proceedings of the

of both potential energy and trajectory calculations. This latter task has recently involved attempts to under-

Na (3t) atoms

photodissociation of metal halides. At present, the quenching of molecular energy transfer on the separation between donor and acceptor molecules; displacement of absorption and luminescence bands by the molecular environment; bonding and structure of condensed molecular systems; chemical reactivity and state at high pressures; radiation damage in organic scintillators; and intramolecular energy transfer, photochromism, and chemi-

Spectroscopic investigation of the changes of intermolecular energy transfer processes in rigid media brought about by com-

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 Br2 as scavenger leads to both abstraction and substitution reactions with hydrocarbons (e.g., DT + CD3 or CD3T + D from T + CD3). As the excess energy is transferred (lowered wavelength), the substitution reaction dissociation appears 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 Br2 to reform radicals. Using flash photolysis or low-temperature techniques and aprotic solvents, we may isolate the key 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-

The continuing objective of this project is to develop a more complete understanding of non-radiative energy transfer in mole-

photostimulated emission detection of tritium. Earlier experiments have shown that the photolysis of TBr with Br2 as scavenger leads to both abstraction and substitution reactions with hydrocarbons. This uses a single photon technique that measures the time elapsed between start and stop signals are collected in a multidetector analyzer. This method will be applied first to studies of electronically excited metal atoms produced with excess translational energy by the photoexcitation of metal platelets. 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 photodissociation of metal halides. At present, the quenching of Na (3p) 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.

The general purpose of this research is the study of atomic and molecular species formed with extra excitation through photo-

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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. In addition, two conjugated organic chromophores incorporated in rigid model compounds in which the interchromophoric separation distance and relative orientation are accurately known, and between two separated molecules of which—either donor or the acceptor—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**


**03:178 PROPERTIES OF EXCITED SPECIES IN THE FROZEN STATE.** Maer, E. 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 photoreduction 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 excited species with solid surfaces. Thermal atomization and electrical discharges are in use as methods of generating excited 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**


**03:179 THE CONTRIBUTION OF ELECTRONICALLY EXCITED STATES TO THE RADIATION CHEMISTRY OF ORGANIC SYSTEMS.** Lipsky, 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 immediately application to the problem of stratospheric photochemistry. Ozone in the presence of water vapor is removed by a direct reaction with an oxygen atom and by catalytic destruction by the oxides of nitrogen (NO and NO₂). To a much lesser extent ozone is removed by transport to the troposphere and by catalytic destruction by free radicals based on water (OH, HO). Other nitrogen-containing compounds (NO₂, N₂O₃, NHO₃) 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 NO₂).

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 NO₂ system with the HO₂ system. In particular, we are studying wavelength-dependent photolysis of nitric acid vapor (200 to 320 nm), of the NO₂ 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 NO₂. We are working on two other reactions of great importance to the problem: the formation of nitric acid (HONO + NO₂ + M → HNO₃ + M) and the interaction of peroxyl radicals with nitric oxide (HOO + NO → HO₂ + NO₂).

**PUBLICATIONS**


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 its 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. The results of these studies are presented in the paper. Once these spectra are located and yields determined, it will be possible to answer such questions as What are the rates of the nonradiative deactivation processes 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


PUBLICATION

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 photo-initiated 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. Confirmation of this unexpected result is being sought using a nonchiral 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 both of the collision partners accept 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 intermixture patterns so that any anisotropic effects may be detected. These studies utilize a special optical system to reduce the effective size of the intermixture pattern by two to three times.

PUBLICATION


PUBLICATION

The production of excited states under gamma excitation conditions is of great interest. We are currently examining the excitation of alkane fluorescence by added CCl4 and O2 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


PUBLICATION


PUBLICATION

PUBLICATION


PUBLICATION


03:183 EXCITED STATES IN p-XYLENE. Gangwer, T., and J. K. Thomas. (University of Notre Dame, Radiation Laboratory). The pulse-radiolysis- and laser-photo-lysis-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 S1 state and the excited states produced by pulse radiolysis of p-xylene. It has been found that nitrous oxide efficiently scavenges this S1 laser-produced state indicating a possible source of error in the use of N2O for electron-scavenging experiments. Solute transfer studies indicate a total yield of excited states of C > 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


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 CCl4 and O2 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


03:185 CORRELATION OF RADIATION CHEMISTRY AND PHOTOCHEMISTRY OF 1,4-DIOXANE. Rentz, 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 1850 Å, corresponding to absorption in the first band of the spectrum, is currently being studied. Studies on the laser-induced 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 φ = 1.0 and a lifetime of less than 10^-8 s; quantum yields of products suggest that C4H8O2 + → C4H4 + 2H2O with φ = 0.75 is the major decomposition mode. In future work, photolysis of the liquid at 1840 and 1470 Å will be studied. In addition to their intrinsic interest, results of these photochemical studies will be used to elucidate (1) the role of excited states in the previously studied γ-irradiation of liquid 1,4-dioxane and (2) chemical behavior of the recently reported emitting species in liquid 1,4-dioxane excited with 1840 Å light or 12-MeV electrons.
PHOTOCHEMISTRY AND ENERGY TRANSFER

PUBLICATION
Hentz, R. R., and C. F. Parrish, Photolysis of Gaseous 1,4-


A study of the photoinitiated, 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 (tens of nanoseconds) fluorescent at ~220 nm are observed from a variety of alkane glasses γ-irradiated at 77K. 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 77K and perhaps 4K. The presence of ionization will be established by spectrophotometric and ESR detection of trapped electrons and the 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.


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 a logarithmic increase in decay time 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 $\tau \propto \exp(-t/\tau_1) + \beta \exp(-t/\tau_2)$ in which generally $\tau_1 > \tau_2$, $\beta$ is always greater than unity and $\tau_2 \approx 10 \tau_1$. The values of $\tau_1$, $\tau_2$, and $\beta$ vary with wave-length 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 reminiscent of naphthalene. However, in this current work a study, over a greater range of exciting wavelength, of the relationship between the 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

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 measuring the rate of photolysis under conditions of constant intensity, 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 48201).

The objective of the project is to study deuterium isotope effect on fluorescence of aromatic and heteroaromatic molecules (as vapors and in solution) to gain additional insight into the problem of electronic energy migration in large polyatomic molecules. This requires determination of quantum yield and lifetime of fluorescence under various experimental conditions. The quantum yield measurements are an essential part of experiments, 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 rates with excitation energy, temperature, and deuteration of the molecule will be deduced for these systems.

PUBLICATION

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 77K 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 305K is exposed to ultraviolet radiation in the absence of 3MP. When a matrix containing Na in 3MP is scraped from the cold finger in vacuum 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 3IMP. Further the kinetics of this process will be correlated with luminescence observations. Such a study of the matrix will be correlated with luminescence observations. Such a study is also underway on the effect of radiative and nonradiative processes on the deuterium isotope effect. The sources of the signals from the metal films are also under investigation.

PUBLICATION

03:191 ROLE OF H ATOMS IN THE RADIATION CHEMISTRY AND PHOTOCHEMISTRY OF ORGANIC GASES. 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 4K or above. However, photolytically produced H atoms are produced in the radiolysis of HI in C6H6 in contrast to C6D6, 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 C6H6 and C6D6, as a function of temperature we have now shown that the absence of HI produced no trapped H atoms for photolysis of HI in C6H6 results from the greater ease of reaction with the H atoms abstract hydrogen from C–H bonds as compared to C–D bonds. This reduces the yield of thermally activated H atoms available for trapping to a negligible value. In future work on this project it is planned to investigate the dependence of the yield of photolytically produced H atoms 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, pose significant questions about the nature of the trapping sites.
HOT ATOM CHEMISTRY

Studies of the chemical effects of nuclear transformation.


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 radioactive nature makes them useful in studying the chemistry of hot atoms.


The study of hot atom chemistry (chemical effects of nuclear transformation) in the solid state allows one to determine whether the chemical reactions of atoms formed in states of high kinetic or electronic excitation energy in crystals, and/or the slow, thermally induced annealing reactions by which such atoms, at rest in the crystal, can be made to change their chemical form. 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 theories. It is desired to include Mössbauer and/or perturbed angular correlation measurements to provide a better understanding of the chemistry of recoil atoms in situ in crystals.

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 whether the chemical reactions of atoms formed in states of high kinetic or electronic excitation energy in crystals, and/or the slow, thermally induced annealing reactions by which such atoms, at rest in the crystal, can be made to change their chemical form. 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.

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PUBLICATIONS


03:196 EFFECT OF DEFECTS ON POSTRON 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 annihilation of a positron is predominantly 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 implantation. The Doppler-broadened spectrum is expected to vary with the nature of the defects, their spatial distribution, the ions, the matrix. 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).

Radicals 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 $^13$C atoms is being investigated. Work on reactions of $^13$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 particular 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 permit 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


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. Radioharmaceuticals are used for detection, in the diagnosis of metabolic disorders and organ malfunction, and in therapy.

$^{13}$C-labeled amino acids, sugars, and other physiologically active compounds are being produced in research quantities. New methods for production of large quantities of carrier-free $^{13}$C-labeled disaccharides and organo$(14)C$ labeled, are being developed. The 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 $^{18}$F-$\text{H}_2$, $^{18}$F-$\text{CF}_2\text{OF}$, and other labeled intermediates to be used in the preparation of compounds such as 5-fluorouracil, 5-fluorouracil, and steroids. $^{13}$N, $^{14}$C, 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 RNL.

PUBLICATIONS


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 systematic 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 $^{13}$C 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 careful, well-chosen experiments, 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 atom substitutions, both F- for R alkyl replacement, and both F- for H abstraction processes are strongly similar in fluoroethanes. Preliminary evidence has also been obtained for hot CI- to HCl abstraction in alkynes, and we are attempting to determine whether the hot CI- for H, CI- for F, and CI- 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 $^9$Be. Preliminary low degree neutron velocity spectra and thick-target yields have been measured for 6,9 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


03:200 CHEMISTRY OF TRITIUM AND HALOGENS FORMED WITH NUCLEAR RECOIL ENERGY. Rowland, F. S. (University of California, 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 reagent. Since the radioactive atoms formed by nuclear reactions usually lose a high proportion of their excitation energy, the hot atom reactions are advantageous used in these studies. An inevitable practical by-product of these experiments is that some knowledge is gained of the chemical conditions under which these reactions occur and how and wherever they occur. Our current experiments rely mostly heavily on the formation of triton atoms by the nuclear reactions $^7$Li(n, p)$^7$H and $^3$He(n, p)$^3$H, and of fluorine atoms from the nuclear reaction, $^1$H(n, F)$^1$H.

We have emphasized precision quantitative measurements of product yields from carefully controlled reactions with simple molecules, usually in the gas phase. These changes have been made because the predictions of different theories concerning the importance of various factors in controlling these reactions are rather similar and can be distinguished only with good accuracy in relative yield measurements.

Recent experiments with triton 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 bond to Si, O, and N. Other experiments are being carried out at ~19°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 $^{19}$F atoms. In some $^{19}$F-substrate interactions, hot reactions are readily observed while most $^{19}$F atoms react while essentially thermal in energy when $^{19}$F has a mole fraction >0.95. Current experiments are emphasizing the substitution reactions of $^{19}$F for-halogen in alkyl halides, the abstraction of H by thermal $^{19}$F atoms, and the various addition processes with olefins. Simple substrate molecules are being used to reduce the number of unusual $^{19}$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


03:201 STUDIES IN HOT ATOM AND RADIATION CHEMISTRY. Koski, Walter S. (The Johns Hopkins University, Department of Chemistry, 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 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 reactions. 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 5 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(n, n)$^{12}$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 ramp up the number and type of reactions 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 initiated by the nuclear processes. The reactions of $^{18}$O 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 ion fluorine probably plays an important role in these processes, it is planned to study the reactions of $^3$H ions with a number of target molecules.

PUBLICATIONS


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 $^3$H+ in T reaction with the 47°C-atom of cyclohexene 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 a proportional counting of the tritium. Cyclohexene and all substituted cyclohexenes are being investigated and two papers have been submitted dealing with sulfur dioxide as a radical scavenger in allene systems and with scavenger effects of H$_2$S, butadiene-d$_4$, 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 temperature up to approximately 210°C.

Recent work has indicated the possibility of obtaining kinetic data directly from hot atom reactions in the gas phase. This work will be continued in this field in 1971 and 1974. The above research is done mainly to Ph.D. candidate, Darrell C. Fox.

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 ($\gamma$,$^7$Li) and isomeric transition (IT) processes, hot atom reactions of chlorine, bromine and iodine are being studied extensively in various gaseous, liquid, and solid halogenated methanes and hydrocarbons. The reactions of $^{35}$Cl, $^{35}$Br, $^{35}$Br, $^{35}$Br, $^{129}$I, and $^{129}$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 $^{129}$I, and $^{129}$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 $\gamma$,$^7$Li-activated reactions of $^{35}$Cl will be investigated by radiogas chromatography in the CI, and IF systems employing the gas chromatography and gas electric spectroscopy techniques. The stereochemistry of hot $^{35}$Br and $^{129}$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.
HOT ATOM CHEMISTRY

PUBLICATIONS


J. 204: POSITRIONIUM 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 the positronium atom 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 μsec. 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 in the gas phase and to study chemical reactions in molecular glass solids. At present, we are using polyglycol as the medium system. From this study, we expect to understand more about the difference between the hot atom reactions in glassy solids, such as 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 in 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


J. 205: REACTIONS OF HIGH-ENERGY RADIOACTIVE ATOMS RESULTING FROM NUCLEAR TRANSFORMATION IN THE SYSTEMS OF SILICON-CONTAINING COMPOUNDS.

Tao, Y.-N. (University of Utah, Department of Chemistry, Salt Lake City, Utah 84112).

The major objectives of this study are to investigate the hot \( ^{29}Si \) and \( ^{33}P \) atom reactions in the gas phase and to study chemical reactions involving other hot atoms with silicon-containing compounds. \( ^{33}P \) atoms are formed from the nuclear transmutation \( ^{35}P \) atoms by fast neutrons or \( ^{20}Ne \) or \( ^{18}O \) recoil atoms in the presence of various other clusten. \( ^{33}P \) may undergo ab- straction reactions to give \( ^{33}SiH \) or \( ^{33}SiF \). This can be trapped by butadiene to form silacyclopent-3-ene or \( 1,1\)-difluoro-2-2-3-cyclopentadiene. The reactions of silicon atoms in the presence of various clusten are also under study. Recent recoil phosphorus atoms are also under study. Recent recoil phosphorus atoms are also under study. Recent recoil phosphorus atoms are also under study.

The controlling factors for \( ^{33}P \) abstraction reactions to give \( ^{33}SiH \) or \( ^{33}SiF \), as the final product. Recent tritium and recoil halogen reactions with silicon-containing compounds such as silane, the methylsilanes, and the halomethylsilanes indicated that the controlling factors are related to the bond dissociation energy and inductive effect of the Cl atoms. Chemical reactions of energetic \( ^{33}P \) atoms with organic molecules will also be studied in view of possible chemical reactions of energetic \( ^{33}P \) atoms with organic molecules will also be studied in view of possible chemical reactions of energetic \( ^{33}P \) atoms with organic molecules will also be studied in view of possible chemical reactions of energetic \( ^{33}P \) atoms with organic molecules will also be studied in view of possible chemical reactions of energetic \( ^{33}P \) atoms with organic molecules will also be studied in view of possible chemical reactions of energetic \( ^{33}P \) atoms with organic molecules will also be studied in view of possible chemical reactions of energetic \( ^{33}P \) atoms with organic molecules will also be studied in view of possible chemical reactions of energetic \( ^{33}P \) atoms with organic molecules will also be studied in view of possible chemical reactions of energetic \( ^{33}P \) atoms with organic molecules will 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applications of this method to the preparation of $^{13}$C-labeled radio- pharmaceuticals.

PUBLICATIONS


03:208 REACTION STUDIES OF HOT SILICON AND GERMANIUM RADICALS. Gaspar, Peter P. (Washington University, Department of Chemistry, Saint Louis, Missouri 63105).

We are studying the reactions of recoiling silicon and germanium atoms in order to understand the interplay between structure and energy as factors which 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, we have used a flow recoil technique in which the range in which these exothermic reactions or reactions releasing both energy and mass is the range in which these endothermic reactions or reactions releasing both energy and mass are the range in which these endothermic reactions are favored.

2. We have been using experimental techniques to complement kinetic 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 ($\text{SiH}_3^+$) 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 $\text{Si}^+$, $\text{SiH}_3^+$, $\text{SiH}_4^+$, and $\text{SiH}_2^+$ with silane and methanol have been studied by ion cyclotron resonance spectroscopy. Knowledge of these and other secondary ion—molecule reactions has permitted the definitive conclusion to be reached that positive ions are involved in the recoil chemistry of silicium.

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 activation functions, the reaction cross sections as functions of energy.

PUBLICATIONS


KINETICS AND MECHANICS

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 chloro and bromo ligands of several square-planar platinum complexes are replaced by water is being measured by rapid titrations of the acidic protons of thequo ligands with automatic titration equipment. This way not only will the extent of aquation at equilibrium be evaluated, but the ratios of replacement of the halide ligands will be determined for the cis-dichlorodiarninoplatinum(III) and for the cis- and trans-di- bromodiarninoplatinum(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 $^{35}$Cl and $^{76}$Br. Attention will be directed to some previously unexplored but recently demonstrated mechanisms in conjunction with which one complex species, for example PbHBr$_2^-$, 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


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 $	ext{N}_2$, $	ext{O}_2$, and $	ext{CO}_2$, the trinitrogen molecules $	ext{NO}$, $	ext{NO}_2$, and $	ext{H}_2$, and the free radicals OH, O, HO, and H, in addition, several pollutants are of considerable importance—the nitrogen-containing compounds NO, NO$_2$, and NH$_3$; the sulfur-containing compounds SO$_2$, SO$_3$, and Se$_2$; the metalloid species 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 exothermic, 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 reactions 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 6.5 to 10 eV, which is the range in which these endoergic reactions or reactions re-
processes occurring in chemical reactions. Three unique chemi-

takes place with high enough cross section to allow detailed study.

characteristics such as the threshold laws, the energy reticably expected sensitivity for scattering in crossed molecular

carbons and halogen-containing organic compounds, respectively. TIBr by Accelerated Xe and Kr Atoms, Chlem. Phys. Lett., 10(3):

reactions of these energetic molecules with organic and inorganic

differences of the aerodynamic machine may make possible studies of nuclides and counting of nuclear disintegrations for detection, the

extraction of the products and to allow completed determinations of the threshold energies and the excitation

detection of beams of H and D atoms. The energy range of D a s on a platinum catcler and later measuring the amount deposited

metastable species may also be studied with this accelerator. An

of metastable species may also be studied with this accelerator. Using the Aerodynamic Chemical Accelerator, we have recently

quiring activation energies take place. Alterations in the machine

where the underline signifies the accelerated collision partner. Chemiluminescence from the reactions (assumed here to be radi-

whereas the products denoted by asterisks) will be ob-

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

be observed by photon counting through interference filters. As the

reactants, the various reaction channels were identified above collisions and the study of associative ionization of fast

able to detect by a photomultiplier after passing through an inter-

measurements of reaction rates in these atoms of suitable half-,

the angular distributions for the negative species formed in the

kinetic energies in the range from 0.5 to 150 eV. This machine may be employed to study the dy-

states of 37 Al being an

in the investigation of the dynamics of inelastic collisions of ac-

kinetic energies 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 skematically. 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

Beatty, J. W., and S. Wexler, Hydrogen Displacement in n-Butane

molecular beams with well-defined energies in the range from 5 to 190 eV and higher have routinely been pro-

molecules, illustration which are double bond addition and hy-

with activated metallic atoms. The angular distributions of positive

PUBLICATIONS

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H2 or D2, and T2 molecular beams with well-defined energy in the range from 5 to 190 eV and higher have routinely been pro-

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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 to the detector. Advantages of using this principle are: (1) high detection efficiency; (2) modest vacuum requirements; (3) good energy resolution; (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 tech-

are currently in operation. The machines are based on three dif-

infrared space spectroscopy. The prototype apparatus has been constructed to study the

atoms and molecules with kinetic energies in the range of 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 investiga-

broad classes of reactions. In addition, sections of the ma-

of reactions of these energetic molecules with organic and inorganic

characteristics of the threshold laws, the energy dependency of the

dependent on the atom and molecule. Experimental testing has verified the theo-

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tions 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**


**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 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 = 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.

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 σ-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 homogenous 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 = C3H5CO2) 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 of the active site. So far it appears that one or 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**


**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.

$$R-N=N-R^\ast = R^\ast + N-R^\ast$$

Depending on the solvent, the pair may diffuse apart or undergo rupture of the second carbon-nitrogen bond. The possibility of a concerted fragmentation of I (II → III) is the subject of another study.

The method of investigation uses an optically active azo compound that undergoes stepwise rupture of its two bonds. The site of chirality is at the carbon-nitrogen bond undergoing cleavage. Rotation of II→I in this case is accelerated significantly. 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 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**


**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 base pairs 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 (Adenyl-5' → 5'-adenosine) and ApApA, and the kinetics of the melting of dAT (copolymer of deoxyadenylate and deoxythymylate).

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 cytchrome 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**


**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. That is the basic reason why 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 potassium can be interpreted to show how the potential energy of interaction between the atoms varies with the distance of their association. A successful attempt in trying to solve a long-standing problem, the variation with temperature of the rates of more complicated reactions such as the combination of atoms of iodine to form iodine molecules, is the conversion of the measured transition to vibrational energy in collisions helps to show how chemical reactions occur.

**PUBLICATIONS**


**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 thermodynamic data relating to acidities and basicities (studies 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**


**03.221 DETERMINATIONS OF ELEMENTARY REACTION RATE CONSTANTS FOR THE REACTION OF HYDROGEN ATOMS WITH VARIOUS SUBSTRATE MOLECULES IN THE GAS PHASE.** Michael, Joc 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 radiochemistry. 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 alynes, and the diatomics, O2, N2, and CO. Several deuterated modifications have also been studied in an attempt to gain mechanistic information on these reactions.

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 sub-
strate reactions. These experiments include shock tube and flash mercury photosensitization techniques. The information gained will be of interest to both experimental and theoretical chemical kineticians.

**PUBLICATIONS**


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 HDJ = 1 J + He = HDJ = 0 J + He has been measured as a function of scattering angle by the time-of-flight method. HDJ = 1 molecules are identified from their laboratory velocities which differ from those of HDJ = 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^+ 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**


03:223 STUDIES OF GAS PHASE COLLISIONS OF NEUTRAL SPECIES, Herm, Ronald R. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division). This is an experimental program 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 various alkali atoms; (b) a chemiluminescence determination of the vibrational distribution in electronically excited HgC1(^3P^+2) formed in the reaction of Hg(^6P^2)+PCl3; and (c) a crossed beam study of the transfer of electronic excitation from Hg(^6P^2)+ to Ti species. 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 with the results of pulse radiolysis. By controlling relative concentrations, it is possible to prepare solutions in which either 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., Ba^2+ + Cl^-) will also be initiated in the near future.

**PUBLICATIONS**


03:224 CHEMICAL REACTIONS STUDIES, Mahan, Bruce H. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division). The subject 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 D2^+ with H2, with the object of elucidating the processes D2^+ + H2 -> D2 + H2 or D2 + H2, 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 efficiencies of the reactions made.

Another reaction currently under study is O^+ + H2O + H^+, 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**


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
KINETICS AND MECHANISMS

$e_{\text{phen}}$ 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 ethylamines will be studied for evidence of mixed-metal 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


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 intramolecular energy transfer are under investigation using crossed-molecular-beam techniques. Recently the velocity dependence of electronic to vibronic energy transfer was investigated for the first time. The reaction was $\text{HgCl} + \text{e}^- \rightarrow \text{Hg} + \text{Cl}^-$ where $M = \text{H}, \text{D}, \text{N}, \text{H}, \text{N}, \text{Cl}$, and $X = \text{Cl}^-$. It was followed by the 2537 A light. Molecular beams produced the cross sections decreased with increasing energy as $E^{-1.8}$ above 0.1 eV in accord with the model predictions by Bystroed 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 (5490 Å) attributable to the electronically excited B state of HgCl is observed. The velocity dependence of the chemical reaction being investigated was observed with an 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 process of high energy (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 Na$^+$ 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


03:227 EXCHANGE OF ELEMENTARY IODINE WITH ORGANIC IOIDES. Noyes, Richard M. (University of Oregon, Department of Chemistry, Eugene, Oregon 97403).

Most free radicals are so reactive that competing reactions govern the very small iodine atom. Iodine solutions 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 benzoil or benzenyl iodide affords an example of a larger function that has been observed for any other reaction of neutral molecules. Either isopropyl or tert-butyl iodide will react with iodine by this mechanism at a conveniently measurable rate in an apotropic 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


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 malonate ion in acidic hydrochloric acid. We 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 and the analogies to biochemical processes like heart beats and nerve impulses. The bromate–malonate acid system is not unique as a chemical oscillator, and we are evolving principles to guide the search for other oscillating systems.

PUBLICATIONS


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 focused, and 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.

03:230 RESEARCH ON HIGH-ENERGY CHEMICAL REACTIONS. David, J., and Endre Kőrös. (Oak Ridge National Laboratory, Chemistry Division).

Most free radicals are so reactive that competing reactions govern the very small iodine atom. Iodine solutions 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 benzoil or benzenyl iodide affords an example of a larger function that has been observed for any other reaction of neutral molecules. Either isopropyl or tert-butyl iodide will react with iodine by this mechanism at a conveniently measurable rate in an apotropic 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.

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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 03:190 through 03:208 and Heavy Element Chemistry: 03:76, 03:77; 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, 03:298, 03:304; Thermodynamics: 03:316: High-Temperature and High-Power Chemistry: 03:333, 03:348, 03:349, 03:351, 03:352, 03:355; Engineering Chemistry: 03:360, 03:365, 03:366; Miscellaneous Chemical Studies: 03:440, 03:450, 03:469.
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 SPECTROSCOPv. Calder, G. Vincent. (Ames Laboratory, Chemistry Division).

The electron impact mass spectra of pure azulene and its derivatives in argon matrices at cryogenic temperatures where it can be maintained indefinitely. The vibrational and electronic spectra of the molecule are currently being examined. As long as the technique of matrix isolation can 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 MCO$_x$, where M = Cr, Mo, W has been prepared successfully by codeposition of metal atoms in CO/Ar matrices. The spectra and stoichiomerty of these compounds are presently under study.

Similar studies on the aza analogs, MCo$_x$, are also under active study by means of matrix-isolation reactions of the vaporized metal atoms with the unstable diatomic CS$_2$.

PUBLICATIONS


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 exceedingly thin crystals, 1 to 10 µ thick that are needed for measurements of polarized spectra of pure single crystals. The forbidden d-δ 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 excitonic structure, which has been 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 optical properties of the crystal. 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 4K (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 Hg$_2$PbBr$_4$ is underway.

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03:232 THE ELECTRONIC ABSORPTION, LUMINESCENCE, AND NONRADIATIVE PROPERTIES OF σ-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 σ-unsaturated enones are in progress. Such experiments on these systems are designed to improve our understanding of (i) the electronic properties, electronic symmetries, and geometries of σ* and σσ* excited states; (ii) the radiative and nonradiative (femtosecond) conversion, intersystem crossing, etc., properties of these states; and (iii) electron-phonon coupling processes in mixed molecular crystals.

The electronic absorption bandwidth of an impurity molecule in a...crystal lattice are determined, in part, by the lifetime of the excited state of 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 fits 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 needed, the azaazulene molecules in order to determine appropriate excited state lifetimes.

Azulene's two lowest excited singlet states are σ* 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 σ* states in azazulenes and nonaromatic analogs in solutions and the electronic and vibrational excitations in the gas phase have been reported. Only in the case of azulene where the heavy metal atoms with the unstable diatomic CS$_2$... has been observed recently in dichloro(ethylenediamine)platinum(II). The forbidden d-δ transitions of the heavy metal atoms can be measured for crystals with this thickness.
convention 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


03:234 RAMAN AND INFRARED SPECTRA OF MOLTEN SALTS AND SALT VAPORS. Maroni, V., and F. 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 polymeric aggregates of SnCl$_4$ molecules and a monomeric species, most probably SnCl$_2$. Raman studies have also been made of solid and liquid NaNH$_2$ and BiCl$_6$ 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$_6$ vapor, intense resonance fluorescence was observed at temperatures above about 150°C. This was attributed to the formation of a subhalide of bismuth (probably BiCl$_3$). 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 I$_2$ is the stable product of the processes I$_2$(g) + 2I$(g)$ or I$_2$(g) + I$(g)$, with reaction rates of the form $k_3 = k_3(T)$ where $M$ is Li, Na, K, Rb, Cs, Ag, and Tl. Evidence was also obtained that any I$_2$ formed during these reactions is immediately reduced to I$_2$.

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.

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The experimental potential 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$_5$ octahedral molecules and AB$_5$ 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$_2$ 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 halogenates, 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 spectra 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


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 (25,000 to 50 cm$^{-1}$) and Raman spectra of materials under high external pressures. 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 pseudocrystals of the type AB$_2$ and AB$_3$ have been observed under high pressures. Such studies are important for developing fundamental concepts of lattice dynamics. The experimentally determined parameter $d

ources$ leads rather directly to an experimental value for the Gruneisen constant ($\gamma$). This can then be compared with the $\gamma$ 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 frequencies 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 (ML)$_2$X$_2$, (ML)$_2$X$_2$ (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 (ML)$_2$X$_2$ where M = Co(II), R

L = tridentate ligand (EtN-(CH$_2$)$_3$N-(CH$_2$)$_3$-PO$_2$H, R = Me, H), have been made. Systems demonstrating spin state equilibria of the type NiBr$_2$ (R$_2$BP$_2$)$_2$ have also been studied and evidence provided that the 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 nature of 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.

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that the surface reactions responsible for their formation. largely devoted to the determination of the relaxation times for the ing bombardment with reactive gas projectiles and to characterize surements have proved more useful and our present program is expected to clarify the nature of the molecular products formed dur- the bending and stretching of the hydrogen bonds. Dynamic mea-

Carstens, D. H. W., and D. M. Gruen, Apparatus for Matrix Isola- Magnetic resonance spectroscopy is a new and important tech-


PUBLICATIONS Study of Metal Complex Ion Equilibria, in A. E. Martell (Ed.),

density batteries. Furthermore, they provide strong evidence e.g., biological systems.

ions produced in an isotope separator. These experiments are ex- the radial wave functions, and further g-values of the heaviest activities are being calculated for comparison with atomic beam results.

PUBLICATIONS


03:238 SPECTROSCOPY OF HIGH-TEMPERATURE SYSTEMS.

Gruen, D., Argonne National Laboratory, Chemistry Division.

Current work is aimed at the elucidation of the chemical effects the interaction of energetic particles with surfaces. One of the goals of the research is a better understanding of the mechanism of the chemical sputtering. In a very recent study, the uranium oxide molecules UO, UO$_2$, and UO$_3$ were produced by sputtering a ura- nium metal cathode with argon gas containing variable concentra-
tions of oxygen. The chemically sputtered uranium oxide mole-
cules, isolated at 12°K in a matrix of solid argon, were identified by means of their vibrational spectra by use of an isotopic sub-
sitution technique. In this way, the frequency of the U-O vibra-
tion was established as 839 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 ex-
pected to clarify the nature of the molecular products formed dur-
ing 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 produced 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 photogra-


Gruen, D. M., and D. H. W. Carstens, Absorption and Lumines-

Carstens, D. H. W., and D. M. Gruen, Apparatus for Matrix Isola-


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 nu-
clear magnetic resonance techniques to studies on inorganic sys-
tems where such studies can provide useful information with re-
spect to molecular structure, electronic configurations, and kinetic behavior. An early study in this direction was the study of the H$_2$ magnetic resonance of the xenon fluorides with the ob-
jective of determining the shielding parameters, structural char-
teristics, and charge distribution on the fluoride ion. More recent-
ly, Chemical Shift measurements have been made on the fluo-
rine and hydrogen nuclei in gaseous and liquid HOF in order to learn something about the charge distribution and molecular properties of this unstable fluoride.

In the present, a definite program is underway to extend the study of H$_2$ chemical shifts and relaxation behavior for xenon oxy-fu-
loride and xenon hexafluoride and for mixtures of xenon hexafluoride and other xenon fluorides is underway. These studies were undertaken to provide informa-
tion on general physical interest. Both static and dynamic nuclear magnetic resonance techniques have been found useful. 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 present 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 in-
creasingly apparent that an understanding of the diverse proper-
ties 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 was found to be limited by the fact that the chemical shifts are sensitive not only to the breaking but also to the formation of the hydrogen bonds. Both static and dynamic nuclear magnetic resonance 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


- A. J. Ziedel, A. Svirmickas, and M. Wood, Relaxation Pro-


Magnetic resonance spectroscopy is a new and important tech-
nique for the study of structure and function of proteins and en-
ymes. The application of high-resolution techniques is greatly facilitated by the use of isotope hybrid proteins containing $^{1}$H-

amino acid side chains or $^{13}$C-prosthetic groups, because chemical shift assignments can then be made unambiguously. Conformational changes in isotope hybrid cytochrome c, ferredoxin, and flavopro-
tein, proteins important in electron transport, are being studied by proton magnetic and electron spin resonance to learn how energy transportation is mediated by the proteins. Horne Radialt Pervorind, Electron spin relaxation studies with fully deuterated flavins and flavoprotein are found particularly valuable because the flavin is a natural spin label. These studies make it possible to determine hyperfine interac-
tions of the unpaired electron of the flavin radicals with nearby protons of ordinary isotopic composition. Other physical parameters such as rotation correlation times can also be measured, which makes it possible to ascertain whether the protein is free or bound in the living organism. Combination of 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 organism. Combination of these two types of 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 freshly deuterated enzyme containing an N-terminal amino acid side chain in its active center and to observe directly the consequences of enzyme–substrate interaction.

PUBLICATIONS


3.242 CIRCULAR DICHROISM SPECTROSCOPY. Katzin, I. I. (Argonne National Laboratory, Chemistry Division).

3.245 CASEOUS ION CHEMISTRY. Friedman, L. (Brookhaven National Laboratory, Chemistry Department).

3.246 MECHANISMS OF METABOLIC AND PHOTOSYN-

THETIC REACTIONS. Fajer, J. (Brookhaven National Labo-

ratory, Department of Agricultural Sciences).

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 $^1$H and $^13$C. These include $^2$H- and $^{13}$C-substituted chlorophylls.

2) Substituents on the porphyrin molecule are altered and gendiction 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 ligand oxidation states. 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 electron transfer and to extend the studies to new cation radicals of metalloporphyrins, chlorins, and bacteriochlorins as models for biological and energy transfer systems.

PUBLICATIONS


03:246 PHOTOELECTRON STUDIES. Hudis, J., M. L. Perlman. (Brookhaven National Laboratory, Chemistry Department).

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. The objective is to study the electronic structure of molecules and ions of importance in the fields of radiation chemistry and photochemistry.

PUBLICATIONS


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. The objective is to study the electronic structure of molecules and ions of importance in the fields of radiation chemistry and photochemistry.

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The ESR spectra of systems 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. Pulseradiolytic 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 recombinational recombination 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. Finck, R. W., McGeorge, J. C., Schmidt-Ott, W. D., Baker, K. J., Xenoulis, A. (Georgia Institute of Technology, School of Chemistry, Atlanta, Georgia 30322).

Current emphasis is on precision measurement of K, L, and M subshells x-ray fluorescence yields and Coerster-Kronig transition probabilities in the lanthanide through the transuranium elements. This is carried out by investigating x-ray and Auger electron emissions, low-energy x 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, gated-valved electron detectors, together with a multichannel, 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 57Fe, a major question was the best agreement of several theoretical calculations for the electron capture decay has been answered; best agreement of M/L capture ratio in the decay of 57Fe, 57Co, and 57Ge is the result of these calculations. The authors predict that the decay of 57Fe, 57Co, and 57Ge is consistent with the theory, and the agreement of the observed electron capture decay results in 57Fe with the literature value is excellent.

During 1972-73 we expect to devote an increasing effort to the USNQ project, the joint university isotope separator-on-line with the 850 MeV heavy ion beam at Oak Ridge National Laboratory.

Our purpose in this program is to carry out on-line studies of new nuclei far from stability, particularly for the Georgia Institute of Technology group, the study of very-high-spin isomers predicted by Goldanskii 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 hope that most of our effort will be devoted to research under the UNISOR program.

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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 capabilities of the ion microprobe mass spectrometer.

One study currently in progress involves an experimental investigation 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 mass and material, and how the conductors and emission surfaces 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 14O enrichment, 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 reactivity produced by complexing the CrO42- will be studied. The lifetimes of water molecules in the first coordination sphere of nickel ion complexed by one immobilized carbon monoxide are being measured to find how much 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


03:253 OPTICALLY DETECTED MAGNETIC RESONANCE (ODMR IN PHOSPHORESCENT TRIPLET STATES AND IN TRIPLET-FRENNEL 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 transient absorption spectrum 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 109 molecules in this manner. 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 nuclear hyperfine interactions, and the nuclear quadrupole interactions. In addition, quantitative analysis of the microwave-induced changes in phosphorescence yields a measure of the rates and mechanisms of 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 allows an 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


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-0 bonding. For example, if this type of bonding is important in SiF4, 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 determining very small changes in atomic charge distributions and in some cases a measure of molecular distortion in these states can even be ascertained.

PUBLICATIONS


03:255 ELECTRON PARAMAGNETIC RESONANCE AND MICROPHOTOMIC SPECTROSCOPY. Myers, Rollie J. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).


Our current work on electron–electron exchange in \( \alpha-\text{NiSO}_4 \cdot 6\text{H}_2\text{O} \) 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 dependence 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 \( \alpha-\text{NiSO}_4 \cdot 6\text{H}_2\text{O} \) Lattice — Electron Paramagnetic Resonance Study of Transition-Metal Ions in \( \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} \). J. Magn. Res., 6, 63(1979).


**03:258 PHOTOELECTRON SPECTROSCOPY IN SOLIDS.**

*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 other areas 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 greatest interest to solid state chemists and physicists and solutions in the field. 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.

**03:259 OPTICAL SPECTROSCOPY.**

*Conway, John G.* (Lawrence Berkeley Laboratory, Nuclear Chemistry Division).

This project employs the experimental techniques of low-temperature nuclear orientation, Mössbauer spectroscopy, and perturbed angular correlations of \( \gamma \) rays to study hyperfine interactions in solids. 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 0.1 mK. 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 Mössbauer spectroscopy with \( ^{57} \text{Fe} \) relatively straightforward. Further experiments are in progress in tantalum alloys and compounds.

**03:260 PHOTOELECTRON SPECTROSCOPY IN SOLIDS.**

*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 theoretical and experimental data 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 properties of states of various 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 photojected from surfaces, and having energies in the range 0 to 2 \( \text{eV} \). The apparent resolution is less than 30 mV from 0.1 to 2 \( \text{eV} \) and less than 0.1 \( \text{eV} \) between 0 and 0.3 \( \text{eV} \). Photoelectron spectra of the substrates have been measured, 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 from the oxide compound at the surface and its emission intensity is temperature-dependent. Stabilization of such an oxidized silver surface with trialkylchromoaluminate results in a monolayer or less than monolayer coverage of the latter groups. Electron penetration of surfaces is selectively attenuated in energy. The general features result in the suppression of all electrons emitted from the unaltered surface with less than 0.5 \( \text{eV} \) 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**

03:261 SPECTROPHOTOMETRIC STUDIES OF SOLUTIONS WITH ALPHA-ACTIVE MATERIALS. Bell, J. T., I. L. Thomas. (Oak Ridge National Laboratory, Chemistry and Physics Division).

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 applications in chemical sciences. 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 is evaluating 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 built for use in electron spectroscopy which should eventually 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.


The 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 UF4 and UF5 in molten LiF - BeF2, it was observed that rapid equilibration among the various uranium species graphite, and insoluble uranium carbides occurred at temperatures below 1000°C. Since these thermodynamic data are available for UF4 and UF5 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 metal, uranium, and molybdenum, whose redox chemistry is still poorly understood, are being initiated; these studies will occupy much of the immediate future.

PUBLICATIONS


03:264 PHOTOELECTRON SPECTROSCOPY. Thomas, T. Darrah. (Oregon State University, Department of Chemistry and Radiological Science, 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 atoms of the molecule. 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


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 determina-
tion of the signs of zero-field parameters in \( n_{\pi} \), 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 adamanate matrix technique for the measurement of EPR and optical spectra of free radicals. A large number of \( \beta \)-carbonyl radicals containing five-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 excited states can be used to detect EPR spectra of electronically excited states of free radicals.

**PUBLICATIONS**


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 phenomena involving 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 compounds \( [\text{C}_{6}\text{H}_{5}]_{2}\text{SnCl}_{2}, \) 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 \( \leq T \leq 100^\circ\)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) \( \text{ti}^{1}\text{V} \) diethylidithiocarbamates; (b) \( \text{ti}^{1}\text{V} \) sulfates and thioglycolates; (c) \( \text{t}^{1}\text{+} \) compounds with a variety of phosphorus-containing ligands; (d) hydrate derivatives of \( \text{Fe}^{11}, \text{Ni}^{11}, \text{and Sn}^{11}(\text{v}) \); and (e) dialkylformamide complexes of \( \text{Sn}^{11} \). Related studies on solid state properties, hot atom chemistry and chemical effects of isomeric transitions and internal conversion are currently underway.

**PUBLICATIONS**


03:267 GASEOUS ION CHEMISTRY: ANALYTICAL APPLICATIONS. Torrey, Ruby P. (Tennessee State University at Nashville, Department of Chemistry, Nashville, Tennessee 37203).

The purpose of this study is to evaluate the performance characteristic 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 \( \text{Ar}^{+} \) and \( \text{Ar}^{2+} \) 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 to 10 torr causes a reduction in the ionization efficiency by approximately 50% for \( \text{Ar}^{+} \) and approximately 75% for \( \text{Ar}^{2+} \).

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, ArNH\(_{2}\), 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.

**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 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**


Hoffman, David K. (Ames Laboratory, Chemistry Division).

03:269 EFFECTIVE EXPANSIONS OF ATOMIC AND MOLECULAR ELECTRON 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 thus at the core of the development of new computational methods. Several methods have been developed 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 quantum coupling have been derived and implemented, using a group theoretical analysis of the permutation symmetry. Furthermore a rapidly convergent optimization procedure for the one-electron molecular orbitals occurring in many configurations had 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


03:270 EVEN-TEMPERED ATOMIC ORBITALS FOR ATOMIC AND MOLECULAR CALCULATIONS. Ruedenberg, Klaus. (Ames Laboratory, Chemistry Division).

The one-electron 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 [−r/2] or exp [−r²]. The optimal choice of large sets of these parameters has been derived both bound 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, 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 basic sets are being refined to yield optimal usefulness in molecular calculations. Such calculations were made predicting the stabilities, dissociation energies, and geometrical shapes of, as yet unknown, trialkali ions Li₃⁺, Na⁺, Na₂Li⁺, Na₃Li⁺, Li⁺, Na⁺, Na₂H⁺, NaH⁺, Li⁺H⁺, NaH⁺, and LiH⁺. In current work orbitals, even-tempered atomic orbitals are being refined in typical molecular environments for such common atoms as carbon, nitrogen, and oxygen, for general use.

PUBLICATIONS


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 deformation. However, when a model has been established that allows the theoretical approach 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 interpretations 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


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 long-range forces between solute and solvent atoms and by minimizing the chemical potential of the solute with respect to dilution. 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 entropic contributions.

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 LMFR's, coolants and blankets for controlled thermonuclear reactors, new methods for the recovery and purification of nuclear fuels, nuclear safety and energy conversion.

PUBLICATION


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 more operational.

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


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 part, 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 geometrical structures.

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 in the condensed phases is the results of calculations over 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 faculty group has 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.


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 fluoride molecules for a collaboration with the Chemical Engineering Division, atmospheric diatomic molecules related to aerocinning modeling, and metal chlorides that are being concurrently studied experimentally in the Physics Division.

The 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 calculations. 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


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 + H2 = LiH + H (collaboratively with LLL), H + Li = LiH and Li + H2, 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, the 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 determining 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. The priority is on the establishment of priority rules that can determine the energy surfaces to a semiempirical (LEPS) surface has been generated and used in related wave functions for small molecules. Upon determination of the numerical integration, by the local energy method, of correlation interactions in the H + CH4 System, Chem. Phys. Letters, 13: 24 (1972).

**PUBLICATIONS**


**03.279** THEORETICAL STUDIES OF ATMOSPHERIC TRIOATOMIC AND DIATOMIC SPECIES. Wahl, A. C., C. W. Wilson and R. Rosteny. (Argonne National Laboratory, Chemistry Division).

The spectra (both electronic and infrared) and kinetic behavior of small atmospheric triatomic molecules under stressfll atmospheric conditions are well understood. The understanding of these phenomena, which is fundamental to aeronomic modeling, requires a knowledge of the energy surfaces governing the collision and recombinati 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 \( \text{H}_2 \), \( \text{O}_2 \), \( \text{O}_2 \), \( \text{N}_2 \), \( \text{N}_2 \), and their ions. This critical review is using as a reference a theoretical description of the electronic structure of these molecules from molecular orbital theory and correlation rules as well as existing calculations. Energy points in the neighborhood of the equilibrium geometry and in dissociation limits can be fixed from experiment.

In a few instances, notably \( \text{H}_2 \), 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 to determine the energy surfaces at pre-specified levels of accuracy. It is expected that priority will be given to the determination of all energy surfaces arising from ground and lowered excited state fragments and to the dominant absorption features of 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 fit 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 employed 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.


**03.281** 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 vibration 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 \( \text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H} \) 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 modeling reactions such as \( \text{H} + \text{Cl}_2 \). 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 \( \text{H} \) atoms with different electronic states (\( \text{H}^1, \text{H}^2, \text{H}^4 \) with alkane substrates and their halogen derivatives.


**PUBLICATIONS**


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 recombinations, fluorescence quenching, collisional dissociation and photoionization. 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 thermochemistry and hot atom studies of reactions of excited states of the hot atom atoms) 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 calculation in the most useful form, computer graphics and animation of numerical data are also an integral part of this program.

**PUBLICATIONS**


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 ions, that is, of the detachment, attachment, and energy-exchange processes of low-energy electrons in matter.

One approach, which has been profitably emphasized here in recent years, is the study of the fine and hyperfine splittings of the rotational-vibrational structure 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.

Most attention has been 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, electronic-electron processes present a barrier to electron escape. Analogous barriers do not 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**


03:284 THEORETICAL STUDY OF FINE AND HYPERFINE STRUCTURES AND THEIR EFFECT ON RADIATIVE INTERAC- TIONS AND ELECTRON-TRANSFER PROCESSES. Chow Chi, 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 interactions were found to give rise to additional 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 is on the excited state.

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 transfer between the different pairs of excited states were 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**


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 up to several electron volts). Current work is involved with developing a general semiclassical theory of molecular energy transfer and progress is being made 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+H2 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 H2 and He; this work employs an accurate potential energy surface and should thus give physically meaningful values to compare with recent shock tube measurements of the vibrational relaxation time. Three-dimensional calculations of the H+H2 reaction are also planned.

**PUBLICATIONS**


03:286 PHYSICAL CHEMISTRY WITH EMPHASIS ON THER- MODYNAMIC PROPERTIES. Fitzler, Kenneth S. (Lawrence Berkeley Laboratory, Inorganic Materials Research Division).

Aqueous solutions of some solutes, usually electrolytes, are of enormous practical importance in situations all the way from the utilization processes to the chemical processes in the human body. While very dilute solutions of all these solutes were investigated intensively and, in most cases, successfully several decades ago, the fundamental basis for concentration 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 a large number of different ions, as well as different electrolytic 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.

PUBLICATIONS


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-molecular interactions under clustering reactions. A simplified dimers-in-molecules (DIM) energy expression was derived to make possible calculations of approximate potential energy functions for each ion. Detailed application has been made for H^+H^-H^+H^- system. The results from this study provide an indication of the character of the results of the DIM model, which can be used as a guide for studying other ions. Both single and dihydrogen ions are investigated by various quantum mechanical methods. The results from this study provide an indication of the character of the results of the DIM model, which can be used as a guide for studying other ions.

03:289 MATERIALS AND METHODS FOR THE STUDY OF ISOTOPE EFFECTS IN BIOLOGICALLY IMPORTANT SYSTEMS. Katz, J. J.; Crespi, H. L.; DaBoll, H.; Komka, J.; Smith, U.; Uphues, R. A. and Norris, J. R. Jr. (Argonne National Laboratory, Chemistry Division). Our research involves the application of stable isotope H^1, D^2, N^14, O^16, Mo^90 to chemical, biological, and biophysical problems. Our current activities fall into three categories: (1) isotope labeling of living organisms of highly unnatural isotopic composition and the extraction of compounds of biological significance from these; (2) structure and function of proteins and enzymes; and (3) the role of chlorophyll in the light conversion 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 180-186-gal. scale in pure heavy water (99.95% H^2O) for the production of deuterated organisms and compounds. The cultivation of organisms of unusual composition has been extended to C^12-algae fed into biological processes. These organisms then serve as the source of deuterated (or H^2O) 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 H introduced by biosynthesis into specified positions of the molecule. Thus, isotope hybrid proteins are obtained by growing organisms in H^2O on H^13-amino-acids, and other isotope compounds that are essentially fully deuterated except for the particular H^13-amino acid(s) biosynthesized into side-chain positions. We plan to put another tank into operation, and to extend our operational to cultivate organisms that are depleted in C^13 (by using C^13O from which the C^13 has been stripped) to serve as a source of C^13-free compounds. Because organisms and compounds of unusual isotopic composition find important use in magnetic resonance spectroscopy, we have active instrument development programs to design new and better stages for making effective use of these substances. We have interfaced our magnetic nucleus and electron spin resonance spectrometers to a central Sigma V computer. We are now in the process of interfacing our superconducting 122-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 magnetic resonance at unnatural abundance (H in small amounts embedded in a deuterated compound) with remarkable simplification of the spectra. We are actively planning to interface our EMTR5 spectrometer to the Sigma V computer, and to develop storage and extraction of spectra for 2H magnetic resonance.

PUBLICATIONS


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 systems of one and two water molecules plus an extra electron for the system 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.


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.; Komka, J.; Smith, U.; Uphues, R. A. and Norris, J. R. Jr. (Argonne National Laboratory, Chemistry Division). Our research involves the application of stable isotope H^1, D^2, N^14, O^16, Mo^90 to chemical, biological, and biophysical problems. Our current activities fall into three categories: (1) labeling of living organisms of highly unnatural isotopic composition and the extraction of compounds of biological significance from these; (2) structure and function of proteins and enzymes; and (3) the role of chlorophyll in the light conversion in photosynthesis. In these studies, proteins and photosynthetic pigments of unnatural isotopic composition are key elements in the research.

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PUBLICATIONS


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 systems of one and two water molecules plus an extra electron for the system 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.

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 terrestrial 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

\[ \text{AH} + \text{BT} = \text{AT} + \text{BH} \]

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 polylysine 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.

In the design and operation of a chemical reactor 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 deuteration and tritium substitu-

ion 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.

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03:292 STUDIES OF CARBON ISOTOPE FRACTIONATION. Takamdu Iishida. 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 \(^13\text{C}\) 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.

As a result, low-temperature distillation of fluorinated hydrocarbons, in particular, chlorotrifluoromethane, dichlorofluoromethane, dichlorodifluoromethane, and fluoroform, is being studied. Systems for chemical purification, two catalytic systems for the decomposition of the fluorinated methanes to carbon dioxide have been assembled. The unit stage separation factor for the fractionation of \(^13\text{C}\) will be obtained from the transient behavior of the distillation process.

The shift in zero-point energy on the transition 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 \(\text{CCl}_2\) and \(\text{CCl}_3\) 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.

03:293 THEORETICAL STUDIES ON ISOTOPIC MASS EFFECTS IN CHEMISTRY. Max Wolsberg. 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 isotopic fractionation 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 almost been completed of the effect of corrections to the Born–Oppenheimer approximation on isotopic exchange equilibria involving a number of diatomic hydrides and deuterides. These 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 tritium molecules and atoms.

PUBLICATIONS

Wolsberg, M., A. A. Massa, and J. W. Pyper, Effect of Vibrational Anharmonicity on the Isotopic Self-Exchange Equilibria \(\text{H}_2 \rightleftharpoons \text{D}_2\) and \(\text{H}_2 \rightleftharpoons \text{D}_2\) (1971).


Chemical exchange between carbon dioxide (CO) and amine carbamates (RNCO\(\text{NH}_2\)) results in a concentration of \(\text{NO}^+\) in the gas and \(\text{CO}^+\) in the solution phase. A solvent carrier system with thermal reflux for stripping the carbon dioxide from the carbonates is used to test the effectiveness of different amines and solvents. D-n-butylamine (DBA) in triethylamine (TEA) as solvent was shown to be practical for the concentration of \(\text{CO}^+\) and \(\text{NO}^+\) by stripping.

A six-section cascade for the preparation of \(90\%\) \(\text{CO}^+\) is being operated to study some of the characteristics of the system. Measurements of single stage separation factors (a) 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 \(\text{CO}^+\) 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% \(\text{D}^+\) has been prepared by the exchange of NO with HNO\(_2\), 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., Fractionation of \(\text{D}^+\) and \(\text{O}^+\) Isotopes by Chemical Exchange of Carbon Dioxide with Amine Carbamates, Separ. Sci., 6(6): 819 (1971).

Mathur, B. P., Effect of Chemical Exchange Between \(\text{D}_2\) and \(\text{H}_2\) on the Thermal Diffusion Separation of \(\text{D}_2\) and \(\text{H}_2\) in a Trennenschaukel, J. Chem. Phys., 55: 3966 (1971).


There are now a number of investigations of proton-transfer reactions in solution which substantiate the importance of tunnel cor-
reactions. 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 (a) tunneling is favored 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 substances that are not 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, part 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 transition states.

Rates of base-catalyzed $H^+$, $D^+$, and $T^+$ transfer from several $\text{cyclotripyridinium}$, acetamidinium, and $\text{cyclotetrapirimidine}$ 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 see whether the effect of the 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 certain 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 barrier will be determined and the see whether derived from Brönsted'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 $\varepsilon$ in studies when tunneling is important.); and (e) to test the validity of Swain's relation systematically. (Since the Swain relationship has had few empirical important;); and (e) to test the validity of Swain's relation 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 chemical 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 reliability of repressing 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 refixxed. Single-stage fractionation factors in the range 1.01 to 1.02 for $^{34}$S/$^{32}$S 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 achievable by ion exchange. Separation factors appear to be measured for the isotopes of cobalt, calcium, and uranium on sulfonated styrene–divinylbenzene copolymers, polystyrene–divinylether–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**


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**


**03:300 LOW-TEMPERATURE ELECTROLYTIC ENRICHMENT OF TRITIUM IN WATER.** Robert L. Wolfe, 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 relationships between stable 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, isotopic effect studies are force probes at the atomic scale. The current experimental program utilizes this property of isotopic effects to study liquid structure in simple atomic and molecular fluids. Measurements of vapor-pressure isotope effects on simple solids (Ar, Kr, CO₂) 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 (V_{UCO₂} - 3V_{UH₂O})/2, not too different from the density index 3.

**PUBLICATIONS**


**03:302 A NUCLEAR MAGNETIC RESONANCE STUDY OF THE GAS–LIQUID CRITICAL POINT IN HYDROGEN AND ITS ISOTOPE MODIFICATIONS.** Max Lipson. (Yeshiva University, Belfer Graduate School of Science, 2455 Amsterdam Ave., New York, N. Y. 10033.)

This work represents a detailed nmr study of the gas–liquid critical region in H₂ and its isotopic modifications, HD and D₂. The nmr measurements encompass spin lattice relaxation times, T₁, 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 H₂ system itself. H₂ is in reality a quantum mechanical two-component mixture of ortho-hydrogen (½, J = 1) and para-hydrogen (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 T₁ and ρ on the ortho-H₂/para-H₂ ratio. We examine the coexistence curve both by measuring gas and liquid relative densities, ρₙ and ρₗ, and by measuring T₁ 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 T₁ and ρ, on the ortho-H₂/para-H₂ ratio.

2. The proton spin–lattice relaxation time T₁ for an ortho-H₂/para-H₂ mixture depends on both two-body and three-body molecular correlations. By examining T₁ as a function of the ortho-H₂/para-H₂ 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 D₁ and D₂ in a similar way. In HD there are no nuclear symmetry considerations and thus only D₂ exists in ortho and para forms. HD is, however, still a quantum mechanical fluid and will be studied both by proton magnetic resonance and deuterium magnetic resonance. In addition to acquiring information on the critical behavior of D₂ and HD, it will be possible to compare the behavior of D₂, D₁, 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 at 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 T₁ and ρ have been made and we are now in the process of obtaining final data on normal hydrogen (H₂) ortho.

The measurements will then be extended to samples of lower ortho-H₂ concentration.

**PUBLICATIONS**


THERMODYNAMICS

03:304 ISOTOPE EFFECTS ON RATE AND EQUILIBRIUM PROCESSES. Marvin J. Stern. (Yeshiva University, Department of Chemistry, Belcher 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 mechanisms 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 physical-chemical 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 deuteron 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.

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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: 02:211; Chemical Spectroscopy; 03:241; High-Temperature and Inorganic Chemistry: 03:261; Structure and Bonding: 03:346; 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, Chemical Engineering 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 $A_2MX$ 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(III), ([CH₃)₂NH]₂MnCl₄, 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) $A_2M_2O_7$ 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, $Na_xW_{2}O_{7}$, with $0 < x < 0.5$. 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 $\text{CrCl}_2\text{NH}_4\text{MnCl}_4$ by a thermal and magnetic study of the deconstruclional compound $\text{CrCl}_2\text{NH}_4\text{MnCl}_4$ in which propylammonium groups lead to interlayer spacings larger than in the methylvammonium compound; (b) revision of a currently operating program for tight binding band calculations of $A_2MO_7$ solids to increase inclusion of four center interactions; and (c) completion of initial susceptibility measurements on a La–Tm alloy to complement a thermal study of the crystal field interaction in rare earth metals.

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03:306 THERMODYNAMIC PROPERTIES OF INORGANIC COMPOUNDS. Trevbaugh, 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 enthalpy measurements 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 $\text{Na}_2\text{C}_2$ in equilibrium with sodium and graphite up to 800°C. This work is important because Na$_2$C$_2$ 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 $\text{Na}_2\text{UO}_4$ and $\text{Na}_2\text{MoO}_4$, which may yield different results 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.

Plans are being made to determine the thermodynamic properties of a number of other compounds of interest in the LMFBR program. These compounds include $\text{CeMoO}_4$, $\text{Cu}_2\text{O}$, $\text{H}_2\text{MoO}_4$, $\text{Ce}_2\text{CrO}_7$, $\text{TcF}_7$, $\text{TeO}_4$, $\text{PuO}_2$, $\text{PuF}_5$, and $\text{PuF}_6$.

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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, and of superconductors; and the study of the thermodynamic and transport properties of the two helium liquids \( ^{4}\text{He} \) and \( ^{3}\text{He} \) 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. Acoustic 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 several discrepancies in the existing theory, and we have definitely eliminated the one theoretical approach. Our goal is to establish unambiguously the excitation spectrum for \( ^{4}\text{He} \) 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 \( ^{4}\text{He} \)-\( ^{3}\text{He} \) and the determination of the quasiparticle-quasiparticle interactions in liquid \( ^{4}\text{He} \). An error in the temperature scale, discovered by us, has brought into question some of the previous work on \( ^{4}\text{He} \). 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.

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Another principle of the 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 \( \text{PuF}_3 \), \( \text{PuF}_4 \), \( \text{Na}_2\text{UO}_4 \), and UFSI; (b) compounds of important fissile products such as cesium, molybdenum, and technetium (e.g., \( \text{CsC}_6 \), \( \text{MoC}_6 \), and \( \text{TeC}_6 \)); and (c) other compounds of interest in reactor technology such as \( \text{NaC}_6 \).

The method is to measure the heat capacity (and related properties such as heats of transition and fusion) between room temperature and the boiling point of the substance. 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 Gibs and Helmholtz energies 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 other quantities 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 \( \lambda \) 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 supply an unambiguous wave function for the system 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


A computer method of evaluating equilibrium constants from spectrophotometric data has been developed for the following type of chemical system:

$$\log K_v = \log \left( \frac{[Y^n]}{[X]^{n-1}} \right) + nX$$

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 \( \log K_v \) are estimated by comparison of values obtained in separate experiments.

Very precise spectrophotometric data (40.001 absorbance units) for the PdBr₃Cl⁻ tetrahedral complexes were obtained for a wide range of lithium/bronze/chloride concentration ratios. The calculated values of \( \log K_v \) 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 PdBr₃Cl⁻ is 10⁴ times greater than that of PdBr₄⁻ 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

$$\text{UO}_2^{2+} + \text{In}^{3+} + 2 \text{H}_2\text{L} = \text{UO}_2\text{L}^- + 3 \text{In}^{3+} + 2 \text{H}^+$$

where two of the protons come from the hydroxyl groups. The logarithm of the constant is -11.38. Infrared measurements on tributarium (tribridonolaminate) extract of the mixed metal complexes have been made and are discussed.

The dimerization constant for the formation of (UO₂⁺⁺⁺) 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

$$\text{UO}_2^{2+} + \text{H}_2\text{L} = \text{UOH}_{\text{L}}^- + \text{H}^+$$

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

$$\text{UO}_2^{2+} + \text{In}^{3+} + 2 \text{H}_2\text{L} = \text{UO}_2\text{InL}^- + 3 \text{H}^+$$

where two of the protons come from the hydroxyl groups. The logarithm of the constant is -11.38. Infrared measurements on tributarium (tribridonolaminate) extracts of the mixed metal complexes have been made and are discussed.

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.

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. Both types of measurements give information 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 project the contributions to an understanding of the properties of materials is obtained by heat capacity measurements at low temperatures. Several metal-insulator transitions, in VO₂ and SnS₂, are being studied by measurements of the heat capacity at pressures up to 25 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 corium, 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 ³He 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 to be studied are dilute solutions of rare earth metals in noble metals.

A series of related experiments on the powdered CMN (cerium magnesium nitrate (Ce₂Mg₃(NO₃)₈·24H₂O)) temperature scale and the Kappa 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 autostereotropy thermometer by adiabatic demagnetization of a cell containing liquid H3O, powdered CMN, and a γ- ray thermomenter attached to copper fins. Some preliminary information on the Cu2+–Hg Kapitza resistance will be obtained in the same experiment. In later experiments the field dependence of the CMN–Hg 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


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 H3O+ 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 CCl4 and isooctane; the existence of H3O+–TBP 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: H3O+ species. We believe this is just an example of a stepwise complexing of the H3O+ ion by TBP, and it spectra indicate essentially the same (H3O+)+ structure. Our present work uses trioctylphosphine oxide (TOPO) as extractant. This is more basic than TBP, and we find that two molecules of TOPO can abstract the proton from water to form an essentially aprotic species, TOPO–H+–TOPN, 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 complexes leads to interesting activity coefficient effects, which 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, H. D. Bayard (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 complex, 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 in such solutions; (3) kinetic 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 complexes, 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


03:317 THERMOCH EMISTRY. Busey, R. H., 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 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 CeO2, CeO2, and CeO2, a series of compounds exhibiting interesting order–disorder transitions. The low-temperature calorimeter will be employed for measurements on rare earth halides, where the scarcity of accurate values of the entropies derived from such low-temperature heat capacity observations makes their acquisition of importance.

PUBLICATION


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 reactions and rational design of processes such as sequence 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 solutions to cover extremes of activity coefficient behavior with cation pairs of various charges, e.g., Na+ and H+, Ba2+ and UO22+, 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 the high solubility of many per-
chlorates allows measurements under conditions in which ions interact in the presence of very little water.

**PUBLICATIONS**


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–MgCl₂ 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 by 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**


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**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 polycrylate, shows great promise for the economical recovery of waste and brackish water via reverse osmosis or hyperfiltration techniques. Polyelectrolyte gels, such as the natural 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, micropolarimetry, 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 applicability in the preparation of an attractive new type of nuclear fuel particles for high-temperature, high-performance gas-cooled reactors.

**PUBLICATIONS**


Bamberger, C. E., R. G. Ross, and C. F. Baez, 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 BeF₂. 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, Cr₂O₃, MgO), fission products (Na₂O), and actinides (ThO₂, PuO₂, PaO₂, UO₂, PuO₂) as a function of melt composition and temperature. The results, along with available formation free energies and entropies for the solides, will yield improved thermodynamic values and activity coefficients for the corresponding dissolved fluorides. Oxide ions of the various metal cations generally are not formed, except for cations of small size and high charge; thus, Na₅O₂ seems to form an axion ion but Pa₂O₇ 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–BeF₂ melts.

**PUBLICATIONS**


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**03:322 HIGHLY CONCENTRATED AQUEOUS ELECTROLYTES**. Brauneinstein, J., and H. Brauneinstein. (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 electropolishing, water electrolysis, and corrosion. The study of solutions, which carry activity in hygroscopic salts, such as Ca(NO₃)₂, and their mixtures with weakly hydrated salts, such as KNO₃, will be extended to deuterium oxide, to aid in characterizing the ion–water, water–water, and ion–ion interactions. The same activities will be used also, with the EMP of cells with transference, to determine transference numbers. Determined association equilibria of Cd²⁺ with Br⁻ in Ca(NO₃)₂–xH₂O electrolytes will be extended to a broader concentration basis (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, H., and J. Braunstein, Isoosmotic Studies of Very Concentrated Aqueous Electrolyte Solutions of LiCl, LiBr, LiNO₃, Ca(NO₃)₂, LiNO₃ + KNO₃, LiNO₃ + Ca(NO₃)₂ + Ca(NO₃)₃ at 100 to 150°C, J. Chem. Thermodyn., 5: 419−431 (1971).

**03.323 TRANSPORT AND THERMODYNAMICS IN MOLTEN SALT MIXTURES.** Braunstein, J., H. R. Braunstein, 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 or charge. 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**


**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 BF₃(g). This gas acts as a thermodynamic probe, reacting with fluoride ions in the melt to form tetrafluoroborate (BF₄⁻) ions. Specifically, BF₄⁻ solubility measurements is a direct means for determining the activity of alkal fluoride in multicomponent fluoride systems. In the range, 0 to 60 mole % LiF−10 mole % LiF−75 mole % LiF−ThF₃, solubility of BF₄⁻ is measured (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−BeF₂.

In LiF−BeF₂−ThF₃ (72−16−12 mole %), solubility measurements showed that LiF activities were about one-half those in LiF−BeF₂. Further study in LiF−BeF₂−ThF₃ mixtures will be used to compare interactions of LiF−ThF₃ with those of LiF−BeF₂.

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**


**03.325 HIGH-TEMPERATURE AQUEOUS SOLUTION CHEMISTRY.** Marshall, W. L., Jr., and L. H. 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 400 atm) through studies of electric conductance and solubility behavior with unique apparatus developed at ORNL. Extensions of solute ionization, solubility relations, evaluations of solute−solvent interactions, and thermodynamic properties of solutions are obtained. These studies show that at high temperatures ion transport in conducting electric currents is to 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 range of temperature and pressure. These predictions are important for better understanding the effect of electrolytes on 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 conductance data for several additional salts, for example, CaCl₂ and MgCl₂. 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 in geochemistry.

**PUBLICATIONS**


**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 HCO$_2$, silicate acid, the alkaline earth cations and also more complex solubility behavior of transition metal oxide systems.

**PUBLICATIONS**


**ALSO SEE**


**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 thermo-couples or in situations where the placement of a thermometer will 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 metallic 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 emittance 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 oxide. The solution of some 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 transmission technique is used for measuring vapor pressures above 10$^3$ mm Hg. This apparatus, which is capable of temperatures up to about 1400°C, will be most useful in determining vapor pressures of refractory and high-melting metals, alloys, and other compounds, such as oxides, carbides, and nitriles.

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**


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 both 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**


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 the mechanisms whereby transition metal compounds catalyze the reactions of carbon monoxide and amines to form organic formamidines, 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 aminocarbamido complexes, $\text{L}_n\text{M} = \text{C}=\text{O} + 2\text{RNH}_2 \rightarrow \text{L}_n\text{M} = \text{C} = \text{O} + 2\text{RNH}_3$ where $\text{L}_n\text{M}$ may be a variety of other ligands. Such reactions occur with $\text{[Cr(H}_2\text{O)}_6\text{]}^3+$, $\text{[Fe}^{\text{II}}\text{(CO)}_4\text{]}^2+$, $\text{[Fe}^{\text{III}}\text{Ru(CO)}_6\text{]}^2+$, $\text{[NH}_3\text{Ni(CO)}_4\text{]}^+$, $\text{[NH}_3\text{SH}_2\text{Ru(CO)}_4\text{]}^+$, $\text{[NH}_3\text{SH}_2\text{Co(CO)}_4\text{]}^+$, $\text{[H}_2\text{Mo(CO)}_4\text{]}^+$, and $\text{[H}_2\text{W(CO)}_4\text{]}^+$ while others such as $\text{[Mn(CO)}_3\text{]}^+$ and $\text{[Fe}^{\text{II}}\text{H}_3\text{]}^+$ form equilibrium mixtures of starting complex and a carbamido product. Finally, there are carbamido complexes that do not react with amines at all; representatives are $\text{RNH}_2\text{Mn(CO)}_3\text{]}^+$, $\text{[RNH}_2\text{H}_2\text{Re(CO)}_4\text{]}^+$, and $\text{[RNH}_2\text{Mn(CO)}_5\text{]}^+$. 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 carbamido 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 carbamido formation. Although this correlation may be rationalized theoretically, its greatest use at present is in predicting the formation of carbamido inter-
mediates 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., \( \text{Cd}_{6}^{2+} \), \( \text{I}_{3}^{-} \), 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.

Largely these anions have been found to enhance the stability of these polyatomic cations, and the ion \( \text{AlCl}_{4}^{-} \) has proved to be particularly convenient for use in synthetic routes involving molten salt media. Nuclear quadrupole resonance (NQR) data are being accumulated for \( \text{AlCl}_{4}^{-} \) in such salts to determine easily whether free \( \text{AlCl}_{4}^{-} \) 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 \( \text{Br}_{3}^{+} \) and \( \text{ICl}_{3}^{-} \) are also being obtained for the structural characterization of cations such as \( \text{ICl}^{2+} \), \( \text{ICl}^{+} \), \( \text{I}^{+} \), and \( \text{I}^{-} \) in their \( \text{AlCl}_{4}^{-} \) salts.

Synthesis of bromine and of other interhalide cations such as \( \text{Br}_{3}^{+} \) and \( \text{ICl}_{3}^{-} \) as well as investigations with counter-ions other than \( \text{AlCl}_{4}^{-} \) are underway. A synthetic, NQR, and x-ray study of compounds reputed to contain the \( \text{GaCl}_{4}^{2-} \) anion is also in progress since other formulations seem not to have been excluded. The x-ray characterization of the cation in \( \text{Bi}_{2}^{2+} \text{(AlCl}_{4}) \) has been frustrated by technical problems, the 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 (e.g., \( \text{Pb}, \text{Sn}, \text{Bi} \)) that are isoelectronic with known cations, further investigations are in progress.

PUBLICATIONS


Friedman, Robert Mark, and John D. Corbett, Bismuth(III) in the Solid State. The Crystal Structure of \( \text{Bi}^{3+}(\text{Bi}^{3+})_{8} \text{(HCl)}_{10} \), Chem. Commun., 421 (1971).


Couch, Thomas W., Donald A. Lokken, and John D. Corbett, The Crystal Structures of Tetraletrilumium(2+) Tetrahalohalolinate and Hexaphloridolinate, \( \text{T}_{4}^{2+} \text{(AlCl}_{4})_{2} \) and \( \text{T}_{4}^{2+} \text{(AlCl}_{4})_{2} \), Inorg. Chem., 11: 357 (1972).

03:322  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 oxidant media. Nuclear quadrupole resonance (NQR) data are being accumulated for \( \text{Cl}_{3}^{+} \) in such solids to determine easily whether free \( \text{Cl}_{3}^{+} \) 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 \( \text{Br}_{3}^{+} \) and \( \text{ICl}_{3}^{-} \) are also being obtained for the structural characterization of cations such as \( \text{ICl}^{2+} \), \( \text{ICl}^{+} \), \( \text{I}^{+} \), and \( \text{I}^{-} \) in their \( \text{AlCl}_{4}^{-} \) salts.

Synthesis of bromine and of other interhalide cations such as \( \text{Br}_{3}^{+} \) and \( \text{ICl}_{3}^{-} \) as well as investigations with counter-ions other than \( \text{AlCl}_{4}^{-} \) are underway. A synthetic, NQR, and x-ray study of compounds reputed to contain the \( \text{GaCl}_{4}^{2-} \) anion is also in progress since other formulations seem not to have been excluded. The x-ray characterization of the cation in \( \text{Bi}_{2}^{2+} \text{(AlCl}_{4}) \) has been frustrated by technical problems, the 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 (e.g., \( \text{Pb}, \text{Sn}, \text{Bi} \)) that are isoelectronic with known cations, further investigations are in progress.

PUBLICATIONS


Friedman, Robert Mark, and John D. Corbett, Bismuth(III) in the Solid State. The Crystal Structure of \( \text{Bi}^{3+}(\text{Bi}^{3+})_{8} \text{(HCl)}_{10} \), Chem. Commun., 421 (1971).


Couch, Thomas W., Donald A. Lokken, and John D. Corbett, The Crystal Structures of Tetraletrilumium(2+) Tetrahalohalolinate and Hexaphloridolinate, \( \text{T}_{4}^{2+} \text{(AlCl}_{4})_{2} \) and \( \text{T}_{4}^{2+} \text{(AlCl}_{4})_{2} \), Inorg. Chem., 11: 357 (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 transitions of simple structural and bonding models, and the 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 (e.g., \( \text{Pb}, \text{Sn}, \text{Bi} \)) that are isoelectronic with known cations, further investigations are in progress.

PUBLICATIONS


03:334  HIGH-TEMPERATURE AND INORGANIC CHEMISTRY. Franzen, Hugo F. (Ames Laboratory, Chemistry Division).

The 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 species, 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 nuclear quadrupole resonance (NQR) spectroscopy, 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-chalcogenides of transition metals and studies of the preparation, structure, and properties of mixed sulfide-phosphide systems are in progress.

**PUBLICATIONS**


**03:35 THE CHEMISTRY OF HEAVY TRANSITION METAL COMPOUNDS**

McCarrory, 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(III), Ta(III,IV), 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 of fused salt media have provided efficient routes to Mo(NH_3)_4^2+ and W(NH_3)_6^3+, (X = halogen) cluster species, whereas previously unknown metal–metal bonded dimers, Nb(NH_3)_4(C_2H_5), Ta(NH_3)_4(C_2H_5), and MoW (CH_3COOH)_4, have been obtained via reactions in more conventional non-aqueous systems. The objective of developing methods for producing more complicated mixed metal cluster compounds by stepwise addition of metal atoms to simple metal halides is a current research focus.

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, ^118Nb, ^187Ta, ^186Re, and ^187Re, which commonly form metal–metal bonds, all may be studied by this technique. The first pure NQR spectra for any compounds of ^187Ta 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**


**03:36 PHASE RELATIONS IN LITHIUM–CHALCOGEN SYSTEMS**

Cunningham, P. (Argonne National Laboratory, Chemical Engineering Division).

The electrochemical couples of lithium and the chalcogenes 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 137°C). A miscibility gap, with a critical temperature above 600°C, extends from about 0.2 to 37.0 atom percent lithium above a monostatic temperature of 364.8°C. The lithium–tellurium system has two intermediate phases, LiTe (mp 120°C) and Li_2Te (mp 459.3°C). The Li_2Te phase has not been reported previously. Two eutectic reactions occur: one at 418.5°C [liquid → Li_2Te + Li_2Te_3] and the other at 448.5°C [liquid → Li_2Te + Li_2Te_5].

**PUBLICATIONS**


**03:37 PHASE EQUILIBRIUM AT HIGH TEMPERATURES**

Ackermann, R. J., and R. H. Winninger, 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°C. The important experimental aspect involves the successful containment of 100- to 300-ng 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_3 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 2874°C have been studied by means of a high-temperature, controlled-atmosphere diffractometer (with C. A. Sorrell, University of Missouri, Rolla). 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 a–ß 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 ß–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 ß–quartz structure.

The existence of holes in structures at high temperatures provides the necessary ingredient for the mechanism of diffusion. The compounds UO_3 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.

**PUBLICATIONS**

Into this category fall such materials as the noble gas compounds, higher-valent actinide compounds, perbromic acid and the perbro- 
molates, astatine compounds, and a variety of reactive fluorine-
doing-containing compounds, such as the recently synthesized hypo-
fluorous acid.

We are now completing work on the infrared, NMR, photoioniza-
tion, and photoelectron spectra of hypfluorous acid, in collabora-
tion with H. E. Appelman, D. M. (Argonne National Labora-
tory, Chemistry Division). PUBICATIONS


Appelman, E. H., The Oxidation of Halates to Perhalates by Xenon 

Appelman, Infrared Spectrum of Matrix-Isolated HOF, Spectrochim.  

Kim, H., E. F. Pearson, and E. H. Appelman, Millimeter-Wave 
Spectrum and Structure of Hypofluorous Acid: HOF and HOF. 

Johnson, G. K., P. A. O'Hare, and E. H. Appelman, Ther- 

03.339 STUDIES OF CHEMICAL SPUTTERING, DEUTERIDE 
AND TRITIDE MOLECULE FORMATION AND TRAPPING IN 
THERMONUCLEAR REACTORS. Green, D. M. (Argonne Na-
tional 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 in-
ventory in a fusion reactor will be strongly influenced by chemical 
compound formation. Some of the areas where compound forma-
tion possibly occurs 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 thermal-
ized at some state of the operation of the machine so that the un-
bound 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 decomposi-
tion at the higher temperatures. The estimated flux of 2×10^{17} 
ions/cm²/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 condi-
tions will, therefore, be entirely different from rates determined 
on clean surfaces. It is, therefore, important, for example, to 
study the wide range of materials for their trapping efficiency 
and to define their optimum operating parameters.

One separation technique that has been developed is chemical 
sputtering with a matrix. Chemical sputtering has been observed 
with this device. In very recent experiments the matrix isolation technique 
has been used in conjunction with an isolated separator that pro-
duces monoenergetic mass-selected particles. This work is aimed 
at developing a new, sensitive, and quantitative method of measur-
ing sputtering yields. Because of the known difficulties in measur-
ing sputtering yields of the hydrogen isotopes, it allows separation 
of molybdenum, and vanadium, the new method, which does not in-
clude target weight loss data, will be applied to these metals.

Studies of the gas phase reactions 2Mg(g) + H₂(g) = 2MgH₂(g) are 
being undertaken in order to study the thermodynamics of the 
reaction, which is expected 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 con- 
trolling plasma contamination.

Work is also underway on a chemical accelerator (with S. Weixler 
and E. K. Parks) utilizing the scattering of ionized and neutral D₂ and T₂ molecules and D and T 
atoms from Nb surfaces as a function of surface coverage and 
temperature, collision energy, exchange of energetic neutrals with the thermal neutron flux, and the desorption of 
sputtered metal atoms with D₂ and T₂ molecules.

Theoretical calculations (with A. C. Wahl) have already yielded 
prefinal confirmation for the existence of chemically bound 
existed states of T, D, and H, molecules, which had also been 
proposed in 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 determine detailed information 
on the uranium—oxygen and related systems (e.g., ternary sys-
teums 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. Hydro-
thermal and related 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, and thermoanalytical methods. The utility of photoelectron spectroscopy (ESCA) to this project will be deter-
ned as it becomes available.

Recently completed was the UO₂—H₂O system has supplied new 
data on each of the six phases in this system, including com-
plete structural determinations (with S. Siegel) on two of them— 
Y₂O₃UO₂H₂ and H₂U₂O₄. A related study on the rare earth uranates 
is in progress. Several series of compounds have been identi-
fied in these systems.

The program for the near future will be directed toward an in-
vestigation of several UO₂—MO₃ systems where it represents 
fixation of some component that will become more important 
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 

——, S. Siegel, and F. X. Gallagher, Reaction of Platinum Di-
oxide with Some Metal Oxides, Advan. Chem. Ser., 98: 49—53 
(1971).
03:342 STUDIES OF CHEMICAL METHODS FOR REMOVING RADON AND XENON FROM AIR. Stein, L. (Argonne National Laboratory, Chemistry Division).

Redox reactions 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. Post- (half-life 3.82 days) is a naturally occurring air contaminant in daughters decomposed by radiation (half-life 9.2 days) and HXe (half-life 9.2 days) are fission product gases that are released to the atmosphere by nuclear power plants during the de-cladding and dissolution of uranium fuel elements. Liquid bromine trifluoride and a number of solid halogen fluoride—metal fluoride complexes, such as CIF$_2$F$_2$, BrF$_2$F$_2$, BrF$_2$BrF$_2$, and BrF$_2$BF$_4$, have been shown to remove radon from air efficiently at 23 to 25°C (through the formation of volatile radon ions or compounds). The solid compounds can be recycled and reused but may be used in combination with desiccants for removal of Post- from recirculated (secondary) air in mines and for analysis of Post- in air. An oxygenyl complex, OsF$_6$, containing the Os$^2+$ cation, has been shown to react with both radon and xenon at 23 to 25°C. This appears very promising as a reagent for removing the heavy noble gases from air because it has a low vapor pressure at 25°C and produces only oxygen as a gaseous reaction product. Efforts are now being directed toward obtaining pyrolysis mixtures with OsF$_6$ and to determine optimum conditions for preparing OsF$_6$ by photochemical methods.

PUBLICATIONS


03:343 THERMOCHEMISTRY AT HIGH TEMPERATURES. Thorn, R. J.; Ackermann, R. J.; Hoekstra, H. R.; McCready, J. R.; Rauh, E. G.; and Winslow, G. H. (Argonne National Laboratory, Chemistry Division).

The program in high-temperature chemistry at Argonne National Laboratory is concentrating on the development of thermochromical investigations of inorganic compounds of the transition metal, lanthanide, and actinide elements at temperatures ranging from 900 to 3000°C.

Current investigations are directed toward understanding the structures of material that may be of interest in both fusion and fission reactors, the vaporization process, and the thermochromism 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 intercalation and extrapolation to new or unavailable conditions of temperature, pressure, and material composition.

Developments in these significant experimental techniques are of current interest in many fields, including temperature and controlling devices, simultaneous measurements of the mass effusion from a Knudsen cell and mass spectrometric analysis of the effusate, and the introduction of photoelectron spectrometry.

Historically, this has been the disadvantage of the optical pyrometer using visual matching and, therefore, individually calibrated by each experimenter. A camera lens assembly has now been substituted in an I$_4$N automatic pyrometer to permit 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 ±0.02°C for the Knudsen cell seems to be attainable and temperature measurements and control are no longer limiting.

A recording microvolumetric balance and a quadrupole mass spectrometer valved off within an ion pump and thus maintained at high vacuum (10$^{-6}$ 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$_2$-$x$), solids with mixed central atoms (e.g., UP$_{6-x}$O$_{12}$), 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


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 gases of a single type of compound (for example, gaseous monoxides) that span the periodic table and are of fundamental importance in general studies of chemical bonding are being studied at Argonne in an effort to develop new chemical groups for use in the study of chemical reactions at high temperatures.

Precise systematic relations among monoxides are derived from measurements of isomolecular exchange reactions such as Y(O + ZrO) = YO + Zr(1). Complete studies from which derived accurate dissociation energies include YO, ZrO, HIO, THO, UO, CeO, and LaO. Thermochromical 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 spectrosopic studies to supplement our existing measurement facilities.

Studies in progress or planned include additional oxides and lanthanide and actinide fluorides.

PUBLICATIONS


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 thermochromical parameters for representative oxides, particularly the lanthanides. For example, for the lanthanide monoxides, mononucleides, 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 chlorides, and trihalides, and an analogous series with a more typical lanthanide.

A systematic approach 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 (UO$_2$-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).

A large number of 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 be-
behavior of nonstoichiometric phases characterized in actinide oxidation 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 ThO2 and correlate lattice parameters as a function of temperature and thermochromic measurement for both UO2+x and UO2-x phases. A phase important in fuel elements for nuclear reactors (often as UO2+xO2-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


03:347 HIGH-TEMPERATURE PHYSICAL CHEMISTRY.

Egan, J. J. (Brookhaven National Laboratory, Department of Applied Sciences), 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 alloy 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-Na, 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


03:348 INTERMEDIATES IN OXIDATION—REDUCTION REACTIONS. THALLIUM(III). Dodson, R. W. and Schwarz, H. A.

Thallium(III) 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(III)—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 x 10^5 cm^3 mol^-1 sec^-1 for the specific rate at which ThIII oxidizes iron(II) in 1 M HClO4. Direct measurement by pulse radiolysis gives 6.7 x 10^6 cm^3 mol^-1 sec^-1. Other reactions measured by pulse radiolysis were: OH + Ti^3+; H + Ti^3+; and 2Ti^3+ + Ti^3+ + 4H^+ + O_2. The absorption spectrum of Ti^3+ in 1 M HClO4 was determined from 225 to 370 nm. The kinetic results, in conjunction with other data, show that the reaction Ti^3+ + Ti^3+ + 4H^+ + O_2 is too slow, by many orders of magnitude, to play a significant role in the normal thallium(III)—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


03:349 KINETIC STUDIES OF SUBSTITUTION AND OXIDATION—REDUCTION REACTIONS INVOLVING COMPLEX IONS IN SOLUTION. Satin, 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 through 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 will be investigated in conjunction with the electron-transfer work. Current work involves studies of the rate of added chloride, azide, and thiocyanate ions on the rate of reduction of Fe(phen)3^2+; Co(phen)3^2+; and porphyrinates of iron(II) and Fe(II). 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


03:350 HIGH-TEMPERATURE THERMAL PROPERTIES OF РеАCTOR 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 become a necessity. 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 2180 ± 2 psi and the critical temperature as 3642 ± 2°F. The vapor pressure fits an equation of state for potassium which is too be extended in the next contract year to sodium, of importance in actinide oxide fuel elements in nuclear reactors. 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 through 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 will be investigated in conjunction with the electron-transfer work. Current work involves studies of the rate of added chloride, azide, and thiocyanate ions on the rate of reduction of Fe(phen)3^2+; Co(phen)3^2+; and porphyrinates of iron(II) and Fe(II). 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


Employing a different original titling capsule technique, the critical density of rubidium was found to be 0.347 g/cc. The critical temperature was obtained as 331°F, in rather good agreement with 331°F obtained earlier by the entirely different pressure tube method for an average of 332°F, probably correct to ±0.2%.

PUBLICATIONS


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 well-established spectroscopic importance of porphyrin-like metal complexes, their selective tumor distribution properties, especially in combination with toxic and radioactive metal ions, make them attractive potential chemothapeutic 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 Mossbauer studies on iron and manganese complexes will determine the validity of the Griffith–Rotani theories for obtaining zero-field splitting parameters from low-temperature magnetic measurements.

PUBLICATIONS


03:362 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 TiO phase at high temperature and to a resolution of the controversy on the dissociation energies of TiO(g) and TiO(g).

Studies will be undertaken to measure the fragmentation patterns of TiO(g) and TiO(g), to measure the oxygen potential throughout wide regions of the TiO system, and to explore the use of the mass spectrometrically determined TiO/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 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


Chen, H., and W. S. Gilles, High Molecular Weight Boron Sulfides, VIII. Vapor Pressures of 8B3(g) and 8B3(g) over Stoichiometric B2S3, J. Phys. Chem., 76: 2035 (1972).


The search for new noble gas compounds, particularly ArF+ and new XeF7 salts, continues but the major emphasis is on the use of known compounds as synthetic reagents. The thermally stable salt KArF+([SbF6]-) is a powerful oxidizer and is being used in efforts to make BrF5+, ClF5+, and XeOF7 salts. Our crystallographic studies have proved that the XeF3 cation occurs in the compounds XeF3[AsF6]-, XeF6[PF6]2-, and XeF5[PF5]6. We have also established the salts [XeF6]3+, [XeF5]2+, [XeF4]1+, [XeF3]1+, [XeOF3]1+, and [XeOF]1- and shown that the binary xenon fluorides, XeF6 is the best fluoride ion donor. Since XeF6 is a good base and a good ionic solvent, it promises to be an excellent reagent (with elemental fluorine) in the generation of hitherto unknown (or uncertain) oxidation states (e.g., Au(I'), Hg(RV); PdF6, and XeF6) probably correct rates.


Chen, H., and W. S. Gilles, High Molecular Weight Boron Sulfides, VIII. Vapor Pressures of 8B3(g) and 8B3(g) over Stoichiometric B2S3, J. Phys. Chem., 76: 2035 (1972).


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. The synthesis 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 donation 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**


**03:355 SOLID STATE MATERIALS SYNTHESIS. Donaghy, 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 for processing of varying structure-dependent 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, , and several chromium halogenide spinels have been studied theoretically and subjected to qualitative 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 GeH3 ion, the Ge(CH3)3 ion will be used as a reagent. We shall attempt to quench some of the reactive intermediates formed in the acid hydrolysis of BH3 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.

**PUBLICATIONS**


**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 which exhibit multiple oxidation states. A current project involves determination of the decomposition/ vaporization mode of samarium oxide and samarium fluoride. 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 SmBr3. Cursory vaporization studies of YbCl and SmBr3 are in progress; a detailed study of TmF3 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 Yb2Si2O7Cl, a phase that forms when YbCl3 and YbCl3 are sealed in quartz under a Cl2 atmosphere, are progressing; a detailed study of Tm2F7 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.

State studies of the decomposition of these compounds 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 La2O2Si2, which contains acetylenic 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**


**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 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 samarium 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 salt-like species Li2Bi between the liquid alloy phases. In the future, similar studies using 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


03:359 PROTACTINUM 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 reactor solutions (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 PaF3 from molten LiF–BeF2–HF–Ar gas mixtures by equilibration with H2O–HF–Ar gas mixtures is being studied, using a transeptation 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 PaO2 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 H2O are about 0.2 atm. In future work, the conditions under which both protactinium and uranium oxides precipitate will be determined with more accuracy. When solid mixtures are in equilibrium with solid PaO2 and the appropriate low-temperature gas mixture, both PaO2 and PaF3 can exist in the salt. The transeptation method will, also, be used to determine the equilibrium constants for the reaction PaF3 + 1/2 O2 = PaO2 + HF. This equilibrium constant, with other available data, allows calculation of the maximum oxide concentration permissible in an MSBR at a given temperature.

PUBLICATIONS


Mallen, J. C., and F. J. Smith, Estimated Free Energies of Formation of Some Lanthanide and Actinide Halides at 2000 to 3000°C is difficult to measure or to predict. Therefore, other compounds of fluoride structure (e.g., BaF2) will be sought in which the conductivity at lower temperatures will model that in UO2 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


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 20K 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, N2, O2, and NO, have been made. We have observed reactions with all of the above small molecules with matrix-isolated NiF2 and NiCl2. In all cases the species formed, NiF2(VI), were previously unknown. We anticipate continued studies in this area with emphasis on trapping transition metal catalytic intermediates.

PUBLICATIONS


03:362 CHELATION OF TRANSITION METALS BY DERIVATIVES OF 3-NITROSO-2- PYRIDINOL AND 5-NITROSO-4- PYRIMIDINOL. 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 metalating portion 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**


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) abnormal oxidation states, the stabilizations 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 (0) species as components of coordination compounds are virtually unknown. We propose to generate the monoxide, UO2, or analogous compounds of the higher actinides, thorium and uranium. For example, the higher oxidation states of thorium 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—whether analogous or not to the higher actinide species—might be of interest in connection with isotope separations using the gas centrifuge.

**PUBLICATIONS**


--- and John S. Thompson, Jr., The Interaction of Liquid Ammonia and Urca and Thiourea Complexes of Copper(I) and (II), Silver(I), Zinc(I), Nickel(I), and Palladium(II), J. Inorg. Nucl. Chem., 33: 1319 (1971).


**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 anamionic acid, a key fungal metabolite of unknown structure; synthetic and natural dimeric alkaloids related to the clinically important anti-cancer alkaloids vinblastine and lomustine; a potent toxin from A. gravis; and oleandromycin, a macrolide antibiotic. In conjunction with these problems we are investigating new methods of analysis, 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 interest are those related to reactions of molecules with strained carbon—carbon bonds or fluxional structures. We are investigating the bromination products of some bunsulvalene and bunsulvaline. 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.


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 similar to those calculated from smaller-dimensional Fourier series can be calculated in one-fifth to one-twenty-fifth of 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**


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 complex. 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(NH3)2SbCl4 indicate that the SbCl4⁻ anion has undistorted octahedral shape with no evidence of lone pair distortions; however, preliminary results on Co(NH3)2SbF6 indicate that the SbF6⁻ 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 pyramidal distortion is too small to be detected. The difference in these two structures containing identical cations could be ascribed to differences in electronegativity between fluoride and chlorine or to a size difference between the two halogens. Future plans include extended structural studies including investigations of K3SbCl6 and Cs3SbBr9.

Refinement of the (CuL3)2ClO4 structural data (L = 2,2'-bipyridylamine) indicates a distorted five-coordinate trigonal bipyramidal geometry with one of the L-inorganic ions at the apical position. Previous geometries found for us for such complexes involve distortions square pyramidal and distorted octahedral. Studies of tripyridylamine complexes of copper such as Cu[tripyramid]Cl4 and Cu[tripyramid]SCNClO4 are planned.


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 analogues are being investigated using neutron diffraction techniques with the applied magnetic field of up to 25 kilogauss at temperatures between 2K 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 isonuclear series, Ce, Pr, Nd, and Ho, (H = 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 for further information regarding the electronic spin interaction. The same technique, the inelastic neutron techniques 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 waves in the thermally and magnetically excited states. The solid solution systems, US-UC and UO2-SCO2, which may well be of interest in a systematic study of refractory uranium compounds, are scheduled for investigation, though not in the immediate future.


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 455K for VH2 and VH3. These measurements cover a range of momentum transfers, for elastic scattering up to 4.1Å⁻¹. The line width results are compared with proposed models involving 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 VH3. The results also suggest that the large Debye-Waller factors found in the present and previous neutron-scattering experiments on VH3 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 TaH2.4 from 293 to 613K. These data are now being analyzed and additional data are being obtained for TaH3.
acterized by unusually short O–H–O bonds and the key H bonds involving the acid protons are the shortest ones and are typically defined by millimeter or larger volumes, single-minimal-configuration structures. 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 proton conduction and transfer phenomena of importance in aqueous liquid and biochemical systems.

Current hydrated proton studies include $H_2PbCl_6 \cdot 6H_2O$, nitramic acid hexahydrate, sulfamic acid trihydrate, and $Pt(OH)_3Cl$, chromic 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.

Extrusions to such compounds as $H_2B_2O_7$, $HBr \cdot H_2O$, and $H_2Mo(CN)_6 \cdot 6H_2O$ 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 (CHICl)$_2$, $BrI_2$, and $(F^- \cdot HF)_2$ ions. Longer range plans envisage a shift of attention to systems of biological importance.

**PUBLICATIONS**


Peterson, S. W., J. M. Holloway, B. A. Coley, and J. M. Williams, Acidic and Basic Coordination About Xenon: The Structure of Nitrosonium Octafluoroxenate(VI), Science, 173: 1238 (1971).


03:370 STRUCTURAL AND SPECTRAL CHARACTERIZATION OF SOME ANHYDROUS DOUBLE NITRATE SALTS OF THE LANTHANIDES. Siegel, S., Cornall, W., Ferraro, J., and Gebert, E. (Argonne National Laboratory, Chemistry Division).

Structure investigations employing x-ray-crystallographic and neutron-diffraction techniques are being carried out in order to aid in relating the thermodynamic properties of the rare earth ion to its site symmetry.

The first compound to be investigated is $K_2Pr(NO_3)_5$. The symmetry of the crystal is cubic with $a = 13.82$ Å and the space group is $O^3$. 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, each 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 (K. Cornall) indicate a strong correlation between the intensities of the transitions and the site symmetry of the rare earth ion. As a result, more studies are to be investigated in detail. $K_2Er(NO_3)_5$, which is monochonic, is currently under study. Similar studies, possibly with actinide sulfates, are also being contemplated.


Current emphasis has been directed towards a study of the $UO_2 \cdot H_2O$ system, covering elucidation of structure and the nature of the hydrogen bonding.

The structure of $UO_2 \cdot 2H_2O$ has been completed. The configuration shows chains of shared octahedra and bipyramids, each with a given configuration, 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. Cu$_2UO_6$ has been studied to exhibit a similar grouping, but with the Cu atoms bonded to the oxygen configuration. A morphological relationship to $UO_2H_2O$ has been found.

The structure of $UO_2 \cdot 4H_2O$ 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 transition of the $\beta$- and $\gamma$-forms of $UO_2H_2O$. With proper choice of orientation, orthorhombic $UCNO_2H_2O$ exhibits pseudo monoclinic symmetry with cell dimensions close to those of monoclinic $UCNO_2H_2O$. However, the $\beta$-angle of the pseudo cell is about 10° larger than that in the $\gamma$-phase. This causes a one Angstrom translational difference between the two structures.

It is believed that one Angstrom shift causes a slight rotation of the U-6(0) octahedron, permitting a shift in two of the four hydrogen bonding directions. A report by Bannister and Taylor, Acta Crystal., 26: 662 (1971), shows that the U-6(0) octahedron, the octahedra of the $\beta$-modification exhibit rotation. Gridding experiments demonstrate the presence of this shear relationship. Two phases in the $UO_2 \cdot H_2O$ system are being considered for future study.


03:372 STRUCTURAL PROBLEMS IN POTENTIAL BREEDER FUELS. Siegel, S., Thern, 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 $UO_2Cl_2$ in order to derive the site occupancy of the oxygen atoms. This would permit a measure of the oxygen deficiency with anions and would need to be understood for the structure evaluation of the nature of the defect. Thus, a study with some general results, the technique could be applied to the mixed $UO_2 \cdot PbO$ fuel itself. The second problem under consideration is the study of the diffusion of uranium in $UO_2$, and the relationship to structure.

03:373 SOLID STATE CHEMISTRY OF RARE OXIDE SYSTEMS. Eyring, J. S., and Eyring, L. (Arizona State University, Department of Chemistry, Tempe, Arizona, 1971).

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 neutron bombardment 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 fluoride-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 definition of the structural principles that relate 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 diffraction and especially high-resolution electron microscopy and selected area electron diffraction. The latter method may be applied to the mixed $UO_2 \cdot PbO$ fuel itself. The second problem under consideration is the study of the diffusion of uranium in $UO_2$, and the relationship to structure.

**PUBLICATIONS**


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'-diphenyl-3,5-dipyraFdiphthalamide was determined. This is a synthetic compound, the tetrasulfide analogue of a 2,5-dipiperazinedione ring with an epip-dithio bridge across the 3,6-positions, the latter being a structural fragment common to glutamic acid and some other amino acids. The structure determination was undertaken to provide a basic 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 in a bronze and pyrochlore structure is being investigated. 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 magnetic moments. 2) The system FeTa₂O₄-FeTaO₄ is currently being modified for low-pressure ionization chamber in which proton transfer measurements will also facilitate the investigation of volatility problems. 03:376  MAGNETIC PROPERTIES OF CRYSTALLINE COM-POUNDS. Elliott, N. (Brookhaven National Laboratory, Chemistry Department).

Magnetic susceptibility measurements supplement x-ray crystal structure determinations in providing an understanding of the magnetic 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)₂H₂MnCl₄ the anion MnCl₄²⁻ is square pyramidal and monomeric. Studies now under way or planned include the following: 03:378 CHEMICAL CRYSTALLOGRAPHY STUDIES BY NEU-TRON 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 crystal structures of magnetic compounds. The interaction of neutrons with an ordered array of spins gives rise to 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 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 are being investigated. The system FeTa₂O₄-FeTaO₄ has been found to exhibit ferromagnetic 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.

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 process has been practically solved by the use of a low-pressure ionization chamber in which proton transfer takes place in a single ion molecular collision. This has led to a solid state mass spectrometer system developed in the IRL 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 derivatized tri- and tetraalanes and Thyrotropin Releasing Hormone have been evaporated from a teflon probe in a teffion collision chamber to provide mass spectra suitable for structural identification and quantitative assay.

03:378  X-RAY DIFFRACTION. Hamilton, W. C. (Brookhaven National Laboratory, Chemistry Department).

X-ray and neutron crystallography often offer the quickest method of determining the arrangement of atomic magnetic moments in solids, ionization of amino acids and peptides can be minimized by selection of appropriate ion reagents.
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(BH₄)₄ and H₂(BH₄)₂ have provided the only reliable information on the mode of attachment of borohydride groups to metal atoms.

Neutron-diffraction investigations oftellurians 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. The structure determination now low of this ice by neutron diffraction, 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

03:379 PRECISION NEUTRON DIFFRACTION STUDIES OF AMINO ACID AND NUCLEIC ACID COMPONENTS. Hamilton, W. C., Koeztle, T. F. (Brookhaven National Laboratory, Chemistry Department).

The structures of amino acids and nucleotides 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 0.024 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 properties of polypeptides and in the variability of amino acid structures as they occur in proteins.

The structures of amino acids 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 mutagenesis in DNA. The work will continue with the analysis of a number of other base pairs, nucleotides, and oligonucleotides.

PUBLICATIONS

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 underway and are 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, MX₂, 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 demarcation between bent and linear species. Preliminary results indicate that the rare earth dihalides 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 subtraction zones are being studied. Rocks from the Alienian are (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 ultramafic and related rocks 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 essential to the structural analysis. 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 tailored for computational convenience. Neutron-diffraction refinements of the structures of these hydrates permit 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
Physiological systems, and x-ray studies related to the structure for the near future are neutron diffraction studies in relation to of this program has broadened to include studies of special inor-
hydrate, the 1:
Brown, G. M., F. L. Hedberg, and H. Rosenberg, Crystal Structure NaBe and CUF Data for the structures of
PUBLICATIONS by the installation of a new Si solid state detector, will resolve
structures of proteins or other molecules of high molecular weight study of
of neutron resonance scattering to the solution of crystal struc-
by other AEC activities. The results of the neutron-diffraction
configurations in solution. For the longer term, the applicability provide the basic parameters for fundamental studies funded

Because of interest in LiF–BeF₂ systems, we have recently shown that the crystal structure of Li₄BeF₆ 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 CuCl.
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 intramolecular forces. An x-ray study of crystalline cyclopen-
tane 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 motions as well as a more precise interpre-
tation of experimental interatomic distances.

PUBLICATIONS

03.384 NEUTRON AND X-RAY CRYSTAL STRUCTURE ANAL-
This project aims to furnish for selected crystals the accurate knowledge of structure required for basic chemical understanding in a number of areas: energies of crystal packing, hydrogen bonding and distribution of hydrogen isotopes among different locations, unusual 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 neutron-diffraction facilities at Oak Ridge are utilized at the ever 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(H₂O)₂⁻–H₂O–(OH₂)₂⁻ (C₂O₄)⁴⁻, which contain the rather rare disordered proton (H₂O(H-OH₂)) and on hydroxamic acids, such as hydroxyurea, H₂NCONH₂, which has been shown to have a pyramidal nitrogen in the –NH₂ group. Other compounds under study include lithium hydrosulfo monocarboxylate, the 1: 1 complex of urea and phosphoric acid, metallo-
tenes, terpenoids, steroids, and natural pigments. Specific topics for the near future are neutron diffraction studies in relation to molecule-substrate interactions and crystal structure and 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
Deiderator, R., J. C. Terry, G. R. Freeman, and H. A. Levy, The Molecular and Crystal Structure of 8-Hydroxyquinoline–N-


Although liquids are involved in virtually all technological fields—energy, environment, and molecular weight—commercial applications are lacking. This program attempts to solve this 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 BeF₂–
LiF over wide ranges of temperature and composition have yielded high-precision correlation functions. Molecular dynamics calculations based on purely interaction potentials derived from crystal data have yielded ion pair correlation functions that agree well with those derived from diffraction. More re-
fined 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 H₂O⁺ ions. The data are being analyzed to obtain a realistic potential of in-
teraction between water molecules.
Diffraction studies of glass BeF₂ and SiF₄ have been inter-
persed 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

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 OkNL programs devoted to fundamental and applied chemistry of molten fluoride mixtures. Emphasis upon such compounds includes more recently, the scope of this program has broadened to include studies of special inor-

PUBLICATIONS
environmental, and nutritional sciences. The spark source mass spectrometer with its broad capabilities occur and to develop schemes for their elimination. These studies overall project concerns automatic control of the spark position being conducted in an effort to understand how these interferences tipply charged ions upon the analysis. The final phase in this are laying the groundwork for applying plasmas and flames to the relative to the instrument ion optics. Preliminary manual ex-

portant insights on: (a) the relative concentrations of stable sodium metal. Isotopic abundance measurements on the five most significant of these observations on practical analytical applica-

tion. 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.

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 techniques for the ultrasound (part per billion level) de-

termination of the lanthanides in various reactor materials suggests a multitude of further application studies. The analytical studies are complemented with explorations on the potential-

tialities of various fluorescent hot systems as radiographic phosphors, neutron detectors, and in-pipe, 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

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 im-

PORTANT INSIGHTS ON: (a) THE RELATIVE CONCENTRATIONS OF STABLE REACTIVE SPECIES IN THE VARIOUS ZONES OF THESE HOT GASES; (b) THE RELATIVE CONCENTRATIONS 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 APPLICATIONS OF THESE DEVICES. MECHANISTIC STUDIES ON SOLUTE VAPORIZATION INTERFERENCE EFFECTS IN FLAMES OR PLASMAS ARE BEING CONDUCTED IN AN EFFORT TO UNDERSTAND HOW THESE INTERFERENCE EFFECTS OCCUR AND TO DEVELOP SCHEMES FOR THEIR ELIMINATION. THESE STUDIES ARE LAYING THE GROUNDWORK FOR APPLYING PLASMAS AND FLAMES TO PRACTICAL SOLUTION OF SIGNIFICANTLY DIFFICULT ANALYTICAL PROBLEMS ENCOUNTERED IN NUCLEAR REACTOR TECHNOLOGY AND IN THE BIOLOGICAL, ENVIRONMENTAL, AND NUTRITIONAL SCIENCES.

PUBLICATIONS


03:356 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.

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 techniques for the ultrasound (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 hot systems as radiographic phosphors, neutron detectors, and in-pipe, 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


These studies are laying the groundwork for applying plasmas and flames to the relative to the instrument ion optics. Preliminary manual ex-

portant insights on: (a) the relative concentrations of stable sodium metal. Isotopic abundance measurements on the five most significant of these observations on practical analytical applica-

PUBLICATIONS

for ionizing all materials to make isotopic abundance measurements that are as good as any made using surface or electron bombardment ionization.

**PUBLICAtION**


**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 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**


**03:392 COPPER ARCHAEOLOGY.** Friedman, A. M.; Lerner, J. L.; Fields, P. R.; Milled, 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 it is possible to 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 it was found that 75% of them had 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 some alloys. Since this is 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**


**03:393 NUCLEAR MEDICAL ISOTOPE RESEARCH.** Friedman, A. M.; B. Rayr 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 radioynthesis of milligram amounts of 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 Fe in bone marrow. We have been able to achieve enrichments of ~200 with respect to surrounding tissue. This will make it feasible to use these Fe complexes to diagnose some diseases of the red-blood-cell-forming structure.

We intend to study the production and use of 51Fe and 54Fe during the coming year, since these isotopes are expected to be useful for studies of tumors and bone growth while their half-life is short enough to cause minimal 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.; Kramer, 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 BLN RARAF accelerator, which presently produces 4-MeV protons. The program will then consist of tying the various techniques into the 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**


**03:395 SULFUR TRIOXIDE, OXYGEN, PLATINUM ELECTRODE IN A FUSED SULFATE.** Salzman, 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 interaction of SO2 into the atmosphere. Although there are numerous methods for the continuous determination of SO3 in ambient air, there is no method for SO2 or (H2SO4). A study was undertaken to examine the Os, SO2, Pt/(Na, Li, K)2SO4 electrode as a possible means for continuous measurement of SO2 in ambient air. The behavior of this electrode was studied at SO2 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 con-
taining a fixed and known concentration of $\text{SO}_4^{2-}$. Through the other electrode was passed a similar gas stream containing a variable concentration of $\text{SO}_3$. The $\text{SO}_4$ passed into each electrode through a platinum inlet tube that converted a fraction of the $\text{SO}_3$ in the gas stream to $\text{SO}_2$. 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 $\text{SO}_4$ and $\text{SO}_3$. It is expected that sulfate is present in ambient air in a variety of forms such as $\text{H}_2\text{SO}_4$, $\text{H}_2\text{SO}_3$, $\text{(NH}_4)_2\text{SO}_4$, ($\text{NH}_3$)$\text{HSO}_4$, 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; the 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 matrix provide a new method of classifying and grouping the objects, 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 thermluninescence and $^{14}$C dating and to apply them to archaeological and art objects.

### PUBLICATIONS


### 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 $^{99}$Co, $^{203}$Tl, $^{241}$Am, and $^{207}$Tl. Work on $^{15}$N, $^{24}$Na, and $^{88}$Sr is in progress and work on $^{1}$H, $^{13}$C, $^{27}$Al, and $^{7}$Li will soon commence. The Westcott conventions for expressing $\beta$-irradiation units and $\alpha$-radiation units of special chemical techniques in activation analysis being developed include work on mercury determination involving neutron activation and x-ray counting and the development of a precision 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 synchrotron solvent extraction is continuing. A procedure will be developed to synthesize tetrachloroaluminate chloride labeled with radioactive arsenic. The study of the use of chloric acid as an extractant for metal cations will be continued.

### PUBLICATIONS


### 03.398 NEUTRON ACTIVATION ANALYSIS

Rowland, F. S. (University of California, Department of Chemistry, Irvine, California 92610).

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. J. Guinn and G. E. Miller). The single swordfish (caught 1946) and seven tuna (caught 1878 to 1909) showed mercury concentrations in the same range (0.1-1.0 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 $^{35}$Cl atoms formed by the reaction $^{35}$Cl(n,$\gamma$)$^{35}$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.

### PUBLICATIONS


### 03.399 CHEMICAL ANALYSIS BY ION MICROPROBE MASS SPECTROMETRIC METHODS

McHugh, J. A.; Stevens, J. F. (Kings 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 amino acid 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. The results indicate that 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 chemical standards 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 $^{3}$He 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 $^{3}$He ions for chemical studies, including non-destructive 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 sulfur, phosphorus, chlorine, bromine— and the determination of various elements as a function of depth from the surface can also be measured. The use of $^{3}$He activation analysis has been demonstrated in several laboratories around the world for studying the effects of trace concentrations of certain elements in surface-sensitive 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


03.041 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.

03.042 NUCLEAR METHODS OF ANALYSIS OF ENVIRONMENTAL SAMPLES. Gordon, G. E.; Viola, V. E. Jr.; Wallers, W. B. (University of Maryland, Department of Chemistry, College Park, Md., 1972).

Instrumental nuclear methods of analysis involving both long-range ionizing 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 minutes 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, Rh, 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 200 MeV electron accelerator. Thus far we have found IPAA capable of analysis for Na, Cl, Ca, Ti, Cr, Ni, Zn, As, Br, Zr, Sb, I, Cs, and Pb, among which Ti, Ni, As, Br, and Pb are difficult or impossible via INAA. The elements Na, 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 Pb and Gd. 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


03.043 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, and 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 GeMAEC, 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 Jyeck-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 GeMAEC 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 GeMAEC analyzer, in search for rapid methods for measuring contamination of natural waters.

Projects on computer-controlled methods is continuing with emphasis on exhaustive electrolysis under control-potential conditions.

PUBLICATIONS


03.044 PHOTOELECTRON SPECTROSCOPY (ESCA) FOR SURFACE ANALYSIS. Bullock, 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 where 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 samples taken from a steam plant equipped with a Catox device for SO2 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 method 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 S02 removal studies that involve adsorption on solid surfaces.
by similar studies using photon activation at the ORELA. Some dation of Methyl Orange was carried out. We find that the extent program to handle the y spectra obtained from these irradiated lytic water products protects the dye from radiolytic degradation. very small samples. We are studying impurities in fossil fuels, explore its special potential; our aim is multielement analysis using measure accurately the radiolytic degradation is very low (~10

in the low Z region of the periodic table. pH indicators, show that dyes as a group are easily degraded (de-

analysis, charged particle reaction analysis, and x-ray excitation analysis whenever possible. For the past year or so the latter has

investigation and exploitation of four different systems: (1) auto-

Baybaz, R. D., J. R. Stokely, and J. R. Peterson, Absorption


In this approach, the unstable intermediate is electrically gener-

in fluoride molten salts. Various electrode as-

we are continuing to collect basic data and further character-

the electroactive species in the different molten fluoridic solvents. We have been primarily concerned with the study of more stable electroactive species (uranium, corrosion products, etc.) which are less adapted to the time monitoring now to study the more unstable constituents, such as Mo, Nb, Tc, and Ru, particularly valence states and disproportionation re-

actions at low concentrations. Ring disc voltammetry and thin layer methods have been utilized to characterize unstable in-

mediates 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. The approach we have chosen is to generate electroactive species generated in situ and spectral data are obtained by scanning the electrode solution interface.

we are continuing to collect basic data and further character-

REFERENCES


Whiting, F. L., G. Mamantov, G. M. Bogen, and J. P. Young, Raman Spectra of Solute Species in Molten Fluorides: O2-, CO2-, CO3

Jenkins, H. W., G. Mamantov, and D. I. Manning, Electrode Poten-


Both the high flux at HFIR, only a short irradiation time is required to achieve great sensitivity; by measuring the induced activity with a computer-controlled 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 NeV 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 ex-

plor its special potential; our aim is to use the HFIR for analyzing 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 y 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 14C/12C and 18O/16O ratios in biological experiments, and the technique is now being evaluated for other applications.

PUBLICATIONS


of protection is a function of Cu\(^{2+}\) concentration, and that by selecting the proper conditions less than 1 ppm copper can be measured accurately. No interference is shown by the presence of nonactive ions such as Al\(^{3+}\), Zn\(^{2+}\), Cd\(^{2+}\), Ca\(^{2+}\), N\(^{2+}\), and Na\(^{+}\). 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 for gamma may lend itself to analytical methods for ppm amounts of the active ions. While the method is by nature non-specific, by the proper selection of conditions it should be possible to cause it to be no worse in this respect than any other reduct method.

PUBLICATIONS


-, Effects of Radiation on Common Analytical Reagents, in Progress in Nuclear Energy, Analytical Chemistry, Series IX, Vol. 19, pp. However, the C-station between 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 ~0.6 M and 0.11 M. 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 ~0.6 M. These models consist of a series of linear terms analogous to Rosritt'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


03:410 SOLVENT EQUILIBRIUM AND EXTRACTOR DESIGN FOR SEPARATING THE RARE EARTHS BY SOLVENT EXTRACTION. Borkhart, Lawrence (Ames Laboratory, Chemical Engineering Division)

The solvent equilibria 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 two-solute system TmCl\(_3\)-YCl\(_3\) 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 reagents are obtained from the log of the equilibrium constant. Different expression for each reagent and the control. Equilibrium data for the two-solute system TmCl\(_3\)-YCl\(_3\)-LaCl\(_3\)

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 for an extraction study has shown that a feedforward loop adds materially to the effectiveness of the control. An approximate model of correcting for the transient portion of the feed-forward loop is being determined.

PUBLICATIONS


03:411 INVESTIGATION OF STABLE, LABILE RARE EARTHS 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 rare earths and fission-produced rare earths (Sc, Y, and La-La) mixtures. Countercurrent processes, such as ion exchange and solvent extraction, used in conjunction with competitive 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(6-2-ethylhexyl)-phosphoric acid anion form relatively insoluble H\(_2\)(EDTA) and H\(_2\)(EDTA) species in pH ranges suitable for facile column operation, and (EDTA) (the prononiated form H\(_2\)(EDTA)) is more soluble than H\(_2\)(EDTA) is selective only for the rare earths La-Sm and Ho-Lu.

Because it appears that lack of symmetry makes H\(_2\)(HEEDTA) more soluble than H\(_2\)(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',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. M. 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 promise for our recovery, 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 separa-
Repeatedly deposited on a fresh surface, dried and desorbed again of tritium in liquid potassium and liquid lithium. Studies with high temperature permits the dissolution and desorption of uranium from fluids proposed for the blanket and coolant of thermonuclear reactors because of the large quantities of tritium required in those reactors. 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 molten salt and 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 potential advantages over conventional ion exchange processes for recovering uranium from wet-process phosphoric acid, Ind. Eng. Chem., Process Design Develop., 10: 582-590 (1971).

Future research will include the phenomenon observed long ago by Kraus and his colleagues that large anions, such as CH₃COO⁻, are absorbed by strong acid cation exchange resins from aqueous chloride phase, J. Nucl. Chem., 25: 2501-2509 (1971).

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 organic-aqueous media leads to weaker 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 CH₃COO⁻, are absorbed by strong acid cation exchange resins from aqueous chloride phase, J. Nucl. Chem., 25: 2501-2509 (1971).

The method has been applied successfully to mixtures in which the ²³⁵U 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.

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 fluorination 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 column reactors, (3) developing procedures for selectively precipitating 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 bubbling 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 columns, and contacting units for industrial scaling and to the design of continuous contacting units.

Increased awareness of the biological hazards of tritium imposed restraints on future nuclear reactors, and now, improved tritium-separating and -handling techniques are needed. These constraints will have especially large impact on thermonuclear reactors because of the large quantities of tritium required and produced by the fusion reactions. The program is based on the premise that the increased attention to the materials and chemistry involved in the removal of tritium from wet-process phosphoric acid, Ind. Eng. Chem., Process Design Develop., 10: 582-590 (1971).

Other research efforts are directed at removal from fluids proposed for the blanket and coolant of thermonuclear reactors, but the fundamental materials information required 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 planar or cylindrical solid surfaces and thermodynamic properties at high temperatures.

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 describe new 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 the study of separation phenomena for bibliographical support. 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 bioseparations). The latter will include specifically: the isolation and purification of "colon-stimulating factor," involved in the maturation of white blood cells and of high medical significance. Increasing attention will be given to processes for environmental problems, e.g., scintillation spectrometry in monitoring of actinide contaminations and metal hydride control in tritium.

PUBLICATIONS


3.419 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 $^{13}CO_2$-$^{13}CO_2$ 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 biochemical studies. A comparison of the chromatographic separation behaviors of CH$_2$OH and CD$_2$OH 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. 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 on-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 silica columns that allow different conditions to be used for different compounds. The separation of xenon from helium, molten salts, or liquid sodium is also planned. The program will also be directed towards the development of a permeator with hollow fiber 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.

PUBLICATIONS

ENGINEERING CHEMISTRY

Basic nuclear and chemical engineering studies.

03:422 BENCH SCALE MIXER-SETTLE 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 operating 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 effects 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


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 study has shown that internal motion and salt concentration 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 motions coincide with corresponding shifts in mass-transfer rates. Such changes have been correlated with fluid velocities and physical properties of the fluid. 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 drops. 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 be used to study transport processes inside opaque liquid metal systems.

PUBLICATION


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 both thermal spin-type units and in convection loops at temperatures in the range of 260 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. Efforts are being made to develop generalized correlations between surface tension and thermodynamic properties.

PUBLICATION


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 and liquid metal eutectics. An experimental model 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 alumina. Use of the residue, hydroxymetallurgical 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 EFUSION CELLS AND THEIR EFFECT ON EXPERIMENTAL THERMODYNAMIC PROPERTIES. Fitzgerald, 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 non-equilibrium in the Knudsen cell makes the assumption of the torsion effusion cell invalid. 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, Henry's law, etc.), it is an effort worth the effort to establish limiting internal cell geometries that would minimize the effect of non-equilibrium on the effusive beam. Initial work is expected to take into account internal cell and sample geometries as well as future work is expected to account to the interaction 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. Shick, Frank O. (Argonne Laboratory, Chemical Engineering Division). Recent work has demonstrated the utility of resistivity composition-temperature measurements for the study of 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 require a considerable amount of experimental testing of design parameters. Possible 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

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, with the Sequential Design of Experiments is an extremely effective and economic approach to solving 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 errors of a specified variance to calculated results in an effort to learn 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

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. Numerical results 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–Li2D, and Li–LiT systems. This work is intended to fill the need for composition–temperature data for 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 results are far more precise than all previous measurements. Moreover, the present study of the effect of hydrogen pressure on the structure of liquid lithium isotherms in the Li–LiH–Li2D system. This work is intended to fill the need for composition–temperature data for 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 results are far more precise than all previous measurements. Moreover, the present study of the effect of hydrogen pressure on the structure of liquid lithium isotherms in the Li–LiH–Li2D system.

PUBLICATIONS

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 layers were obtained. A final phase being completed is a study of the surface waves generated when the surface is unstrained, 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 N2–N2O5 is under way. There 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 metallic systems in these phase change studies on the condensing heat transfer, condensing condensation or accommodation factors, and thermal conductivity of mercury vapor up to the 500 to 1000 psia pressure range are commencing.
PUBLICATIONS


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 drift properties of high-temperature mercury 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 thermal processes. Laser-heated fused lanthanide samples are used to study the gas phase reactions induced by proton irradiation (e.g., O3 → O2 and CO2 + H2 → H2O + CO) and are used in mass spectrometric sampling to permit detection of free radical intermediates.

03:436 CHEMISTRY OF RADIOGRAPHY IN HIGH-RADIATION-LEVEL SEPARATION PROCESSES.

Submit, J. M. (Oak Ridge National Laboratory, Chemical Technology Division).

The purpose of this program is to obtain a better understanding of the 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 process off-gasses 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 gaseous and aqueous phases are being determined. The studies have shown the importance of small amounts of organic impurities, which are readily formed 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 guides to minimizing their effects on process performance.

Iodine reactions in other systems are continually being examined in a search for new and more efficient iodine-transporting processes.

03:437 CHEMICAL ENGINEERING RESEARCH.

Watson, J. S.; McNees, L. E.; Lindauer, R. B. (Oak Ridge National Laboratory, Chemical Technology Division).

This program includes several studies generally pertinent to applied programs of the ARC; 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 large, engineering-scale systems is under study. It is likely that some existing approaches can be made more economical and some marginal processes may become practical. Recent experimental efforts have included study of thorium nitrate anion exchange in small (10 to 50 μl) resins. This system closely resembles the plutonium anion exchange process, which is limited by slow diffusion rates in the resin particle. Plutonium anion exchange studies have had practical significance for recovery 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 for mercury--water, mercury--natural nonaqueous solvents, and 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/cm³) and dibromomethane (density, 2.5 g/cm³). 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) chemical behavior of structural refractory metals—niobium, molybdenum, vanadium, and tungsten, synthesis of the more stable lower valance fluorides of these metals; solubility and reactivity of these refractory metal compounds in fused fluoride blanketing coolants, (LiF, Li2BeF4); 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.

Axmann, 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 reactors are more related to solid-state physics than plasma physics. 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, up to energies up to 50 keV and with current densities equivalent to those expected in practical fusion devices. Samples of various candidate materials, such as niobium, molybdenum, vanadium, and stainless steel, are exposed to these high fluxes 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 important influences in the assessment of the environmental effects of fusion devices.

PUBLICATIONS


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).

The present 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 ultrasonic metal surfaces. Techniques used most extensively are field emission electron microscopy and flash filament adsorption 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 is being established, correlated with LEED structure measurements on these surfaces, and the research supplemented by extended Huckel calculations of bonding models for $H_2$, $N_2$, and $NH_3$ adsorbed on these faces.

Physical adsorption of organic nonelectrolytes at the mercury-electrolyte solution interface 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 surfaces 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


MISCELLANEOUS CHEMICAL STUDIES

03:441 DEVELOPMENT OF THE ON-LINE CHEMICAL LABORATORY COMPUTER FACILITY. Day, P., J. Hines and A. Zielon (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 four experimental installations utilizing our Sigma-5 computer. The program calls for a continuing development of the existing interfaced equipment and for 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 programs to new and existing system resources through an optimized storage (diurnal, secondary, 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 regard to their mineral contents, meteorite components, and textural evidence indicative of metamorphism.

The mineralogy and chemical composition of selected meteorites is another principal interest. Just completed is a study of the Allende meteorite, a rare Type-2 carbonaceous chondrite. The 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 highly temperature-conditioned 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


tions.  

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).  

Metamers 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 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. 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, NH₃, and H₂ 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 biogenetic 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


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—biopolymers and nonvolatile decay products, which would permit high-resolution dating of different, possibly earlier, events in the early solar system. For the latter purpose we are investigating 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 electrophoretic mobility of the mercury surface. If the mechanism of physiological activity involves adsorption on membrane sites, there may be a correlation.

PUBLICATIONS


03:446 LOCALIZED CORROSION. Issacs, 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 require 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 loads to the development of transgranular stress corrosion cracks along slip lines. A general approach 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 Science).  

Direct substitution of fluorine into organic molecules is notoriously difficult, and only within the last three years have useful methods been discovered. We have found that some of these methods, involving the use of xenon difluoride (XeF₂) as fluorinating agent, to develop procedures for introducing F atoms into a variety of molecules. These procedures involve the reaction of XeF₂ 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 derivates but not for pyrimidines. For the latter purpose we have been able to achieve the substitution of lead directly and rapidly into such molecules would be of very great value. We are currently attempting this using XeF₂ with 18F-tetrahydrocannabinol, the active ingredient of marijuana. Another fluorination method involving working on, photochemical fluorination with CF₂OF, 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, Carnegie 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 components of meteorites and their meteorite parents, including the chronology of the meteorite formation, are yielding precise determinations of the 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. For the latter purpose we are investigating 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 electrophoretic mobility of the mercury surface. If the mechanism of physiological activity involves adsorption on membrane sites, there may be a correlation.
chemical and possibly nuclear processes in the early solar system.

The 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 astronauts' data on the metal contents of dated galactic 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 $^{238}_{10}$U/$^{235}_{92}$U alpha activity ratio in the uranium in young and old tectites are being made, in an attempt to determine whether significant amounts of soil or other weathering materials with low $^{238}_{10}$U/$^{235}_{92}$U ratios were incorporated into them.

The Moosbeauer spectra of iron in coal is being investigated in order to determine the chemical form of the nonpristine iron reduced, by 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, diffusional, 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 to be formulated 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 recently been overcome. The formation in the laboratory and particle size analysis of submicron aerosols is a formidable feat. The collection efficiencies measured were extremely low, dropping off sharply from a value of $3.1 \times 10^{-2}$ for a $2.54$-$mm$ droplet to a minimum of $6.3 \times 10^{-4}$ 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 $0.7$-$mm$ radius), indicating that the mechanism of collection of these particles involves Brownian motion rather than inertial impaction as is the case for larger particles. The low values of 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 in progress under way will explain 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, this study has a number of advantages in that it leads to a basic understanding of the mechanism involved in the suppression of dust in industrial and mining environments by water sprays.

PUBLICATIONS


03.449 STUDIES ON COLLOIDAL PARTICLES: SCAVENGING OF AEROSOL PARTICLES BY A FALLING MICROSCOPIC PARTICLE. Kerker, Milton (Clarkson College of Technology, Department of Chemistry, Potsdam, New York 13670).

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, diffusional, 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 to be formulated 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 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 $3.1 \times 10^{-2}$ for a $2.54$-$mm$ droplet to a minimum of $6.3 \times 10^{-4}$ 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 $0.7$-$mm$ radius), indicating that the mechanism of collection of these particles involves Brownian motion rather than inertial impaction as is the case for larger particles. The low values of 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 in progress under way will explain 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, this study has a number of advantages in that it leads to a basic understanding of the mechanism involved in the suppression of dust in industrial and mining environments by water sprays.

PUBLICATIONS


03.450 INVESTIGATION OF SECONDARY ELECTRON YIELDS INDUCED BY ION IMPACTS ON THIN-FILM OXIDE SURFACES. Diets, L. A., J. C. Sheffield (Knolls Atomic Power Laboratory, Mechanisms Spectroscopy).

When an ion with low 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 been used as an important tool for determining the electronic structure of target films 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 monoatomic 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 BOUNDAIRES. 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 electrolyte film formation. In a study of chemisorption of carbon monoxide, a good quantitative correlation was found between ellipsometric and Auger electron spectroscopic measurements. Ellipsometric measurements of a NiSQ 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


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 correlation of rotating iron and copper dislocations is being investigated theoretically. A device for concentrating electropositive cations using porous, fixed, flow-through, carbon electrodes is being studied experimentally. Mass transfer occurs as being calculated for a system of two concentric cylinders, the influence of which rotates. The transient response of potential to an interruption in the current is being calculated for a rotating disk electrode. Diffusion coefficients of aqueous KOH solutions are being measured for concentrations of 1-3 M.

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


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, Auger electron spectroscopy and (2) investigations of chemical surface reactions of carbon surfaces, which are being carried out using low-energy electron 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 (carbonaceous) 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 O₂ to Cl₀₂ on platinum has been found to be sensitive to the surface structure of platinum. The decarbonylation of cyclohexene to benzene and the oxidation of ammonia are being studied using platinum crystal surfaces. The reaction of atomic steps on a surface in examining 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 study the mechanism of energy transfer between the gas and the surface in surface chemical reactions such as in the dissociation of nitrogen oxides during surface reactions of diatomic molecules (O₂, H₂, N₂, and CO).

PUBLICATIONS


MISCELLANEOUS CHEMICAL STUDIES

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 subject 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 Uc = 100,000, in 0.02-1 cm separation. Concentration fields in laminar boundary layers along extended surfaces are being analyzed by means of laser--Mach--Zeidler Interferometry. Effects of electrolyte composition, flow, mass transfer, and microgeometry on the reaction 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 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 solvents. The program seeks to extend previous work on electropositive elements to anodic reactions to alkaline--alkali earths, and alkali--alkaline earth metals is now receiving renewed emphasis. Characteristic of this program is the high potential reaction of certain transition metals that will be initiated on the kinetics of dissolution of Cd(OH)₂.

PUBLICATIONS


03:455 TRANSPORT PROCESSES IN ELECTROCHEMICAL SYSTEMS. ELECTROLYTIC PROCESSES IN NONAQUEOUS SOLVENTS. Tobias, Charles W. Lawrence Berkeley Laboratory, Inorganic Materials Research Division.

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PUBLICATIONS


03:456 SURFACE AND INTERFACE PROPERTIES IN HETEROGENEOUS SYSTEMS. Campbell, D. G., L. I. Thomar, J. P. McHale, (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 selective interaction of n-pentane and o-xylene (or acetone) by (n,y) reactions within molecular sieves, so that recoil moves product atoms to more accessible sites and permits selective elution. A second line of study is the mechanisms of retention and release of volatile materials in metal catalysts, 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 interaction 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 model 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.
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 applications. 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 hepta- mediaites, which undergo oxidation during each step of the overall reaction, should allow determination of specific surface interactions to solid state electrolytes as well, and confirmatory measurements are planned. In a continuing investigation, the effect of pH on potentialistic current--time transients in the microsecond time domain is being examined. Such measurements should allow determination of specific surface interactions, and confirmatory measurements are planned. Present studies are concerned with analysis of B and D solutions and with effects of some of the more common interfering species present in municipal and industrial waters or process streams.

MISCELLANEOUS CHEMICAL STUDIES

PUBLICATIONS


ELECTROCHEMICAL KINETICS AND CORROSION.


The program of this group is concerned with fundamental physical-chemical 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, 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 interactions, and confirmatory measurements are planned. 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


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 flowing streams and with the corrosion 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, 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 interactions, and confirmatory measurements are planned. 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.

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 surface diffusion over a thin adsorption layer. 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 at high temperatures, is essential. Electrochemical studies have shown that anodic polarization curves for pure copper have Tafel slopes of 6.6 log i equal to 2.3 RT/F and that the reaction rate is limited by mass transport of CuCl 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.
will be followed by later work at higher concentrations and with different species in the series iodine, xenon, cesium, barium, and curium, which have widely varying affinities for carbon.

03-461 SURFACE CHEMISTRY. Holmes, H. F., L. Fuller, Jr., and P. A. Agnon (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 surface 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 adsorptive gases. Calorimetric measurements of the heat of immersion of thorium oxide in water at temperatures up to, and including, 200°C; calorimetric measurements of the heat of immersion of zirconium oxide in water at 25, 50, 100, 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 gravitational 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


03-462 MOLECULAR DYNAMICS. Malinauskas, A. P. and B. K. Anniis (Oak Ridge National Laboratory, Reactor Chemistry Division)

The molecular dynamics program seeks to be a broad sense to understand and describe the 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 necessary to develop microscopic 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 distinct 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


03-463 RESEARCH IN THE FIELD OF CATALYSIS. Turkovich, 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 20-GeV Proton bombardment 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


03-464 HIGH-ENERGY NUCLEAR INTERACTIONS WITH MATIER 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, titanium, uranium, and many other targets. The results on the spectrum of products 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 12C1 and 13C1 by cosmic rays is being studied. A new method for counting 35Cl in the gas phase as methyl chloride has been successfully developed and is being applied to measurement of the 35Cl1 proton production cross section from iron and nickel targets as well as a study of the depth variation of the cosmic-ray-produced 35Cl1 in the El Tato meteorite. Cosmic-ray-produced 12C1 found in tree rings is under investigation. It is planned to extend the previous study (which showed a short period variation in 12C1 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 differential losses of cosmic-ray-produced tritium or 3He during the lifetimes of certain meteoroids.

PUBLICATIONS


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 Kf to Kα 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 Kf to Kα 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 hyperrelativistic peaks in the x-ray spectra arising from the radiative deexcitation of atoms having two initial K-shell vacancies.

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