SUMMARIES OF THE USAEC BASIC RESEARCH PROGRAM IN CHEMISTRY (OFF SITE)

March 1963

Office of Chemistry Programs
Division of Research,
AEC Washington, D.C.
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FOREWORD

The Atomic Energy Act directs the Atomic Energy Commission to support and foster research in the field of atomic energy. The Division of Research of the Atomic Energy Commission is responsible for accomplishing this objective in the physical sciences. Research is supported at the AEC National Laboratories, at other Government Laboratories, at universities, at research institutes and foundations and at industrial laboratories.

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 AEC-owned facilities. The "off-site" program is carried out elsewhere and consists primarily of research projects performed through contracts with educational institutions.

This document summarizes the objectives and current status of the individual research projects supported by the Office of Chemistry Programs of the Division of Research under its "off-site" program.

It is the purpose of this document to inform the scientific community of the current researches being supported. Although it was not possible to have up-to-date summaries for each contract in time for this publication, all contracts in effect on February 1, 1963, and several others terminated shortly before February 1, 1963, are identified.

For convenience, the summaries have been organized into the following categories and coded as indicated:

1. Nuclear Chemistry (N)
2. Geo- and Cosmochemistry (G)
3. Radiation, Photo-, and Hot Atom Chemistry (R)
4. Isotope Effects (IE)
5. High Temperature Chemistry (HT)
6. Coordination Chemistry (CC)
7. General Inorganic Chemistry (I)
8. Structural and Theoretical Chemistry (ST)
9. General Physical Chemistry (P)
10. Physical-Organic Chemistry (O)
11. Analytical Chemistry (A)
12. Chemical Engineering and Separations Chemistry (CS)

These classifications, of course, are partly arbitrary but they do reflect the main programmatic interests of the Division of Research in the chemical sciences.

Many individual research contracts might logically be assigned to any of several categories; other research programs specifically cover several different areas of investigation. In such instances, the assignment was made on the basis of apparent greatest emphasis.

Each summary is on a separate page and includes the name of the institution at which the work is carried out, the principal investigator
or investigators, the AEC contract number, and the date on which the summary was received.

One index appears at the end of the directory. It is arranged alphabetically by contractor. Contracts are with organizations and not individuals.

All of the research presented in this document is unclassified. As a normal procedure, periodic progress reports of information resulting from these contracts are not prepared for general distribution. Investigators are encouraged, however, to report their results in the open literature at the earliest opportunity for wide dissemination of the information. The interested reader is referred to Nuclear Science Abstracts or to Chemical Abstracts as sources of information concerning publications resulting from the work summarized in this document.

Inquiries or comments concerning the researches described should be directed to:

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*Summary not available
NUCLEAR REACTIONS AT HIGH ENERGIES

Research under this contract may be divided into the following subjects:

1. The relative yields of the following pairs of isobaric nuclei, Ti\(^{45}/\text{Ca}^{45}\), Cr\(^{48}/\text{V}^{48}\) and Fe\(^{52}/\text{Mn}^{52}\) produced in various targets under bombardment by high energy protons and alpha particles are being determined. To date relative yields for each pair have been measured using copper targets and protons of 700, 500, 300 and 225 Mev. The relative yield of Ti\(^{45}/\text{Ca}^{45}\) in copper using 900 Mev alpha particles has also been determined. The data so far obtained indicates that the relative values for each pair are remarkably independent of energy or projectile. In order to complete the study, targets of mass greater than copper are now being irradiated and relative values being determined.

2. A program has been undertaken to study the production of the isomers Co\(^{58}\) and Co\(^{58m}\) produced in cobalt and heavier elements by high energy protons and alpha particles. Preliminary data for the relative yields of these isomers produced in cobalt by 700 Mev protons is in reasonable agreement with data obtained by Meadows\(^1\) at 100 Mev.

3. A study of secondary reactions produced in copper by high energy protons has begun. Production cross sections for several isotopes of gallium, germanium and arsenic have been measured using 700 Mev protons. The data appears to be consistent with work carried out at lower and higher proton energies\(^2,3\). Cross sections will also be measured at a number of energies below 700 Mev.

Nuclear reactions induced by protons from Carnegie Tech's 440-Mev proton synchrocyclotron are being studied. Measurement of excitation functions of spallation products and determination of cross sections for specific products from different target nuclides are underway as part of a general survey of high energy nuclear reactions. Some specific studies include determination of excitation functions of simple high energy reactions such as \((p,n)\), \((p,pn)\), \((p,2p)\) and \((p,2n)\) reactions, measurement of the integral recoil properties of \((p,2nucleon)\) reactions, measurement of the recoil behavior of specific spallation products, and theoretical calculations, using a Bendix G-20 computer, on different models of \((p,2nucleon)\) reactions. The discovery, preparation and characterization of new nuclides are also to be expected.
This research has two main lines which are nuclear reactions induced by high energy particles from the University of Chicago 170" synchrocyclotron, and extraterrestrial problems.

Research at the synchrocyclotron is of two types: internal beam irradiations with protons up to 450 Mev energy and external beam irradiations with protons of approximately 450 Mev energy or $\pi$ and $\mu$ mesons of both charges and various energies. Radiochemical isolation methods are used to determine yields of specific nuclides.

*Internal* beam studies are on high-energy fission and spallation reactions, as functions of target nucleus and proton energy. *External* proton beam studies are on the angular distribution of fragments from nuclear reactions and the interaction of high energy protons with specific nuclides in large bodies of matter. The meson beam studies are concerned with the fundamental interactions of these particles with nuclei as evidenced by the reaction products.

The extraterrestrial studies involve determining the abundance of elements in meteorites by neutron activation and the production by cosmic rays of radionuclides in meteorites and satellites.

Study of the cosmic-ray production of radionuclides in meteorites emphasizes recovery of meteorites soon after their fall for the isolation of short-lived radionuclides. The synchrocyclotron proton bombardment of thick targets is directed toward the understanding of the nature and distribution of radioactivities produced in cosmic-ray bombardment.
The external beams of the University of Chicago 170" synchrocyclotron include a \( \sim 450 \) Mev proton beam directed into a "proton station" a considerable distance away, and meson beams (\( \pi \) and \( \mu \)) of both charges and at specified energies extracted from the machine and directed into the "experimental area" separated from the machine by a 12-foot steel wall. The existence of these beams has made possible radiochemical research at the University of Chicago that cannot be done elsewhere. Also, the steady operation of the machine at high intensity has made feasible the production of long-lived species from spallation reactions.

The lengthy irradiations involved in these studies can be carried out only at night in order not to interfere with other research at the synchrocyclotron. This contract supports the additional operating time of the machine necessary for long meson and proton irradiations. The radiochemical work itself is supported under Contract AT(11-1)-104 (see page N-3).
NUCLEAR CHEMISTRY AND RADIOCHEMISTRY

With the object of building understanding of nuclear energy levels, formation cross sections of isomeric pairs produced by protons, alpha particles and heavy ions, are being studied. The ratio (Ce\textsuperscript{137m})/(Ce\textsuperscript{137}), resulting from the compound-nucleus reactions La\textsuperscript{139}(p,3n), Ba\textsuperscript{136}(α,3n), and Te\textsuperscript{128}(C\textsubscript{12},3n) is being determined. The isomeric ratio of several tellurium nuclides will be determined in direct reactions such as (p, pn) and nucleon transfer in heavy-ion reactions.

Yields of products in the proton and heavy-ion induced fission of target nuclides in the rare earth region and in the region of mass 110 are being investigated at bombarding energies near threshold. The measurement of recoil ranges of shielded nuclides in the fission of uranium with 150-Mev protons will be continued.

Adjunct analytical radiochemical studies of alkaline earth elements include use of chelating ion exchange, solvent extraction, and specific precipitants. The objective of this part is a highly specific method for strontium in the presence of large amounts of calcium and a satisfactory low-level separation and solid-state counting procedure for radium from samples of geochemical interest.
MECHANISMS OF NUCLEAR REACTIONS

These studies are concerned with developing an understanding of the relative importance to nuclear reactions of the two extreme mechanisms that may be postulated for them, direct interactions and compound nucleus formation. Nuclear reactions induced by particles with energies ranging from several Mev to several hundred Mev are being studied. Of particular interest are the partial cross-sections for the production of the various radioactive products that may be formed from a given particle and target. Reactions are studied through isolation and assay, by radio-chemical techniques, of these products.
EXPERIMENTAL STUDY OF NUCLEAR MODELS

General studies are under way on the structure and spectroscopy of the nucleus, on carbon isotope separation by ion exchange methods, and on the spectra and structure of metal carbonyls.

During the current period the following work is being undertaken:

(1) Experimental studies of nuclear energy level systematics utilizing the Browne-Buechner spectrograph as the analyzer at the end of our Tandem Van de Graaff with particular emphasis on the transition from spherical to deformed nuclei, deformed odd-odd nuclei and the shell model in the Zr and Sn regions.

(2) Observation of the effect of resin crosslinking and temperature on the carbon isotope separation factor; a general theory of the separation factor in ion exchange separation is being sought; and

(3) Preparation of new substituted metal carbonyls, and study of their structure and preparative kinetics through the use of infrared spectroscopy.
The radiochemical studies of nuclear reactions, initiated in previous years, will be continued. Among the specific experiments to be performed are excitation functions for the reactions:

\[
\begin{align*}
\text{Mo}^{98} \ (p, \alpha) \ & \text{Nb}^{95,95m} \\
\text{Mo}^{92} \ (p, \alpha) \ & \text{Nb}^{89,89m} \\
\text{Rb}^{87} \ (\alpha, \gamma) \ & \text{Y}^{90,90m} \\
\text{Y}^{89} \ (d, p) \ & \text{Y}^{90,90m}
\end{align*}
\]

The results will be subjected to a theoretical analysis in the manner of Huizenga and Vandenbosch\(^1\) and Need\(^2\). Also to be investigated are isomer ratio studies involving He\(^3\) projectiles of the Florida State University 12 Mev Tandem Van de Graaff accelerator. Finally, an attempt will be made to measure the cross sections over a range of energies for radiative capture reactions using heavy ions as projectiles. A recent measurement of a radiative capture cross section\(^3\) in p\(^{31}(N^{14},\gamma)Ti^{45}\) failed to disclose any unusual effects. It is hoped that an extended study of this sort will establish a definite mechanism.

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TERNARY FISSION AND THE INTERACTION OF FISSION FRAGMENTS WITH MATTER

Investigation of fission phenomena using nuclear emulsion techniques, radiochemical procedures solid state detectors and coincidence circuitry is in progress.

Multiple fission decay modes are being investigated by fabrication of special emulsions in which a fissionable material is incorporated into a thin insensitive layer sandwiched between two nuclear emulsions. Exposure of this "sandwich" emulsion to the thermal neutron beam of the University of Florida Training Reactor permits the measurement of individual fission fragment tracks by identifying the origin of the fission event.

With the completion of a two-nanosecond time resolution triple-coincidence circuit and a three-dimensional analyzer, a determination of the mass division in ternary fission modes of decay is well under-way using solid state detectors for energy analysis of the ternary fission fragments. Using this instrumentation, it is planned to make a study of the interaction of fission fragments with matter and to extend ternary fission studies to the correlation of neutron and gamma ray emission with fission fragment energies.

The investigation of charge distribution is in progress based on "fast" chemistry separations of fission fragments during the irradiation of a fissionable material with neutrons.
NUCLEAR CHEMISTRY RESEARCH

One aspect of this project involves the application of nuclear techniques to analysis. Studies of thermal neutron activation emphasizing the use of short half-lived radioisotopes are being continued with the Ford Nuclear Reactor of the University of Michigan. These studies have required development of rapid radiochemical separation procedures for a variety of samples including rocks, petroleum, biological tissue and ashes, and metals. In addition, the application of low cost neutron generators and isotope neutron sources to activation analysis and neutron research in general is being studied.

A second area of interest deals with the characterization of nuclear decay schemes for short-lived radioisotopes (from both neutron and charged particle activation as well as fission) produced in the Michigan reactor and the Michigan cyclotrons.

The third area involves the development of optimum radiochemical procedures for a number of elements and the evaluation of these procedures to determine pertinent decontamination and interference values. Of particular interest is the amalgam exchange separation, a new type of radiochemical procedure developed in this laboratory. This method has proved to be quite specific and rapid and its application to a number of elements is being studied. The adaptation of other separation procedures, particularly those now being used in other areas of chemistry, to rapid separations is also being studied.
The project will include spectrographic studies of the radioactive decay of several members of the actinium family (Ra$^{223}$, Fr$^{223}$ and Rn$^{219}$) and of Tm$^{173}$ and related nuclides. Application of the unified nuclear model to these nuclides will be made. In addition, a study of the nuclear pairing energy, currently underway, will be continued.
The properties of nuclear recoils from 15-MeV deuteron-induced nuclear reactions are being investigated by direct counting with semiconductor detectors. The ranges of these recoils in their source materials (targets) are being determined by counting and taking energy spectra of the recoils at specific angles in a scattering chamber as a function of target thickness. Recoils of various energies are selected by selecting the kinematically appropriate angle; in this way range-energy curves are being obtained.

The charge-state distributions of the recoils are also being determined as a function of recoil energy and target thickness by experiments in a high-resolution magnetic spectrometer.

Studies of 15-MeV deuteron-induced nuclear reaction cross sections by radiochemical methods are also in progress. Among these are a survey of radiative deuteron capture cross sections and a study of isomeric yield ratios from certain selected processes. Both of these studies are being carried out, insofar as possible, as a function of deuteron energy and target mass number.
CHEMISTRY AND NUCLEAR CHEMISTRY OF THE HEAVY ELEMENTS

This work is concerned with obtaining independent fission yields from actinide elements in the 100 to 140 mass regions. Information already obtained on independent fission yields in the tantalum to gold region will be extended. Chemical procedures for obtaining ultra high purity target materials containing less than parts per trillion of heavy elements will be developed.

In physical-inorganic research, work will be initiated on making completely isothermal ultra-microcalorimeters for exothermic reactions by using thermoelectric cooling. Such research should lead to even greater mass sensitivity than previous devices developed in these laboratories. Work will continue on obtaining thermochemical data on actinide compounds and ions.
NUCLEAR SPECTROSCOPY AND THE APPLICATION OF
RADIOISOTOPES TO THE STUDY OF REACTION KINETICS

In the field on nuclear spectroscopy a systematic determination of
L/K-capture ratios in the low and medium atomic number regions is
being carried out by the use of a high pressure proportional counter.
At the present time Cd$^{109}$ is being investigated to see if accurate
measurements in the second transition series are feasible. In addition,
various beta spectra are being investigated. The determination
of the spectrum of Si$^{32}$ by liquid scintillation spectrometry is just
being completed. Thus far it has not been possible to determine the
beta spectrum of Re$^{187}$ in a proportional counter either as ReO$_3$Cl or
CH$_3$Re(CO)$_5$, both having proved efficient counter poisons.

The study of the pyrolysis of tagged alkyl iodides (RI) continues
with the pyrolysis of n-propyl iodide. It is hoped that the method
which was used with ethyl iodide to inhibit back and side reactions
will provide the first reliable R-I bond energies for the heavier
alkyl iodides by the pyrolysis method. An attempt is being made to
obtain experimental values for the equilibrium constants for the
reaction: \[ M + O_2^- = M O_2^-, \text{ where } M = O_2 \text{ or } N_2. \]
STUDIES OF SPALLATION REACTIONS

The objective of this research program is insight into the mechanisms of spallation and fission reactions.

A study is being made of spallation reactions brought about by protons of moderate energy (up to 250 Mev.), in particular some relatively simple reactions, such as \((p,pn)\), \((p,2p)\), \((p,2n)\) etc., especially with neutron excess and neutron deficient target nuclei are being examined.

Specific parts now under active investigation are these:

1. \(^{29}\text{Cu}\) \(^{63}\) \((p,p2n)\) compared to \(^{29}\text{Cu}\) \(^{63}\) \((p,3p)\) reactions from 60 to 440 Mev:
   Radiochemical cross section determinations are being carried out with protons of 60 to 440 Mev energy. The results will be compared with Monte Carlo cascade calculations plus statistical-evaporation calculations to determine the effect of nucleon binding energies on reaction products.

2. Reactions induced in \(^{28}\text{Ni}\) \(^{58}\) and \(^{42}\text{Mo}\) \(^{92}\) with 10 to 42 Mev protons:
   A wide range of reaction product cross sections are being measured radiochemically. The experimental excitation functions so measured are being compared with statistical model calculations to verify reaction mechanism and importance of gamma ray de-excitation.

3. Low energy proton spectra from compound nuclear reactions:
   A survey of proton evaporation spectra is to be undertaken to determine the effects of angular momentum selection on inhibiting low angular momentum particle emission. This should be seen experimentally as a cut-off on the low energy end of the spectra.

4. Statistical model calculations:
   Statistical calculations of particle emissions with angular momentum effects are being undertaken.
The cross sections for the production of isotopes of neodymium, praseodymium, cerium, and lanthanum by 100 to 240 mev proton bombardment of neodymium-150 are being determined. Particular attention is being given to the mass 143 chain. A rapid method of separating the lighter rare earths by using a centrifugal, high-speed chromatograph is being developed.

During the coming year, the quantitative nature of the rare earth separation mentioned above will be determined. The mass 143 yield measurements should be completed. Probably some attention to the decay characteristics of the nuclides produced in the Nd$^{150}$ spallation will be given. In particular, the rapid lanthanum separation devised should make possible a study of lanthanum-143. An attempt will probably be made to make and characterize praseodymium-134. Attempts to theoretically calculate the (p,2pn) and (p,3p5n) spallation cross sections will be made.
Two different types of mass division have been observed to occur in the fission of heavy nuclei. In the fission of uranium and heavy elements at relatively low excitation energies, the most probable division is such that two fragments are formed which have a mass ratio of two to three. In the fission of bismuth and lighter elements, the most probable division is such that the two fragments have nearly equal mass. This latter type of fission has been termed symmetric fission while the former has been termed asymmetric fission. In the fission of radium (an element which lies between bismuth and uranium) the mass division is such that there is a composite mixture of both symmetric and asymmetric fission.

Because the mass division in fission is such a fundamental aspect of the fission phenomenon and is still not understood on a theoretical basis, studies are being carried out to investigate some of the parameters upon which symmetric and asymmetric fission depend. The relative yields of various mass fragments from 16, 20, 21.3, 23, and 26 MeV bremsstrahlung excitation of Ra\textsuperscript{226} and from 32 MeV bremsstrahlung excitation of Bi\textsuperscript{209} have been determined. From this, and other existing data, correlations are drawn which better characterize the asymmetric and symmetric fission process. For example, symmetric mass fragment-to-asymmetric mass fragment ratios indicate that symmetric and asymmetric fission are two separate and distinct reactions. The fission probabilities of these two reactions vary differently with excitation energy of the compound nucleus and with charge and mass of the compound nucleus.
LOW-ENERGY NUCLEAR REACTION STUDIES

Compound nucleus decay will be studied both by assay of radioactive product nuclei and by measurement of angular and energy distribution of product particles via scattering techniques. Experimental data will be compared with statistical model theory, by means of electronic computer calculations.

The dependence of measured nuclear level-density parameters and other decay features on several experimental factors will be investigated, among them the effect of different modes of compound nucleus formation (utilizing various target-projectile combinations), of changing bombardment energy, of varying angle at which particles are observed, and of special nuclear structure (such as shell-closure) in the compound system or residuum.

Specific reactions that will be examined are:

1. Rh\(^{103}\) + \(\alpha\), Pd\(^{106}\) + p, Pd\(^{105}\) + d leading to Ag\(^{107}\)*;
2. Ag\(^{107}\) + p, Pd\(^{104}\) + \(\alpha\), leading to Cd\(^{108}\)*; and
3. Cd\(^{110}\) + \(\alpha\), In\(^{113}\) + p, leading to Sn\(^{114}\)*.

It is also intended to explore the following as possibilities for the examination of residua with closed-shell structure:

1. Mo\(^{92}\)(\(\alpha,\alpha'\)) or (p,p')
2. Sn\(^{112}\)(\(\alpha,\alpha'\)) or (p,p')
3. In\(^{115}\)(\(\alpha,p\))
4. Tl\(^{205}\)(\(\alpha,p\)) and
5. Bi\(^{209}\)(\(\alpha,\alpha'\)), and (p,p') or (p,\(\alpha\))

The study of the radioactive decay of Cs\(^{136}\) will be continued, supplementing present electron magnetic spectrometry studies with studies by scintillation techniques. In particular, the sum-coincidence method due to Hoogenboom will be employed.

It is also intended to commence studies, solely via the scintillation method, of the decay of Pd\(^{115}\), Ag\(^{117}\) and possibly also of Te\(^{114}\) and Sb\(^{112}\).
Radiochemical studies of yields and decay properties of fission products will be continued, with emphasis on the shorter-lived products. Of particular interest are fractional chain yields, which give information about nuclear charge distribution in fission. Development work will continue on rapid chemical separation, mechanical handling, and radiation measuring techniques for short-lived nuclei.
NUCLEAR CHEMISTRY (INORGANIC)*

Much of our work is concentrated on studies of fission with the aim of better understanding the fission mechanism and its relationship with nuclear structure. These studies include measurements of ranges and kinetic energies of fragments, calculations on prompt neutron emission, and determination of the distributions of mass and nuclear charge. Recently, investigations of x-rays emitted in fission, using bent-crystal spectrometers, were initiated.

Another major research area is that of measuring decay properties of short-lived activities produced in fission or nuclear reactions. Currently, work is in progress on Br$^{86}$, Br$^{87}$, Cd$^{117}$-In$^{117}$, Te$^{131}$, Te$^{133}$, Nb$^{95}$, Ag$^{115}$, and Sb fission products. Studies of nuclear-reaction mechanisms will be resumed in a few months when the M.I.T. cyclotron is back in operation.

Our chemical research, usually involving use of radioactive tracers, includes study of solvent-extraction and ion-exchange phenomena. The solvent-extraction work is aimed towards development of improved radiochemical separations, in addition to investigation of the chemical species involved in extraction mechanisms. The interest in the ion-exchange work is mainly that of obtaining further information on electrolyte solutions.

* Other phases of the overall program include organic and analytical chemistry.
## Section 2

**GEO- AND COSMOCHEMISTRY (G)**

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See also: Section 1, pages N-3, N-5
The primary purpose of this project is to develop techniques for dating and correlating ore deposits and volcanic rocks, and to establish a chronology of ore deposition and volcanism, particularly for the southwestern United States.

The helium age method is being reinvestigated taking into consideration mineralogic, geologic and crystal chemical factors which were, in large part, neglected during the early history of the helium method. For example, the diffusion of U, Th and He and the occlusion of He in cation-anion vacancies is being investigated. In addition to the helium method, the potassium-argon and lead isotopic methods are being used to date ore deposits. The potassium-argon method will be used to establish the absolute age of volcanic formations which extend over a wide area and correlation techniques will be applied to extend the time marker over the widest possible area.

The relation of radiation damage to production of color centers and cell dimension changes in fluorite will continue to be investigated. An attempt will be made to produce the 3050Å color center by proton bombardment. If the time-radiation dependence can be made quantitative, the color center method will be used as a dating technique.

The above studies will be applied to an investigation of the relationship of ore deposition to volcanism.
NUCLEAR GEOCHEMISTRY

Under this contract the mass-yield curve for the spontaneous fission of uranium-238 is being studied. Attempts are being made to determine the fission yields of the following nuclides:

1. Masses 141, 143 and 144 (cerium isotopes);
2. Mass 147 chain (neodymium-147 and promethium-147);
3. Masses 89 and 90 (strontium isotopes), and
4. Masses 95, 97 and 103.

The mass-yield curves for the 14 Mev and 3 Mev neutron-induced fission of uranium-238 and thorium-232 will also be studied and the study of neutron-induced fission in nature will be continued.

Studies on the possible existence of some of the long-lived transuranium elements in the rare earths fraction isolated from pitchblende will be continued. The nuclear geochemistry of radium and its decay products will be investigated further. Further studies on the nuclear geochemistry of chlorine, iodine, mercury, technetium, rare gases etc. will be carried out.
The natural radioactive decay of the uranium isotopes of mass 238 and 235 to the respective lead isotopes of mass 206 and 207 has been used in geologic age dating of minerals. However, puzzling disagreements between the two ages calculated from the ratios: 
\[
\frac{\text{lead}^{206}}{\text{uranium}^{238}} \text{ and } \frac{\text{lead}^{207}}{\text{uranium}^{235}}
\]
have appeared. These disagreements cannot be attributed to errors in decay constants or analytical techniques. Detailed studies of these isotope systems in the mineral zircon (\(\text{ZrSiO}_4\)) have been made in the Division of Geological Sciences at the California Institute of Technology. The substitution of uranium and thorium for zirconium in the zircon crystal structure is a variable which depends on the crystallization history of the zircon. Techniques developed for separating the zircons from rock samples into different fractions reveal significant differences in uranium content in these fractions. Isotopic analysis of uranium and lead in zircon fractions from each of a variety of granites have shown consistently that the disagreement of ages determined from the lead-uranium isotope ratios is a systematic function of the comparative radioactivity of the zircons. For several fractions from a given rock, the disagreement increases with increase of radioactivity. This provides the important generalization that the most consistent ages for a rock will be obtained from the zircons with the lowest uranium concentration.

These systematic relationships make possible an analysis of the factors introducing discordances among isotope ratios in the zircons. These factors prove to be the physical-chemical conditions which have prevailed during geologic history. For some rocks, it is now possible to determine the time of original crystallization of the zircon and to recognize and date an important subsequent episode of chemical activity affecting the rocks. It may prove possible to characterize the nature of this younger chemical activity. Thus, the lead-uranium isotope systems may be a powerful tool for investigating the shrouded history of the older rocks in the earth's crust which generally have experienced much chemical modification or metamorphism.
STUDY OF THE NATURAL ABUNDANCES OF THE ELEMENTS AND ISOTOPES AND THE PROPERTIES OF METEORITES AND OTHER ASTRONOMICAL BODIES

The total activity on this project on meteorites can be divided into four groups:

1. Study of cosmogenic and primordial rare gases and other cosmic ray produced stable isotopes;
2. A continuing project of investigation of stable isotope abundances of several elements in meteorites: this is to see if meteoritic and terrestrial abundances are similar.
   
The elemental and isotopic abundances of the light elements (particularly lithium and boron) as well as those elements with large numbers of isotopes like tin and germanium are being investigated. These studies bear heavily on nuclear synthesis.

3. Equations of state for gas spheres. These have been worked out and the effects of collisions of objects on the earth and the moon are now being studied.

4. Using some of the most advanced techniques in microbiology and micro-probe analysis, the nature and composition of the fossil-like forms in carbonaceous chondrites are being determined.
A variety of problems involving artificial and natural radioactivities are being investigated. Studies are concerned with meteorites and chronology of the earth, solar system and galaxy. Cosmic ray induced radioactivities in meteorites, with reference to the past intensity of cosmic radiation, cosmic history of meteorites and their terrestrial ages and associated impact products, are being studied. Nuclear reactions with thick targets induced by high energy protons and their secondary radiations are being investigated; these simulate cosmic ray interactions with meteorites. Identification and characterization of unknown or incompletely characterized nuclides is under way; particular attention is being paid to those which might be of use as tracers or in geology. Additional manifestations of extinct natural radioactivity are being sought and the chronology of nucleosynthesis in the galaxy and the solar system is being studied. An attempt is being made to improve the Thorium isotope method of dating marine sediments.

Other current investigations are concerned with improving low-level radioactivity measurement instruments and techniques, performance characteristics and theory of operation of proportional counters and investigation of short-lived alpha emitters produced using the Carnegie Tech 440 Mev synchrocyclotron.
RADIOCHEMICAL AND GEOCHEMICAL STUDIES

Research is devoted primarily to a study of cosmochemical problems by radiochemical techniques, and extends into three principal areas. These are:

1. Cosmic-ray exposure age of meteorites from their $\text{Al}^{26}$ and $\text{Ne}^{21}$ content.

2. Origin of meteorites, that is, a reconstruction of the chemical and physical processes that led to their development. Experiments planned in this area include electron microprobe measurements, and determination of Ag, In, Tl, and Bi by neutron activation analysis.

3. Determination of the micrometeorite influx rate, and its secular variation, from the Ir content of deep-sea sediment.
A variety of problems concerned with isotopic geochemistry are under study. These include such subjects as the study of the lead isotopic composition of sedimentary and metamorphic pyrite, the U-Pb system in zircons to learn about the nature and extent of age discordances, the study of the early history of the Norwegian basement, and the application of the K-Ar method to basaltic rocks. Also, the helium method of age determination is being applied to magnetite from ancient terranes, the discordances between the Rb-Sr and K-Ar chronometric systems are being studied, and the time range for the emplacement of the porphyry copper ores in the Rocky Mountain region is being investigated. Since recent work has demonstrated the oldest known rocks to be in Southern Rhodesia and the ancient basement of Tanganyika, further work will be undertaken to exploit this development. Finally, the geologic time scale for Cambrian and more recent stratigraphically defined rocks is being studied.
ALTERATION AND MINERALIZATION OF PRIMARY URANIUM DEPOSITS

In the Colorado Plateau uranium province solutions responsible for uranium precipitation have frequently produced mineral changes in surrounding rocks. These changes, the associated geological setting and the uranium mineralization provide significant phenomena now under study near Moab, Utah; Grants, New Mexico and at other critical places.

Stratified uranium deposits southeast of Moab overlie sedimentary rocks in which solution effect changes extend downward deeply from uranium ore bodies. Microscopic, x-ray, thermal and infrared studies of the minerals in such altered areas establish mineral transformations which bear on the origin of the ores. Significant changes may also be observed along a major fault which truncates the ore bodies.

Near Grants uranium-bearing strata have been invaded by a sequence of Tertiary volcanic intrusive features. Some volcanic rocks have been dated at $3\frac{1}{2} - 4\frac{1}{2} \times 10^6$ years (K/A method). Numerous pipe-like bodies (non-volcanic) with associated mineral changes also invade the sedimentary strata. One of these is known to contain uranium. Also, ore-bearing limestone near Grants together with an underlying sandstone exhibit significant mineral changes of importance in the interpretation of the origin of the uranium deposits.

Such studies provide information on the mechanism of uranium emplacement which should prove useful in future exploration. Also cumulative data to date indicate that exploration should not fail to consider original deep seated sources for the uranium ions notwithstanding extensive lateral distribution.
The potassium-argon ages of selected iron meteorites will be determined by neutron activation analysis, employing the $^{41}$K$(n,\gamma)^{42}$K and $^{40}$Ar$(n,\gamma)^{41}$Ar reactions. Corrections for cosmic ray effects and for primordial argon will be made based on the cosmogenic $^{36}$Ar and primordial $^{36}$Ar contents, as simultaneously measured by the $^{36}$Ar$(n,\gamma)^{37}$Ar reaction. To determine whether or not there is any significant atmospheric Ar component in the measured data, the argon will be measured differentially as the meteorite is heated slowly to its boiling point.
During the contract year 1961-1962 a cooperative program of research on the geochemistry of curium and plutonium was established with Argonne National Laboratory. This work is being continued with one investigator, W. K. Sabine, having spent the summer of 62 at Argonne. The main activities are to obtain, prepare and analyze by mass spectrography further samples of minerals that have a high probability of containing curium, plutonium or their disintegration products. In addition, work on the crystal chemistry of natural and synthetic rare-earth carbonates will be continued.
Carbonates which are highly thermoluminescent in the natural state are ideal compounds for studying radiation damage effects on geologic materials.

The primary function of studies carried out under this project is to answer some of the questions concerning what parameters (pressure, temperature, etc.) control the intensity of luminescence measured. Information of this nature can furnish data of value in developing suitable phosphor materials for radiation studies.

To properly evaluate these controlling factors, a knowledge of carbonate geochemistry and luminescence theory is essential; consequently, for several years a basic study of relationships between trace element content and crystal imperfections in carbonates has been underway. This study has furnished information helpful in describing the thermoluminescence effects which have been observed.
Highly sensitive radiochemical techniques and neutron activation analysis methods are being applied to geochemical and cosmological problems.

The development and refinement of neutron activation analysis, particularly as applied to the less common elements in the sub-microgram region is under way. Composite activation analysis schemes for the determination of several trace elements simultaneously is being studied.

Techniques developed above will be applied to solve various problems in geochemistry and cosmology, particularly those related to elemental abundances in meteorites, tektites, deep-sea sediments, and the lithosphere. These studies are directed to determinations of cosmic abundances, geochemical distributions, and experimental tests of theories relating to the origin of the meteorites.

The study of cosmic-ray-induced radioactivities in meteorites and terrestrial materials by use of refined low-background counting techniques is also under way. These studies lead to information on cosmic radiation levels in space, dating methods for events in the life history of the meteorites, and mechanisms of high energy nuclear reactions.
INVESTIGATIONS IN ISOTOPIC ABUNDANCES OF STRONTIUM, CALCIUM AND ARGON IN CERTAIN MINERALS

It has been discovered by Hurley that variations in the ratio $\text{Sr}^{87}/\text{Sr}^{86}$ provide a powerful new means of investigating the development of the earth's crust. This ratio reflects the differentiation history of the planet, and details studied so far have indicated an approximately steady increment of continental crustal material, oceans and atmosphere at the earth's surface throughout the last 2800 million years of earth history. It appears that average continental materials contain at least 50% new additions from deep sources, with less than 50% ancient reworked material. The method goes so far as to indicate the genesis of most rock types. These findings are all in outline form with minimum supporting data and investigations must be extended in several directions to arrive at incontrovertible answers.
COPRECIPITATION OF METALLIC IONS WITH CALCIUM CARBONATE

The compound CaCO₃ commonly occurs naturally as the polymorphs calcite and aragonite. Both polymorphs usually contain a variety of trace element impurities which have substituted for Ca²⁺ in the structure. The main aim of this work is to study the factors which influence the coprecipitation of foreign elements with calcite and aragonite from aqueous solutions between room temperature and 350°C, and to use the results of these experiments toward defining the chemical composition of the solutions from which natural calcites and aragonites have precipitated.

The coprecipitation of Sr²⁺ with calcite and aragonite has been studied between 25°C and 250°C. The distribution coefficient k⁰⁺⁰Sr, defined by the equation

\[ \frac{m_{\text{Sr}^{2+}}}{m_{\text{Ca}^{2+}}} \text{aragonite} = k_{\text{Sr}} \frac{m_{\text{Sr}^{2+}}}{m_{\text{Ca}^{2+}}} \text{solution} \]

passes through a minimum near 100°C. For nearly strontium-free aragonite it has the value 0.59±.02 at this temperature and for aragonite in equilibrium with strontianite a value of 0.80±.04. The corresponding values of the distribution coefficient for calcite are nearly an order of magnitude smaller.

The distribution coefficient of Mn²⁺ between solution and calcite is 16±2 at 25°C and decreases continuously to 2.2±0.2 at 325°C. The distribution coefficient of Zn²⁺ between solution and calcite at 170°C is 55±5 in dilute solutions, but is very much smaller in the presence of large chloride concentrations.

Our results are being compared with the observed coprecipitation in two areas of natural carbonate precipitation: caves and shallow marine environments, and are being applied to study the changes in the chemical composition of the fluids during ore deposition in hydrothermal ore deposits.
GEOLOGIC DATING OF CORALS AND OTHER CALCAREOUS MATERIALS

Recently proposed procedures for dating events occurring up to 300,000 years ago are based on the observation that newly deposited corals contain uranium but are essentially free of Th$^{230}$ and certain other uranium daughters. As these deposits age, the uranium daughter elements accumulate. It is possible to use the Th$^{230}$/U$^{238}$ ratio as a measure of age, provided the following conditions are satisfied:

1. The original materials contain a measurable amount of uranium and were essentially free of Th$^{230}$ or contained this isotope at a known level, and
2. There was no subsequent migration of uranium or thorium into or out of the specimen.

This work is aimed at establishing a reliable method for dating Pleistocene events beyond the range of the radiocarbon method. It is directed toward establishing criteria by which one may judge whether or not a given calcareous marine specimen satisfies the requirements for dating by the Th$^{230}$/U$^{238}$ method. During the past year, uranium, isotopic thorium, radium and crystal structure determinations were made on modern marine shells from 14 geographic locations. Similar analyses are being made on corals and ancient shells from a number of well defined marine horizons. The Th$^{230}$/U$^{238}$ ages are being compared with ages based on stratigraphic considerations and in some instances on C-14 analyses.
SULFUR ISOTOPES AND THE ORIGIN OF SANDSTONE-TYPE URANIUM DEPOSITS

The sulfur isotope abundance data for various sulfur-bearing constituents of vein-type and sandstone-type uranium deposits have been obtained to determine the importance of bacterial processes in the localization of ore deposits and to provide additional knowledge concerning the distribution of sulfur isotopes in several geologic environments.

A relatively narrow range of $^{32}S / ^{34}S$ ratios was found, near the meteoritic value (22.21), for primary sulfides of vein-type deposits and is indicative of magmatic hydrothermal mineralization.

Sulfides associated with sandstone-type deposits characteristically exhibit broad $^{32}S / ^{34}S$ ratio variations and are commonly enriched in $^{32}S$ relative to meteoritic sulfur. The evidence would suggest that the mineral constituents were deposited from ground water solutions in local reducing environments. The precipitating agent was hydrogen sulfide, variably enriched in $^{32}S$, generated by sulfate reducing bacteria.

Isotopic equilibrium constants derived from sulfide-sulfate mineral pairs do not provide satisfactory estimates for the temperatures of mineralization due either to noncontemporaneity and/or nonequilibrium conditions of deposition.

A mechanism involving the bacterial reduction of a finite quantity of sulfate is proposed to account for the anomalously low $^{32}S / ^{34}S$ ratios for sulfides of the Woodrow mine.

A cursory study of the $^{12}C / ^{13}C$ ratios of carbonates associated with sandstone-type deposits indicates that, in general, the quantity of calcite-carbon derived from organic material is small as compared with that derived from sedimentary carbonates in the enclosing sediments.
## Section 3

Radiation, Photo-, and Hot Chemistry (R)

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* Summary not available
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BOSTON UNIVERSITY, Boston 15, Mass. AT(30-1)-2383

Norman N. Lichtin 5/16/62

RADIATION CHEMISTRY OF ORGANIC COMPOUNDS

The principle emphasis has been the study of the radiolysis of methanol using $^{10}\text{Be}(n,\alpha)\text{Li}^7$ recoils and cobalt-60 gamma rays. The research involves the effect of scavengers (such as $\text{O}_2$, $\text{Fe}^{2+}$, $\text{I}^-$, $\text{I}_2$, $\text{ArH}$, etc.) on the nature and yields of the radiolytic products. Particular attention is being focused on oxygenated systems.

Concurrent with the investigation described above is a program of research involving the reaction of nitrogen atoms (produced by micro-wave discharges) with $\text{C}_1^4$ labelled substrates. Initial efforts will be directed towards refinement of earlier work on labelled propylene.
EFFECTS OF MERCAPTANS AND DISULFIDES ON FREE RADICAL, LIGHT AND HIGH ENERGY RADIATION INDUCED REACTIONS

The non-chain photochemical conversion of benzophenone in 2-propanol to benzopinacol and acetone is retarded and inhibited by mercaptan and disulfide. The initial mercaptan or disulfide is not consumed during the inhibition but is converted to a mixture of the two. An optically active alcohol, while not racemized by irradiation with either benzophenone or disulfide, is racemized when irradiated with both present. The x-ray induced formation of benzopinacol and acetone is inhibited similarly. Each molecule of mercaptan or disulfide may negate the chemical action of many quanta of light or high energy radiation. A mechanism has been proposed for these reactions and the relation to protection against damage indicated.¹

More detailed study of the racemization of the alcohols and related ethers under these conditions will be made. The acetophenone-l-phenylethanol system will be studied to ascertain whether the presence of different kinds of radicals is needed for the sulfur compounds to act as inhibitors. The chemistry of ketones which are not readily converted to pinacols by this reaction will be studied. The effect of sulfur compounds on the light induced monomolecular reduction of ketones will be examined. The effects of metal cation desensitizers will be compared with those of sulfur compounds. More detailed study of the x-ray initiated reactions, and the effects of mercaptans on them, will be made.

Mercaptans catalyze the light initiated decarbonylation of aldehydes. Benzophenone also catalyzes this reaction, and mercaptans do not inhibit the effect of the benzophenone. The effects of mercaptans and metal desensitizers on the benzophenone catalyzed reaction will be studied. Other aldehydes will be examined.

SOLID STATE POLYMERIZATION

1. Crystalline derivatives of $\alpha$-fluoroacrylic acid will be polymerized in the solid state and the microstructure of the polymer (stereoregularity, fraction of head-to-head addition) will be compared by NMR analysis with corresponding polymers prepared in solution.

2. The determination of the crystal structure of vinyl stearate will be continued and the extent of the retention of the crystalline order during the solid state polymerization of this monomer will be investigated.

3. A study of the solid state polymerization of bifunctional vinyl monomers, particularly compounds with two non-equivalent double bonds, will be initiated.

4. Solid state condensation reactions will be studied by crystallographic techniques, with particular attention to the possible effects of preirradiation on the nucleation of such processes.
The project has begun a long range program to attack, in an organized and concerted way, the problem of radiationless energy transfer between molecules, bringing together the results of investigations in several sub-fields.

1. **Dependence of Efficiency of Energy Transfer on Intermolecular Spacing**
   By varying the spacing between molecules in a condensed scintillator, the relation between range and efficiency of radiationless energy transfer is being investigated.

   A study of the concentration dependence of transfer efficiency between donor and emitter molecules is expected to yield information about the number of individual transfer steps involved in the long distance energy migration.

2. **Relative Displacement of Absorption and Fluorescence Bands**
   The interaction of excited molecules on their surroundings and the effects of this interaction on radiationless transfer will be studied in polymer matrices containing scintillation systems.

3. **Temperature Dependence on Non-Radiative Transfer Efficiency**
   It is planned to investigate the (very small) activation energy which may characterize radiationless transfer. Such a requirement would rise from the necessity of activation from equilibrium to "Franck-Condon" states before transfer was possible.

4. **Participation of Long-Lived States in Energy Transfer**
   Through flash-excitation experiments, the participation of long-lived species (triplets, dimers) in energy transfer will be investigated.

5. **Vibrational Relaxation in Excited Molecules**
   Using flash-technique, the collision dependence of vibrational degradation and the relation of this process to energy transfer will be examined.

6. **Intramolecular Energy Transfer**
   Both theoretically and experimentally, it is planned to attack the problem of the transfer of excitation energy among various coupled vibrational modes of a simple molecule.

7. **Radiation Damage**
   The decline of scintillation efficiency resulting from radiative damage of organic crystals is strongly influenced by non-radiative energy transfer and this problem is being experimentally investigated.
Radiationless processes in polyatomic molecules is one of the main fields that has been examined in this laboratory during the past year. The effect of interchanging energy levels on the emission properties of molecules has been examined for some nitrogen heterocyclics. It was found that if the lowest singlet state of the molecule is of the \((n^1\Pi^0)\) type, the presence of a \((\pi^*\pi^*)\) triplet level of lower energy enhances the intersystem crossing process \((S_1 \rightarrow T)\) and thus increases the phosphorescence intensity on the expense of that of fluorescence. Similar effects are also observed if the molecule has a lowest singlet state of the \((\pi\pi^*)\) type with an \((n\Pi^0)\) triplet level below it.

The importance of vibrational overlap integral between the ground vibrational levels and the lowest triplet zero point level is also examined. It is found that high pressure effects on the life time of the phosphorescence as well as on the phosphorescence - fluorescence intensity ratio can be explained by proposing a displacement of the equilibrium internuclear distances of the triplet level with respect to that of the ground state. This is found to greatly enhance the radiationless processes between molecular energy levels because of the vibrational overlap factor.

The last part of the study was concerned with polarization measurements of electronic transitions in aromatic molecules. The results found on the phosphorescence raised the question of its origin. Polarization on the triplet \(-\) triplet absorption indicated that while the Pariser's method for calculating energy levels is very good for the singlet states, it is not equally good in predicting triplet levels.
The fundamental purpose of this research program is to evaluate the relative importance of ionic, free radical and electronically excited intermediates in the radiation chemistry of gases and liquids. In order to accomplish this goal, several methods of approach are being used. These are, a comparison of the photochemistry of selected compounds, use of deuterated compounds to trace the path of the reaction, and the use of free radical and ion scavengers to inhibit product formation via these mechanisms.

Compounds presently being studied are acetylene, ethane and $\text{H}_2\text{-D}_2$ mixtures. Future studies will include organo-metallic compounds of the type $\text{R}_2\text{Hg}$. 
APPLICATIONS OF FISSION PRODUCT SOURCES IN ORGANIC RADIATION CHEMISTRY

These studies are concentrated on the design and performance of beta-ray sources suitable for use in experimental studies in organic radiation chemistry. Sources consisting of Pm-147 in the surface layer of glass reaction vessels, and in other supporting solids, are of prime interest. The study of the problems of dosimetry relevant to such sources and the investigation of new chemical effects of possible utility in dosimetry are current projects.
Radiolysis of 1,2-dihydronaphthalene, 1,4-dihydronaphthalene and isomeric cresols with gamma-rays gave low yields of gas (primarily H₂) and some high boiling products (G value ~ 0.1). The structures of the high boiling products are being investigated.

It is planned to initiate a study of the flash photolysis of o-substituted benzophenones and to attempt to detect reactive intermediates spectroscopically.
THE EFFECTS OF RADIATION ON THE CHEMICAL ACTIVITY OF CERTAIN SOLID OXIDE CATALYSTS

The purpose of this research is to learn about the fundamental processes involved in radiation-induced changes in catalytic activity. A combination of nuclear reactor and gamma irradiations with precise chemical and physical measurements is expected to provide a clearer and more systematic picture of these processes.

The effects of radiation on solid oxide catalysts will be studied by measuring the first-order rate constant of the $\text{H}_2\text{-D}_2$ exchange reaction before, during and after neutron and gamma irradiation. The exchange reaction will constitute the chief method for measuring the chemical activity of the catalysts. Measurements will be made in the temperature range 25-200°C. For each catalyst, runs will be made in the gamma-neutron field of a 5 Mw research reactor and in the pure gamma field obtained from spent fuel elements or from the reactor during periods of shut-down. With some of the catalyst materials the effects of intentionally added impurities will be studied. As soon as possible after each irradiation attempts will be made to characterize the radiation-induced defects using physical methods of conductivity and electron spin resonance measurements. Particle size, pore structure and surface area measurements will be made before and after each irradiation.
A variety of experimental techniques are being applied to study the primary chemical and physical processes in the radiolytic decomposition or isomerization of various organic compounds (cyclic ketones, ethyl iodide) and aqueous solutions (acetone, D$_2$O + H$_2$O, cystine, cystamine). Careful kinetic analysis of gaseous and liquid products will be made. Radical scavenging and isotopic labelling will be used and the effect of varying temperature and phase will be investigated. Comparisons will also be made with the short wave length photolysis of systems identical to those being studied radiolytically.
The current emphasis in this program is:

1. The study of EPR hyperfine spectra and color centers in irradiated alcohols and correlation of this information with trapped free radicals generated by independent means,

2. The radiation chemistry of selected aromatic compounds and binary mixtures of aromatic and alicyclic hydrocarbons in an effort to determine the partition of energy deposited by ionizing radiation in condensed systems and

3. Vapor phase studies.

In addition, studies, by EPR, of reactions of free atoms and radicals at -196°C in organic matrices and their relation to radiation induced changes and the identification by emission spectroscopy of electronically excited intermediates in irradiated organic gases have been initiated.
EXPERIMENTAL EFFECTS OF PILE RADIATION ON PURE FLUOROCARBONS

Fluorocarbons from CF₄ through C₆F₁₄ in the alkane series and other derivative molecules of fluorocarbons have been purified and irradiated. Analyses of the products have been obtained only for CF₄, C₂F₆, and C₃F₈. The work to be done during 1962-63 is the analyses of the remaining compounds and a study of the effect of isomerization of C₆F₁₄ on radiation damage.
The radiation chemistry of two highly branched hydrocarbons--2,2,4-trimethylpentane and 2,2,4,6,6-pentamethylheptane--has been studied with 50 kvp x-rays. As many of the radiolysis products as possible were identified and G values determined. From the results, most of the radiolysis products, both saturated and unsaturated, of saturated branched hydrocarbons of general formula C_nH_{2n+2} with carbon content less than C_n could be related to some structural portion of the parent hydrocarbon. The major radiolysis products of carbon content less than C_n evidently are formed by fission of the carbon-carbon bonds at sites where the greatest degree of branching occurs. Most of the radiolysis products of carbon content greater than C_n are most likely formed by a combination of a fragment of less than C_n with a C_n component or a dimerization of two C_n components. This phase is continuing with irradiations of 2,2,4-trimethylpentane with a 12-kilocurie Cs-137 source, and will be extended to include radiation chemistry studies of 2,2,4,4-tetramethylpentane.

The program will also include a study of the radiation chemistry of alcohols and this phase will be initiated with an investigation of neopentyl alcohol.

The radiation chemistry of the cyclohexane-cyanogen system is now being investigated. The yields of hydrogen, cyclohexane, and dicyclopentyl from cyclohexane are decreased when cyanogen is present and cyclohexyl cyanide and hydrogen cyanide are formed. After completion of the study of this system, the radiation chemistry of other systems of cyanogen-organic substances will be investigated.
The purpose of this project is to investigate the changes in molecular structure produced in organic polymers by nuclear irradiation. Using a Beckman IR-4 spectrophotometer, infrared absorption spectra of thin films of various organic polymers are being measured before and after irradiation with Co\textsuperscript{60} gamma rays.

Analysis of the infrared spectra of the following polymers after irradiation will be made to determine their double bond concentrations: vinyl chloride/vinylidene chloride copolymers, polypropylene, polyacrylonitrile, styrene/acrylonitrile 71/29% copolymer, and polyvinyl carbazole. The spectrophotometer will be calibrated with N.B.S. pure olefins for determination of vinyl and trans-vinylene unsaturation determinations. The spectra of polyvinyl carbazole, after irradiation to a dose of approximately $2 \times 10^{10}$ rads, will be studied to determine if the C=C stretching band at $1670 \text{ cm}^{-1}$ and the CH stretching band at $3025 \text{ cm}^{-1}$ are observed in support of the assignment of the $800 \text{ cm}^{-1}$ band to $\text{R}_2\text{C}=$CHR\textsubscript{3} formed during irradiation.
Recent studies under this contract have shown that in uranyl sensitized photolysis of oxalic acid the only gaseous products are carbon monoxide and carbon dioxide. The relative amount of these two gases produced varies from 8:1 (CO:CO₂) at low pH's to a minimum of 1.4:1 at higher pH's. This suggests two competing mechanisms.

It is assumed at present that there are two or more photosensitive uranyl-oxalate complex species and it is planned to combine results from photolysis, absorbance and pH measurements to determine the nature of these species.

Because the nature of the reaction varies with pH, quantum yield may also be dependent upon pH of the system. If the nature of the variable mechanism can be ascertained, monochromatic quantum yield measurements will be initiated over the pH range 0 to 4.5.
The aim of the proposed work is three-fold:

1. To use previously prepared ILLIAC (high-speed electronic digital computer of the University of Illinois) programs to solve the diffusion-kinetic equations which presumably describe the radiation chemistry of aqueous solutions, and, therefore, develop an understanding of the early happenings of the chemical stage of the radiolysis of these solutions. These programs will be rewritten for an IBM 7090.

2. To use a low-energy electron impact spectrometer, recently constructed, to investigate the optically forbidden electronic levels of molecules in the gas phase and to study their possible importance in Radiation Chemistry. The technique consists in shooting a mono-energetic beam of low-energy electrons into a gas at low pressure and energy analyzing the scattered electrons. The energy losses correspond to the excitation of electronic levels. Comparison with optical spectra furnishes information concerning the optically forbidden levels.

3. To investigate elementary processes in the vacuum ultraviolet photochemistry of hydrocarbons using light of variable wavelength and to determine the effect of ionization on these processes. Also, to perform analogous experiments with mixtures of DI and H₂ or hydrocarbons aimed at studying the reactions of "hot" D atoms. Finally, to build an electric quadrupole mass spectrometer for use as a molecular beam detector.
RADIATION CHEMISTRY

For the current year the research will follow two principle lines. The first involves studies of energy transport processes in non-crystalline solids such as the linear organic polymer, polymethylmethacrylate. Energy transport by both ions and excited states are being considered. The experimental aspects of the work involve the study of the light emitted by certain systems and the damage produced in these systems under irradiation by ultraviolet light and by ionizing radiation such as fast electrons. The systems being studied at present are polymers of polymethylmethacrylate that contain small amounts of scintillators or other energy sinks, either in solid solution or as part of the polymer molecule.

The second part of the research work involves a study of dosimeters of high-energy electrons. This is vital to the first part of the work if really quantitative work is to be done. Changes in the optical properties of plastics and glasses exposed to such radiation are primarily being considered. The change in the index of refraction is presently being examined in solid samples of polymethylmethacrylate. Optical absorption changes in glasses containing small amounts of cobalt are also being studied.
This work involves the study of the chemical reactions of energetic atoms produced by nuclear recoil or by heterogeneous flash photolysis. Primarily, it is desired to determine the mechanisms by which energetic recoil species lose their energy and react chemically in various media. Furthermore, it is desired to learn more about the chemistry of some of the less-familiar elements, polonium, for example.

The hot atom chemistry of thallium, lead, bismuth, and polonium recoiling from alpha decay in the presence of various inorganic and organic compounds, such as CO₂, CO, the hydrocarbons, oxides of nitrogen, air, water, H₂ and other gases is being investigated. These reactions are to be compared with the reactions of the above-mentioned metallic atoms, and others such as zinc and tin, in the same media when vaporized by exposure to a high intensity light flash.

Gaseous intermediates produced by the flash heating experiments are to be studied using techniques of flash photolysis and kinetic absorption spectroscopy in the ultraviolet and visible regions.

Other work involving the hot atom chemistry of tin recoiling from radiative neutron capture in various inorganic crystals is in progress.
The influence of various radiations on the boron hydrides is being studied. Pentaborane and decaborane bombarded with deuterons give two new boron hydrides, i.e., decaborane-16 and icosaborane-26 respectively. The radiation chemistry of this system will be studied. Attempts are now underway to synthesize some of these new higher boron hydrides by conventional chemical means. Some of their properties, such as ionization potentials, appearance potentials and behavior under electron impact, will be studied. The electron impact fragmentation of tetraborane, pentaborane-9, pentaborane-11 and hexaborane-10 is being investigated. The products that are produced when a strong shock passes through various boron hydrides are also being studied and some of the hydrides such as hexaborane are being synthesized in this manner.

The chemistry of nitrogen recoils in carbon compounds is being investigated. Most of the work has been done with \( ^{13}N \) produced by the reaction \( C^{12}(d,n)^{13}N \). The products produced are generally cyanides, i.e., HCN, C\(_2\)CN. No evidence has been obtained for the formation of N-H or N-Cl compounds. Recently, indication has been obtained from other studies that possible compounds such as NF\(_3\) might be present; consequently, CF\(_4\) will be bombarded with deuterons and the reactions products in this system will be studied.
This contract is concerned with fundamental investigations of the chemical interactions of energetic atomic and molecular species. The major portion of the research is concerned with the reactions of energetic atoms produced in nuclear transformations, especially tritium from $\text{Li}^6(n,\alpha)\text{H}_3$ and $\text{He}^3(n,p)\text{H}_3$.

The reactions of recoil tritium are being investigated in the gas phase with various gaseous hydrocarbons and other low boiling liquids, e.g. cyclopropane, cyclobutane, ethylene oxide, acetone, dimethyl ether, benzene, silane. Other investigations are concerned with the reactions in all phases with particular structural features in organic molecules, such as double bonds, particular substituent groups, etc. Particular attention is being given to the competition of different organic molecules and functional groups in "hot" reactions.

Other nuclear recoil species under investigation include $\text{P}^{32}$, fission products, and $(n,\gamma)$ halogen and osmium activities. Direct radiation-induced synthesis of organic compounds labeled with fission product radioactivity is being studied.

High specific activity ethylene, acetylene, etc., are being used in studies of the effects of radiolysis on trace components in the system. Free radical reactions are being studied through the addition of radiolytic hydrogen atoms to labeled olefins.
Reactions of energetic hydrogen atoms will be studied using the technique of hot filament atomization of molecular hydrogen. Energies of the hydrogen atoms are varied by changing the filament temperature. Tritium will be used as a tracer to enable product identification by counting techniques. Test for molecular inversion accompanying hydrogen exchange will be made. Isotopically pure tritium will be used in developing methods for preparing non-specifically labeled organic compounds. Quantitative measurements will be made of hydrogen atomization rates and rates of reactions of hydrogen atoms with solids. The effects of changing the temperature of the solid will be studied. Previously, target temperatures of 77 K have been used for the most part.

Electron impact on molecular hydrogen will be used as a source for energetic hydrogen atoms. By this technique the reactions of hydrogen atoms possessing kinetic energies of 3 to 11 ev will be studied. Isotopically pure tritium will be used to enable radiochemical identification of the products from a small number of reactions.
The effect of electron energies on the mass spectral cracking patterns of a number of fluorine-, sulfur-, and phosphorus-containing substances, is under investigation as are theoretical calculations based on the quasi-equilibrium theory of mass spectra. It is also planned to study the shapes of ionization efficiency curves and to determine relative electronic transition probabilities for diatomic and the simpler polyatomic molecules.

In addition, hot-atom studies with carbon-14 resulting from the (n,p) process on various organic, biochemical and inorganic compounds, in order to determine the radio-labeled products and the distribution of radioactivity in the various products, will be continued as will charged-particle bombardments of condensed systems using Tesla-coil irradiation.
The two most important primary decomposition processes in radiolysis of gaseous hydrocarbons are:

1. H-atom formation and


Using 1470 A light, the study of direct photolysis of ethane in the presence of added ethylene and also at conversions below 0.001% has been directed at the determination of the contribution by process 1. above. While no evidence for hydrogen atoms was found, experimental precision allows no more than a 20% contribution by this process. That essentially all of the ethane decomposing does so by molecular detachment of hydrogen, process 2. above, is in striking contrast to about 36% and about 10% by this process in gamma-radiolysis and mercury photosensitized decomposition, respectively.

Current work is concerned with observation of the contributions by processes 1. and 2. in cyclic hydrocarbons as well as to a better understanding of the fragment left behind in molecular detachment.

Study is also being made of the diffusion of photolytic products away from a lamp window at which light is absorbed inhomogeneously.
The radiation chemistry of several organic processes are under study. These include:

1. Radiation-induced reactions of amides and unusual hydrocarbons, neither of which have been studied before, to give products and polymers and

2. Radiation-induced polymerizations of unusually reactive monomers such as ethenesulfonamide and bicycloheptadiene. The mechanism of the polymerization of ethylene in chlorohydrocarbon solvents and of methyl methacrylate is being studied at temperatures from -50 to 25°C.
RADIATION CHEMISTRY: COBALT SOURCE DESIGN AND THE STUDY OF GRAFT POLYMERIZATION

Research in radiation-induced graft polymerization will be extended to obtain detailed information on the kinetics of grafting and the properties of graft copolymers. Rate constants will be determined by steady state and rotating sector measurements. Attempts will be made to determine the free radical or ionic character of reactive sites on polymers from the nature of subsequent grafting reactions. The diffusion and solubility of monomers in polymers will be measured.

Measurements and calculations have been made of the dose rate from scattered gammas in the labyrinth of the University of Maryland Co$^{60}$ irradiation facility. Attempts will be made to fit the data to a simple empirical equation of more general use.
The effects of ionizing radiations on various systems are being investigated by physical and chemical methods. In much of this work attention is focused on the nature and the reactions of free radical intermediates. A unique facility has been developed which allows the examination of liquid systems with electron spin resonance techniques during irradiation with fast electrons. As a result, a considerable amount of new detailed information has become available on the free radicals present during irradiation and on their reaction kinetics. This spin resonance work is being paralleled with scavenger studies which incorporate radioiodine and radiocarbon. Other investigations in progress include studies of ion-molecule reactions by mass spectrometric techniques, studies of competitive reactions which occur in aqueous systems, studies of radiation chemical effects in organic halide, amine and aromatic systems and studies of reactions induced by irradiation in gases at low pressures.
Atoms and ions, activated by nuclear processes, react chemically, frequently according to mechanisms not observed at thermal energies. On the basis of the type and extent of products formed in the reactions it is possible to suggest mechanisms for the high-energy reactions.

Mathematical models of such reaction, analogous to neutron cooling-down equations have been developed.

Reactions currently being studied include those of gaseous alkanes and haloalkanes with Br$^{80}$ activated by both isomeric transition and (n,$\gamma$), Cl$^{38}$ from the Cl$^{37}$(n,$\gamma$)Cl$^{38}$ process, and I$^{128}$ from the I$^{127}$(n,$\gamma$)I$^{128}$ process.

A gas chromatography unit for separation of tracer amounts of radioactive gases has been constructed. Incorporated as part of the unit are a specially constructed high-pressure constant-flow regulator and a programmed temperature regulator.
In studies of the radiation chemistry or organic liquids, there is still no system for which it has been possible to evaluate the relative importance of ions with respect to electronically excited neutral states in determining the observed yield of a particular product. One of the techniques that this project will employ is based on the observation that the lowest excited singlet state of many organic liquids survives long enough to transfer its energy to certain additives present in low concentration. It is proposed to measure the effect of several additives on the radiation (✓) and photochemistry of some organic liquids and then to independently measure the efficiency of energy transfer from these liquids (optically excited) to the additives. Furthermore, by comparing the luminescence of optically excited organic solutions with gamma ray induced luminescence, it is possible to determine the efficiency with which gamma rays produce low lying electronic states regardless of whether these states lead to observed products or not. Moreover, luminescence quenching studies may permit us also to determine what fraction of the low lying electronic states produced by gamma rays have had ionized states as precursors.
STUDY OF DECOMPOSITION AND RECOMBINATION REACTIONS OF WATER IN
THE VAPOR PHASE IN THE PRESENCE OF RADIATION

The overall purpose of the research program is the study of the
radiation chemistry of gaseous mixtures of hydrogen, oxygen, and
water vapor. Sufficient knowledge of the rates and mechanisms of
the recombination reactions of these gases (which occur in nuclear
reactor superheaters) is not available.

A high vacuum system capable of producing pressures less than $10^{-6}$ mm
of mercury has been built in order to introduce pure reactant gases
into the reaction vessel, and the system enables the gases to be
sampled and analyzed. The reactants will be irradiated with gamma
rays obtained from a 9500 curie Cs$^{137}$ source.

The main experimental studies to be undertaken are the determination
of the radical pair yield of water vapor and the study of mechanisms
and rates of reactions between hydrogen, oxygen, and water vapor
under gamma irradiation. The latter is to be carried out with both
saturated and unsaturated water vapor at various conditions of
temperature, pressure and composition.
EFFECTS OF RADIATION ON CHEMICAL SYSTEMS

The effects of gamma radiation upon simple aliphatic amines is being studied to determine the mechanism. Product identification is by gas chromatographic analysis. Carbon 14 is being used as a tracer. Various other gases are added as scavengers and to study possible energy transfer in the gaseous systems.

The gamma radiolysis of aqueous and alcoholic solutions of some azo dyes is being studied. Reactions are followed colorimetrically and by gas chromatographic analysis of gaseous products. Paper chromatography and electrophoresis are used to identify products in solution. The mechanism of the solution reactions are proposed from the results.

Gamma radiolysis of solutions of stannous ion are being studied. The effects of acid concentration, inert salts and scavengers is determined. 'G' values for the solutions are being determined using ferrous ion and other related systems.
MECHANISM OF HIGH ENERGY RADIATION EFFECTS IN HIGH POLYMERS

The ultimate goal of this research is to discover the mechanisms of the chemical reactions and other effects produced during the irradiation of solid synthetic polymers by high energy radiations. One research planned is to investigate the growth and decay of unsaturation in polyethylene in the presence of NO gas. It is believed that the NO gas will quench free radical reactions, thus revealing that part of the reactions involving unsaturation due to ionization or excitation.

Another research involves the study of the kinetics of the decay of free radicals at different temperatures in order to determine the activation energy of the decay reaction (which, contrary to expectation, is first order rather than second order), and to correlate the temperature at which free radical reactions first appear on heating from liquid nitrogen temperature with other phenomena.

A third research planned will consist of a study of radiation effects in polypropylene oxide. The latter material can be obtained in three forms, atactic, isotactic and optically active.
Systematic and detailed investigation of the effects of phase, molecular structure, temperature, dosage rate, and solute concentrations on the radiolysis kinetics of relatively simple structurally related organic molecules is under way. The purpose of this research is to obtain information about reactive intermediates and their mechanisms for attaining stability in organic media. Proposed investigation for the forthcoming year include:

1. Tritium Beta-ray induced reactions in CH$_4$-D$_2$ mixtures at -196°C to -78°C.

2. Effects of temperature on the yields of organic products of the radiolysis of CCl$_2$Br$_2$.

3. Effects of temperature on the kinetics of the radiolysis of CCl$_3$Br-Cl$_2$ solutions.

4. Comparative study of the photolysis, pyrolysis, and radiolysis of nitromethane.

5. Effects of dosage rate and temperature in the Co-60 gamma-ray induced decomposition of chloroform.

6. Effects of phase, temperature, and solute additives on the radiolysis of n-pentane and of n-hexane.
This project is concerned with a number of reactions of elementary halogens in inert solvents.

Some effort is devoted to understanding the detailed processes associated with the formation and recombination of iodine atoms including measurement of quantum yields for dissociation and of rate constants for atom recombination. The use of the photochemical space intermittency effect to measure the diffusion coefficients of free atoms will permit a more rigorous test of current theories of diffusion controlled reactions.

Other effort is being directed toward understanding reactions of elementary halogens such as the effects of substituents on the highly polar exchange of iodine with benzoyl iodide and the elucidation of the mechanism of interhalogen formation.
HYDROCARBON REACTIONS FROM FISSION FRAGMENT IRRADIATION

The purpose of this work is to obtain experimental information on reaction yields and to identify products resulting from fission fragment irradiation of hydrocarbons in static systems.

Two major areas of investigation are being followed. The first is a continuation of study of the reactions of methane; the second, fission fragment irradiation of hydrocarbon-oxygen mixtures.

Effect of temperature on reaction G value will be measured; the type and distribution of products formed with fission fragments will be compared to those produced with gamma radiation and fission fragments present in the gas will be identified.

These investigations will be initiated using a batch reactor; subsequent plans include studies in which gas is continually circulated past a fission plate, and products continually removed. Two irradiation cells have been constructed and are now in use.
This project is concerned with a study of the fundamental chemical effects of radiation on solids. The effects of ultra-violet rays, X-rays, and bombardment by electrons, protons and neutrons on solids are being studied to determine the nature of the changes that occur.

The development of new techniques for the study of radiation effects is one important aspect of the program. The comparison of radiation effects with those produced by thermal degradation is another aspect.

Accomplishments to date include the study of neutron bombardment of zinc sulfide phosphors and a survey of the decomposition of a variety of molecules when exposed to electron bombardments. Currently, methods of determining damage by radiation are being applied to catalytic systems such as charcoal and alumina-silica that have been subjected to varying degrees of radiation damage. Considerable use is being made of electron spin resonance to characterize systems under study.
CHEMONUCLEAR REACTIONS IN INORGANIC GASES

Work is underway on the radiation chemistry of fission fragments and of fast neutrons. The long range objective is to obtain a sufficient understanding of the primary processes of energy transfer from fission fragments to chemical systems that possible applications of "chemonuclear reactors" may be explored on a less empirical basis than at present. Whereas most earlier studies of fission fragment energy loss focused on the fragment itself, the present approach emphasizes the identification of chemically significant species produced by the fragment. Specific studies include:

1. A kinetic investigation of the \( \text{H}_2 + \text{D}_2 \rightleftharpoons 2 \text{HD} \) reaction catalysed by fission fragments, and

2. A measurement of the efficiency for the production of nitrogen atoms in pure nitrogen gas as a function of fission fragment track length. As an aid to these studies a concurrent analytical and experimental study has been made of the energy loss of fission fragments in thin films.

The radiation chemistry of fast neutrons is related to the fission fragment work in two ways:

1. Chemical reactions induced by fast neutrons are to be expected in "chemonuclear reactors" and

2. The mechanism by which fast neutrons transfer energy to chemicals is similar in certain respects to that by which fission fragments near the ends of their tracks transfer energy.

Current studies on this aspect include the radiolysis of aromatic hydrocarbons by fast neutrons, and dosimetry of fast neutron irradiations.
The investigations have covered photochemical aquation (and, where non-aqueous solvents are involved, solvation) racemization, and redox reactions of a number of transition metal complexes. Types of compounds studied include various Cr(III) and Co(III) species, PtBr$_2$ and several square co-planer Pt(II) complexes, octacyanides of Mo(IV) and Mo(V) and of W(IV), and a few Rh complexes. In general, quantum yields were determined at at least two wave-lengths in the visible region, and for each type of reaction, where more than one occurred.

The most complete series is that of Cr(III) and Co(III) Complexes. For the former, the photoreactions are invariably aquation or solvation, and, in the case of the tris-oxalato complex, racemization. Quantum yields are relatively high (0.01 to 0.1 usually), slightly temperature dependent and nearly wave-length independent over the range 370 $\mu$m to 700 $\mu$m. The results are consistent with heterolytic bond fission as the initial act, with the nascent penta-coordinated species either recapturing the original ligand or a new one already present in the solvent cage. In the case of Co(III) compounds, either aquation or redox decomposition occurs, depending on the ease of oxidation of the ligand. This progression is most notable in a series of acidopentammines, and an intermediate member, such as the bromopentammine, undergoes comparable amounts of both modes of photolysis. Quantum yields are slightly temperature, and generally very wave-length dependent. The overall behavior is consistent with homolytic bond fission as the initial act, followed by competition between ligand return (no net change), electron return (aquation as net process) or ligand escape (redox net process).
RADIATION INDUCED DECOMPOSITION OF INORGANIC SALTS

The purpose of this research is to determine the mechanism of radiation induced decomposition of inorganic solids. The decomposition of the nitrates, perchlorates, and sulfates are currently being investigated. The method of investigation involves determination of stored energy by measuring heats of solution of the irradiated salts, study of the kinetics of the decompositions, study of the changes which occur in the lattice as a result of decomposition (X-ray and infra-red analyses), and detection of unstable intermediates by dissolution of the irradiated salt in nonaqueous solvents such as liquid NH₃, liquid SO₂, and alcohols.
A study will be continued of the alpha particle induced decomposition of gaseous benzene and cyclohexane at low intensity (about 1 rad per second). The effect of strong electric fields on the yields will be investigated. This provides information that may be used in learning something of the elementary processes taking place during irradiation. These results will be compared with the work of others at much higher intensities. Scavenger studies will also be undertaken.

A study will be made of the alpha induced decomposition of ammonia in the presence and the absence of added hydrogen. The effect of strong electric fields will be studied here for the same purpose as above.

Electron impact studies of negative ions formed in N₂O, NH₃, H₂S, and H₂O, will be made using a mass spectrometer. Special attention will be given to ionization efficiency curves, appearance potentials, and the effects of pressure on the ion currents produced. Ion molecule reactions involving negative ions will be investigated as well as the possible formation of clusters of negatively charged ions.
A study of the radiation-induced polymerization of cyclopentadiene \((\text{C}_5\text{H}_6)\) at \(-78^\circ\) has revealed the extreme potency of ammonia as a retarder of the reaction (J. Am. Chem. Soc., 84, 4355 (1962)). Thus, while the polymerization yield for pure \(\text{C}_5\text{H}_6\) corresponds to \(G(-\text{C}_5\text{H}_6) = 2.0 \times 10^4\), the addition of \(1.0 \times 10^4\) mole fraction of ammonia depresses \(G(-\text{C}_5\text{H}_6)\) to 160. It is proposed that the retardation reaction is ionic, and that ammonia acts as a base in this system; first, by causing proton transfer from propagating ions which may be considered as protonated intermediates (Bronsted acids), and secondly, by combining with carbonium ions to produce substituted ammonium cations. Ammonium-type cations would be inactive to polymerization growth, and presumably persist until neutralization. The cyclopentadiene-ammonia system is being studied over a range of ammonia concentrations in order to establish the kinetic details. Results indicate that the ratio of rate constants \(k_{\text{ret}}/k_{\text{prop}}\) is about 500, which suggests that \(k_{\text{prop}}\), the propagation rate constant, is of the order of \(10^6\) liters mole\(^{-1}\) sec\(^{-1}\), since \(k_{\text{ret}}\) is probably near the diffusion limit of \(10^9\) liters mole\(^{-1}\) sec\(^{-1}\) often characteristic of proton transfer reactions in solution. It is planned to extend this work to evaluate the effect of ammonia on the radiolysis of other hydrocarbons; the possibility of isotopic exchange will be investigated through the use of deuterated compounds.

Evidence for hydride-ion transfer reactions is now being sought by irradiating alkyl halides in the presence of likely donors. Additional investigations will center on other possible reactions of carbonium ions generated by the action of ionizing radiation.
Vapor phase, liquid phase, and solid phase irradiations of organic compounds will be continued using soft X-rays or Cobalt-60, whichever is more suitable for the study being performed. Irradiations of solids made into pellets with KBr will be studied analytically by infrared spectroscopy.

Studies on a series of derivatives of base compounds such as ethylene have disclosed important trends and this approach is being extended to acetylene derivatives. Studies on energizing of vapor phase reactions by admixture of noble gases will be extended to include interacting mixtures.

Gas chromatography and infrared spectroscopy are disclosing important analytical information and their applicability will be developed further.

Inorganic radiochemistry will be concerned particularly with separation techniques, such as ion exchange and solvent extraction, for purification of radioactive sources from accelerators to make them suitable for beta-ray spectroscopic studies.
The Vanderbilt higher pressure mass spectrometer is now equipped to begin a comprehensive study of the rates and mechanism of chemical hydrogenations involving $H_2^+$, $H_2$, or $H$-atom reacting with various intermediate ions or with molecules activated by a catalytic surface. The following program of new work will be undertaken:

1. Determination of the relative proportions of intermediate $H$-atom, $H_2^+$ and $H^+$ generated in a hydrogen carrier gas stream passing over a selected catalytic surface as a function of hydrogen gas pressure and temperature.

2. Measurement of the relative rates of hydrogenation by $H_2^+$ and $H$-atom with a selected olefin or aromatic molecule such as 2-butene and benzene. In these studies, identification of all intermediates would be attempted and, by using a newly designed recirculation method, the yields of final chemical products for a reaction carried out in a mass spectrometer will be measured. Comparative work using deuterium in place of hydrogen may be helpful in these studies.

3. Extension of the experimental approach to other functional groups such as the carbonyl group in ketones and esters.
A KINETIC AND REACTION MECHANISM STUDY OF THE FORMATION AND DECOMPOSITION OF URANIUM OXIDE, U$_3$O$_8$, IN ORGANIC MEDIA

The following light sensitive reactions are being studied:

1. $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{organic media} \xrightarrow{hv} \text{U}_3\text{O}_8 \cdot \text{XH}_2\text{O} + \text{organic oxidation products such as aldehydes and carboxylic acids},$

2. $\text{U}_3\text{O}_8 \cdot \text{XH}_2\text{O} + \text{organic media} \xrightarrow{\text{in absence of light}} \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{organic products, possibly the reactants in reaction 1.}$

The work has progressed as follows: Initial work in the summer and fall of 1961 dealt with a complete literature search and study of the problem. Following this, a suitable U.V. source was found, and an optical system built for irradiation of the UO$_2^{++}$ organic media system. More recently devised was an analytical procedure to qualitatively and quantitatively evaluate the reaction products. The organic products are separated and quantitatively analyzed by means of gas chromatography. A Barber-Coleman chromatography apparatus has been adapted for this work. Specifically, this consists of devising a column and eliminating problems due to the presence of uranium in the product. It was found that a stainless column packed with chromasorb-W of 60-80 mesh size coated with silicon oil 550 and polyethylene glycol-400 served this purpose. Within the next several months, the data obtained will be evaluated. This should result in learning the reaction mechanism and kinetics involved in the ethyl alcohol uranyl ion system. Immediate plans call for expanding the work to the study of other organic media.

Further expansion of the work will entail:

1. Investigation of conditions for causing the reverse reaction (in absence of light) to proceed faster,

2. Measuring the emf of a cell involving U$_3$O$_8$, UO$_2^{++}$ in organic media.

*Mainly ethyl alcohol, however, other alcohols and organic solvents should be tried.
APPLICATIONS OF RADIOACTIVE ISOTOPES TO CHEMICAL PROBLEMS

The objectives of this project are to obtain a better basic understanding of the mechanisms of chemical reactions initiated by radiative neutron capture and by isomeric transition; the mechanism of reactions initiated by beta and gamma radiation and the mechanisms of reactions of radicals, atoms, and excited molecules produced by photochemical processes.

The investigations are planned to obtain information about energy transfer and charge transfer between atoms and molecules, caging effects of liquid and solid solvents, activation energies of reactions of thermal atoms and of free radicals, characteristics of reactions of atoms, radicals and molecules with high kinetic, electronic or vibrational energy, and properties of free radicals formed in solid matrices as observed by electron spin resonance.
RESEARCH IN NUCLEAR CHEMISTRY

This program is concerned with hot atom chemistry of hydrogen, carbon and nitrogen atoms, nuclear reactions of heavy ions, and atmospheric chemistry.

Studies of the chemical properties of high kinetic energy hydrogen atoms are underway. The consequences of recent findings under this contract on the effect of substituent mass on orbital availability in hot atom capture are being explored. Means other than nuclear reaction for generating hot hydrogen atoms are also under study. Work on the chemistry of atomic carbon as produced by nuclear reaction, under conditions of low radiation flux, is now beyond the preliminary stage. During the coming year the properties of hot carbon atoms compared to those thermalized by moderators will be investigated. The study is being extended to aromatic and halocarbon systems. A preliminary study of the chemistry of nitrogen atoms is now in progress.

Studies of grazing reactions of heavy ions are continuing with emphasis on the yield and recoil ranges of products from events in which the target and projectile do not fuse completely. A program for the discovery and characterization of new isotopes also is being established.

Efforts are under way in the field of atmospheric chemistry. The path of natural radiocarbon and particularly its residence as $^{14}\text{C}^{-}$ is being studied. Other work is concerned with the mechanism which is responsible for the high tritium content of atmospheric methane and hydrogen.
Section 4
Isotope Effects (IE)

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See also: Section 1, page N-7
NUCLEAR CHEMISTRY RESEARCH

Reaction mechanism studies in organic chemistry using tracer and isotope effect techniques are being continued. The nature of the disproportionation reactions discovered in the treatment of ketones with acids is being investigated by tracer and gas chromatographic techniques. Comparative rate studies of the acid-catalyzed rearrangements of isotopic isomers of ketones are expected to yield valuable mechanistic information. Oxygen-18 exchange studies are being carried out on substituted aromatic ketones and aldehydes in media of different acidity. Chlorine isotope effect studies of the displacement reactions of aliphatic chlorides and substituted benzoyl chlorides are being continued to see if the previously discovered relationship between mechanism and size of chlorine isotope effect holds generally. Carbon, nitrogen and chlorine isotope effect studies of the S_N2', Curtius, Hofmann and Lossen reactions are also in progress.

Research involving the Cockcroft-Walton accelerator continues the systematic study of fast neutron reactions, including cross-section measurements and discovery and decay scheme characterization of nuclides formed. A major part of these studies involves nuclear spectroscopy on the nuclides involved. Included are β and γ decay scheme studies, scintillation spectrometer studies, α-ionization chamber studies and multiwire proportional counter studies of orbital electron capture. Investigation is continuing of such rare neutron reactions (at 14.7 MeV) as (n,t), (n,np), (n,d), (n,n'α), (n,2p), etc. New techniques in target mounting are being investigated in an effort to increase the neutron flux of the accelerator.
SEPARATION OF ISOTOPES BY CHEMICAL EXCHANGE

The research program on "Separation of Isotopes" in the Chemistry Department of Columbia University has been concerned with a fundamental investigation of chemical exchange equilibria and their use in the concentration of the isotopes. Special consideration has been given to exchange reactions of the oxides of nitrogen for the concentration of nitrogen-15 and to the exchange reactions of carbon dioxide for the concentration of oxygen-18.

Although the exchange of nitric oxide with nitric acid solutions has been used to prepare 99.9% nitrogen-15, the mechanism of the exchange and the factors which influence it are not well known. Recent experiments have shown that an increase in acidity through the addition of sulfuric significantly increases the overall separation for six to eight molar but not for ten molar nitric acid. The effect of operating parameters and of other additives such as metal salts, are being investigated in an effort to learn more about the mechanism of the exchange.

Theoretical calculations show that significant isotope effects should result from the exchange of nitric oxide and nitrogen dioxide with liquid dinitrogen tetroxide or its complexes with certain organic molecules. Enrichment factors for dual temperature systems and systems with complexing agents have been set up for testing the effectiveness of these exchange reactions for the concentration of nitrogen-15.

One of the most promising exchange reactions for the concentration of oxygen-18 is that between carbon dioxide and water which has an enrichment factor of 1.038 at 25°C. However, the exchange rate is low and efforts to catalyze it sufficiently have been only partially successful. Further work is in progress. Experiments on the use of amines as catalysts led to an investigation of exchange distillation systems involving amine carbamates in methanol and other solvents. Even though the enrichment factor is only 1.013 at 25°C, the rapidity of the exchange and the simplicity of the system makes a study of these non-aqueous systems worthwhile. The behavior of amines in different solvents has been investigated.
MECHANISM OF ACID-BASE CATALYSIS AND STUDIES IN DEUTERIUM OXIDE AS SOLVENT

Research on acid-base catalysis can serve both to elucidate the mechanisms of the interesting class of reactions and to provide insights into the properties of the acids and bases. These properties are of particular consequence in solution of concentrated acids where the normal measurements of acidity are inadequate and new ones must be devised. A recent study in concentrated acid solutions has involved the reversible interconversion of 1,2-cyclohexanedione to its mono-enol. This ketone exists in solution as its mono hydrate and data were obtained on its hydration equilibrium, keto-enol equilibrium and the kinetics of the acid catalyzed interconversion. The data permit assignment of a mechanism and lead to the interesting conclusion that the transition state for the reaction is itself hydrated. Another acid catalyzed reaction which is currently being studied in depth is the exchange of the hydrogens of a group of aromatic hydrocarbons, azulene and several of its substitution products. These molecules reversibly form conjugate acids in concentrated acid. NMR and UV spectral studies have shown that the normal structure of the conjugate acid involves direct attachment of the hydrogen ion to a ring carbon to give a bonded methylene group. Equilibrium protonation data for the azulenes establish an interesting new acidity function. Data on the kinetics of isotopic exchange of tritium labeled azulenes demonstrate that the exchange involves a one-step slow proton transfer, occurring via the stable conjugate acid as an intermediate.

For these and similar studies, investigation of both rates and equilibria in the solvents D2O and its mixtures with water serves as an important mechanistic tool. The data for the solvent mixtures also yield information of the basic properties of water itself. Current investigations in this area involve comparison of the relative hydrogen bonding of H and D and a study of the solvation state of the proton in aqueous solution.
THE RATES OF GAS PHASE ISOTOPE CHANGE REACTIONS, AS STUDIED IN THE SINGLE-PULSE SHOCK TUBE

Few gas phase isotopic exchange reactions have been studied under conditions in which the rates were not affected by heterogeneous factors arising from the hot walls. For this reason the mechanisms of atom exchange in binary molecular collisions are not as well established as they need be nor are the quantitative parameters known except in a few cases. The feasibility of measuring in shock tubes such exchange reactions under conditions which guarantee homogeneous conditions has been demonstrated. Estimates of activation energies can be made and proposed mechanisms can be checked.

Experimental work and data reduction on the reactions $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$ and $\text{HCl} + \text{D}_2 \rightarrow \text{HD} + \text{DCl}$ have been completed. These typify "four-center" reaction complexes. The first of these has been investigated via the "single-pulse" technique over the temperature range 1200°-1500°K; the latter from 1200°-2100°K, both by the "single-pulse" technique and by measuring the intensity of infrared emitted by the generated DC1. On combining these new data with lower temperature data (Rideal and Steiner) an activation energy of 55.4 kcal/mole was obtained. The pre-exponential factor is $5 \times 10^{14} T^{1/2}$, but the single-pulse and infrared results as yet do not check each other as well as it is hoped they will eventually.
Isotopic exchange kinetics are being studied in several systems in which one of the species involved also undergoes a chemical change under the same or similar conditions. Examples include the haloacetic acids and haloacetate ions which undergo thermal halogen exchange with the corresponding halide ion and, at the same or slightly higher temperature, a hydrolysis reaction. Differences in exchange energetics between the molecular and acid forms are consistent with electrostatic effects. Susceptibility toward both exchange and hydrolysis decreases in the order iodide, bromide, chloride. It is hoped that conclusions may be made concerning the dependence or independence of the two reactions.

The photochemically induced exchange in the chloroacetic acid and chloracetate system is being studied with light of 2537A and quantum yields for exchange compared with those known for hydrolysis.

Heterogeneous exchanges are being studied in which a hydrocarbon solution of a simple organic halide is exposed to a solid phase consisting of a corresponding alkali halide. Exchange occurs readily at room temperature and the position of exchange equilibrium may be varied by addition of solid phase or altering the concentration of solute in the liquid phase. We hope to obtain energetics and possible rate constants for these reactions.
Research under the subject contract will continue to be concerned almost completely with the isotopic fractionation accompanying chemical reactions (kinetic isotope effect).

Work will be continued on the interpretation of presently complete experimental results for kinetic isotope effects in the following systems: decarboxylation of malonic acid vapor, photolysis of uranyl oxalate, pyrolyses of metal oxalates, photolysis of formic acid vapor, decarboxylation of per-deutero malonic acid, metal-ion oxidation of formic acid, neutralization of malonic acid (i.e. ion formation isotope effect), and nitrogen dioxide oxidation of formic acid in the gas phase.

Experimental work will be continued and, where possible, interpretation and theoretical work begun, on the kinetics and isotope effects in the following reactions: decarboxylation of oxalic acid in the vapor phase, isomerization of cyclopropane, and the gas-phase oxidation of formic acid by nitrogen dioxide.

Subject to the availability of personnel, work will be started or continued on development of techniques for study of oxygen isotope effects using $\text{O}^{18}$ at the natural abundance level and construction of apparatus for study of photolytic isotope fractionation under conditions of monochromatic illumination.
COMPARISON OF TRITIUM AND DEUTERIUM ISOTOPE RATE AND ARRHENIUS PARAMETER EFFECTS

It is proposed to determine via a competitive method the reaction rate ratios for 1-bromo-2-phenylpropane-2-d and 1-bromo-2-phenylpropane-2-t in the elimination reaction with sodium ethoxide in absolute ethanol. This will be done at several temperatures in the interval 5-55°, in order to obtain the Arrhenius parameters of the deuterium-tritium isotope effect. A comparison of these results with those already obtained for the hydrogen-deuterium effect in this reaction should provide an important test of isotope rate effect theory. In particular, the evidence from isotope rate effect studies that tunnelling is important in proton transfer reactions will be critically tested by these results.

The development of the synthesis of 1-bromo-2-phenylpropane-2-d necessitated an investigation of the mechanism of a glycidic acid decarboxylation. This has been shown to involve the intermediate production of the enol, as follows:
The purpose of this project is:

(1) to investigate experimentally and theoretically the properties of solutions of the nuclear spin isomer of the isotopic homonuclear hydrogens in order to observe and account for the nonidealities arising from quantum effects in the liquid and solid states.

(2) to investigate experimentally and theoretically the properties of solutions of the hydrogen isotopes in their lowest rotational states, particularly in the solid phase where a phase separation occurs due to zero point effects.

(3) to investigate the crystal structure of solid deuterium from the triple point through the \( \lambda \) transition, which occurs at liquid helium temperatures, by neutron diffraction techniques. This investigation will cover a wide composition range of the nuclear spin isomers from pure ortho deuterium to as nearly pure para deuterium as is possible using the techniques that we have already developed.

(4) to continue the theoretical investigation by statistical mechanical methods of the nature of the \( \lambda \) transition in solid hydrogen and deuterium enriched in ortho and para content respectively. The knowledge of the crystal structures of these solids is very important to the investigation.

(5) to continue the theoretical investigations of isotopic separations at low temperatures.
ISOTOPE EFFECTS IN ELIMINATION REACTIONS

The initial approach in this project, the measurement of the isotope effect for elimination on $C_6H_5-CH_2-CH_2-S^+(CH_3)_2$ by HO\(^-\) in H\(_2\)O and DO\(^-\) in D\(_2\)O, has been started. The protons on the carbon atoms to the sulfur are expected to undoubtedly exchange for deuterium in the basic D\(_2\)O solution, but it is believed this will introduce a very small error in the isotope effect because there appears to be very little carbon-sulfur bond-breaking in the transition state, according to sulfur isotope effects. The major isotope effect should be due to DO\(^-\) being a stronger base than HO\(^-\) by a factor of ca. 1.8. It is planned to check the results in a number of ways, such as by checking the $\alpha$-deuterium isotope effect in the corresponding eliminations of $C_6H_5-CH_2-CH_2-N^+(CH_3)_3$ and $C_6H_5CH_2CD_2N^+(CD_3)_3$ with HO\(^-\) in H\(_2\)O. The deuterium exchange of the ammonium compound should be much slower than the rate of elimination.

It is also planned to measure the DO\(^-\) vs. HO\(^-\) isotope effects for $C_6H_5-CH_2-CH_2-N^+(CH_3)_3$, $C_6H_5-CH_2-CH_2-Br$, and $C_6H_5-CH_2-CH_2-Cl$, the object being to use these isotopes effects to decide whether the transition states are generally product-like or reactant-like. A product-like transition state should have an isotope effect $k_{DO^-}/k_{HO^-}$ close to 1.8, as observed for ketone enolization. A reactant-like transition state should have an isotope effect close to 1.0.
SEPARATION AND EXCHANGE OF ISOTOPES

The single stage fractionation factor for exchange between liquid N$_2$O$_3$ and NO has been measured at various temperatures and pressures. Decreased temperature and increased pressure both tend to increase the isotope separation phases toward the simplified system: N$_2$O$_3$ in liquid and NO in gas. Results obtained confirm the possibility of operating the exchange system at elevated pressure, without refrigeration, for concentrating nitrogen isotopes.

Fractionation factors for oxygen exchange between azeotropic acid solutions and their vapors have been compared and correlated with available spectroscopic data for oxonium ions.

Calculation of partition function ratios for C and O isotope exchange between nickel carbonyl and CO have been completed, and the calculations verified by experimental measurements of the effective single stage separation factors.

A study of chemical exchange in a thermal diffusion column, using exchange between N$_2$O$_4$ and NO$_2$, is planned. Primary emphasis will be on measuring relative fractionation of oxygen and nitrogen isotopes, and interpreting fractionation in terms of molecular structure.

The kinetics and mechanism of isotopic exchange between NO$_2$ and O$_2$ will be explored further.
STUDIES DEALING WITH THE ISOTOPES OF HYDROGEN

The rate of exchange between deuterium gas and hydrogen in liquid water is being studied over rhodium and other catalysts. The influence of pressure and temperature on the rate is under investigation, as well as that of small concentrations of organic compounds.

The labeling of organic compounds by catalytic exchange with tritium gas or tritiated organic acids is being investigated. Exchange is followed by decarboxylation or similar processes to give the tritium in non-labile positions.

The separation of all forms of hydrogen isotopes by gas chromatography is being studied. Present emphasis is on separation and detection of very low levels of tritium. Separation of labeled hydrocarbons by gas chromatography is also being investigated.
### Section 5

**High Temperature Chemistry (HT)**

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* Summary not available
ULTRASONIC SPECTROSCOPY IN LIQUIDS AT HIGH TEMPERATURES

It is proposed to continue investigation of ultrasonic absorption and velocity in molten salts, molten oxides, and certain liquid metals and their mixtures. From the data the structural and shear relaxation times and viscosities will be obtained. Work to date indicates that certain molten salts and oxides can exhibit a single relaxation time for both volume and shear viscous processes. Future work will allow testing of the hypothesis, resulting from work under this contract, that the origin of the distribution of relaxation times is related to cooperative behavior of the structure of these molten salts and oxides.

The data in the NaK system will be studied to see how the volume viscosity varies with changes in relative composition of Na and K.

Ultrasonic data on molten boron-trioxide is now being obtained.
HIGH TEMPERATURE THERMAL PROPERTIES OF HELIUM AND OTHER GASES

A more extensive theoretical analysis of the frequency response technique used for measurement of high temperature gas thermal conductivities has been completed. This analysis has explained completely certain discrepancies between experimental results and the previous theory. It is expected that experimental values of the thermal conductivities of helium and nitrogen up to 2000°F and 50 atmospheres will be completed in the near future.

The present effort is directed to the development of a new cell which will withstand higher pressures and temperatures. Thermal conductivities of additional gases and possibly, mixtures of gases will then be determined.

Another cell will also be designed to permit measurement of the thermal conductivities of metal vapors such as sodium and potassium with the frequency response technique.

The critical density and temperature, as well as densities of the liquid and vapor phases in equilibrium at lower temperatures, will be determined for cesium and rubidium from measurements of the electrical resistivity of both phases up to the critical temperature. The critical pressure will then be estimated by extrapolation of the vapor pressure curve already obtained under the contract.

Fabrication of an outer pressure vessel used to contain the high pressure argon which balances the internal pressure of the capsule containing the liquid metal has been completed. Fabrication of the 90 Ta-10W liquid metal capsule and a tungsten tube to be used as a 4-pass heater will be completed shortly.

The platinum capillary efflux viscometer has been reconditioned and is substantially ready for recalibration. High temperature viscosity runs on helium will be run in the near future.
TRACER ELEMENT DISTRIBUTION BETWEEN MELT AND SOLIDS

The self-exchange of sodium ions between molten salts and solid aluminosilicates will receive further study. Improved characterization of artificially prepared sodalite (Na₄Al₃Si₃O₁₂Cl) should permit the successful use of this compound in the solid phase. The rate at which a radiotracer is exchanged between the two phases is limited primarily by self-diffusion in the solid, and serves to measure the diffusion rate. Measurements will be made at different temperatures on samples with various ranges of particle size in order to test the validity of the theoretical interpretation. Similar measurements will be extended to compounds of related structure, in order to indicate the factors that affect the diffusion process. A zinc borate with the same structure as sodalite (Zn₄B₆O₁₂O, or 4ZnO·3B₂O₃) has been prepared, but the exchange of zinc ions with a molten zinc salt has not been successfully observed.
The infrared spectra of a number of polyatomic inorganic ions as solid solutions of the ions in alkali halides have been obtained and studied. Ions studied include nitrate, carbonate, sulfate, cyanate, phosphate, vanadate and chromate. The solid solutions were formed by mixing together the sample and the alkali halide crystals and heating to a temperature at which the sample dissolves in the fused halide. The solution is then quickly quenched and a pressed disk is made from the powdered sample.

This technique of quenching fused salt solutions permits the room temperature study of equilibria existing at the melting point of the solvent. A study of solutions to which known amounts of inorganic reagents have been added is expected to yield information on high temperature reaction products. The interpretation of solid solution infrared spectra can yield, therefore, data on the solubility and reactivity of inorganic compounds in the melt. In order to secure this type of information based upon the interpretation of spectral data it is required first that basic studies of solid solution infrared spectra be undertaken. Results obtained include solid spectra of nitrate and carbonate ions in KBr and other alkali halides.

Plans during the next year include continuation of cataloging of spectra of more than 100 inorganic compounds. These spectra will embrace the region 2 to 40 microns; it is planned

1. to analyze spectra of ions which show wide variations in response to aging,

2. investigate the possibility of using other solvents than the alkali halides for the formation of solid solutions, and

3. obtain the spectra of a number of molecules which are polymers at room temperature and monomers at the melting point of the matrix.
The thermochemistry of the chlorides and oxides of various fission product elements is being studied in the temperature range 500 to 1500°C. In these studies, dissociation and vapor pressures are measured, condensed phases and vapor species are identified, and thermodynamic values (enthalpies and entropies of formation) are determined. Work has been completed on the chlorides of ruthenium, rhodium, palladium, and osmium and on the oxides of ruthenium. The chlorides of iridium and the oxides of palladium are currently being studied.

Several interesting and unexpected features of the chemistry of these systems have been revealed by these studies. For instance, the vapor species RuCl$_3$ and Pd$_5$Cl$_{10}$ were observed, previously reported solid RhCl$_2$ and RhCl were found not to exist, and solid OsCl$_3$ was found to exhibit a wide range of homogeneity.

In addition to the thermochemical studies, a thorough study, from both a theoretical and an experimental standpoint, has been made of diffusion effects and kinetic effects in the transpiration method of vapor pressure measurement.
MOLECULAR SPECTROSCOPY OF SUBSTANCES 
EXISTING AT HIGH TEMPERATURES

The microwave and radio frequency spectra of several molecular species existing only at high temperatures have been determined with relatively high accuracy. The species for which investigations are complete are lithium hydride and deuteride, lithium fluoride, and barium oxide. For these species electric dipole moments, internuclear distances and electric quadrupole coupling constants have been measured in several vibrational states. The measurements on lithium hydride do not include microwave spectroscopy. The quadrupole moment of the lithium nuclei, masses 6 and 7 have been determined by combining calculations of electronic wave functions for lithium hydride with the above measured quadrupole coupling constants.

Investigations of strontium oxide, lithium chloride, sodium chloride and lanthanum oxide are partially complete. All of the above investigations have been by resonance techniques. An investigation of the alkaline earth dihalides by electric deflection has revealed the unanticipated result that all of the dihalides of barium, the chloride and fluoride (iodide and bromide were not studied) of strontium and the fluoride of calcium are non linear molecules. This is in contradiction to electron diffraction studies and most chemical intuition.
The research is divided into two major areas; fundamentals of effusion and thermodynamics of materials at high temperature.

The Knudsen effusion method has been used widely in the high temperature field to determine vapor pressures. It is essential that one have greater knowledge of the effusion phenomenon to increase the accuracy and precision of pressure measurements. It is proposed that angular number and momentum distributions, and velocity distributions as a function of angle be measured for molecules effusing from well defined orifices by using a velocity selector. It is anticipated that these results will enable one to make sound conclusions regarding the effusion technique.

In the study of materials, it is proposed that thermodynamic information be obtained by vaporization studies of metal selenide and telluride systems. It is hoped that trends in the vaporization behavior may be determined as one goes down group VI a: O, S, Se, Te. The dissociation energies of S₂, and Se₂, and Te₂ will be determined by a simultaneous torsion-effusion technique. To gain some knowledge about the solid and liquid states and on metallic bonding, a determination of the activities of Ga-and Sc-H systems will be made from equilibrium hydrogen pressures as a function of temperature and composition.
The procedure for determining the standard free energy of formation of a binary salt by a pulsed electrolysis technique (A. P. Wilde and R. L. Seifert, J. Electrochem. Soc., 108, 1059-63 (1961)) will be studied so as better to define its possible limitations and the conditions required to obtain the most favorable cell emf decay curves. This will involve a search for an inert semi-micro electrode having greater reversibility than present graphite electrodes, a study of the effect of trace impurities on the shape of the emf decay curve, and a study of diffusion and convection in the cells that are used. Studies will also be made of cell overvoltage during the charging and discharging cycles. The method will be applied to determine electrochemically the standard free energy of formation of various halides.

Work will continue on the redesign, rebuilding, and testing of the apparatus used in preliminary work to determine the feasibility of measuring the rate of weight loss and recoil of a sample due to free evaporation from its surface. The mean molecular weight of evaporating molecules, which can be calculated from the data obtained by this procedure, should help elucidate the mechanism of vaporization and also give additional experimental data needed to verify one proposed explanation for small condensation coefficients.
It is the objective of this project to construct a high temperature resistance furnace (100° C. - 2,700° C.) for the purpose of obtaining high temperature electron diffraction photographs of various molecular species. This data will then be analyzed to obtain the details of molecular structure at high temperature. The temperature of the furnace will be controlled to ±10° C. and measured by use of a tungsten vs. tungsten, 26% rhenium thermocouple.

Studies on the structure of small inorganic molecules and their tendency to dimerize will be carried out along with studies of the effect on the electron scattering patterns due to the presence of thermally excited vibrational states. The effect of temperature on internal rotation in various organic molecules will also be studied.

The use of an electron velocity analyzer of the Mollenstedt type to eliminate electro-magnetic radiation from the high temperature furnace will also be investigated.
The vaporization of lanthanum monosulfide will be studied by effusion techniques. Tungsten effusion cells will be inductively heated in both a vacuum balance apparatus and an apparatus for collection of the vapor on targets for subsequent analysis. A Bendix time-of-flight mass spectrometer is being converted for use in determining the vapor species and their relative amounts. The data should yield free energies, enthalpies, and entropies of formation of the solid and molecular species of the vapor. The stability of gaseous LaO indicates that the species LaS will be observable, and it is desired to obtain quantitative data for comparison of the properties of oxide and sulfide.

A similar study of barium sulfide will be undertaken.

A high temperature e.m.f. study will be initiated for measuring the free energy of certain non-stoichiometric rare earth sulfides. The effect of introducing small amounts of oxygen into stoichiometric monosulfide may also be investigated.

A high-temperature (ca. 1500°C) x-ray diffraction study of the interaction of uranium dioxide and monosulfide will be performed as a supplement to the principal investigator's previous work on vaporization processes in the uranium-oxygen-sulfur system. Of particular interest is the determination of the phases present at the elevated temperatures in vacuum, as the nature of the solid must be known (i.e. whether US, UO₂ and UOS, or fewer of these are in equilibrium) in order to calculate the thermodynamics of the vaporization processes.
The goals of this research are to establish the composition of high temperature chemical species, to measure the thermodynamics and kinetics of their reactions, to study their structure, and especially to investigate the vaporization processes involving them.

Recent accomplishments include the discovery of many high molecular weight boron sulfides, the establishment of the vaporization behavior of the titanium sulfides and the measurement of the dissociation energy of TiS(g), the study of the evaporation of Ce₂O₂S and MnS and the measurement of their vapor pressures, the clarification of the uses of the closed crucible technique, and the determination of the space group and lattice parameters for the recently discovered phase Ti₂S.

The proposed work lies in five areas: vaporization studies, phase investigations, crystallographic measurements, mass analysis, and kinetics researches.

Vaporization studies, phase investigations, and crystallographic measurements will concern the rare earth-B, rare earth-B-C, Ti-B and B-S systems. Mass spectrometric studies will employ the B₂S₃, isotopically enriched B₂S₃, and possibly the B-O-S, Al-S, B-Se, and B-Te systems. The research on kinetics of high temperature reactions will probably begin with vaporization processes.
ELECTROLYTE SOLUTIONS

This project is an investigation of the relation between ionic interactions in molten salt solutions and in concentrated aqueous electrolyte solutions.

Since concentrated aqueous electrolyte solutions may be considered as molten salt solutions in which water is one component, it may be simpler to treat ionic association in concentrated aqueous electrolyte solutions in terms of models of simpler molten salt solutions.

Association constants of cations such as $\text{Cd}^{2+}$, $\text{Pb}^{2+}$, $\text{Tl}^+$ with halide ions in molten alkali nitrate solvents are being measured potentiometrically as a function of temperature, composition and variation of the solvent cation. These associations are being measured also in solvents consisting of concentrated aqueous solutions of alkali nitrates. The associations in the molten salt solutions may be represented in terms of a quasi-lattice model, and a similar model appears to be useful in describing the associations in aqueous solutions where water is considered as a ligand competing with the halide or nitrate ions for association with the cations.
Experiments will be made to determine the partial pressure of samarium according to the equation: $2\text{SmB}_4 \rightarrow 2\text{SmB}_6 + \text{Sm(g)}$, using a boride container as an effusion cell. Attempts will be continued to prepare both erbium and thulium hexaborides which cannot be prepared by reported techniques (arc-melting, sesquioxide and boron, boron carbide, etc.) and to determine, if possible, the standard free energy of formation of each of these phases.

Equilibrium studies according to the equation: $\text{MO}_x(s) + (x+2)\text{C(s)} \rightarrow \text{MC}_2(s) + x\text{CO(g)}$ will be made in an effort to obtain thermodynamic data on uranium as well as various rare earth carbides.

A phase study of a rare earth-oxygen-nitrogen system will begin in an effort to determine some of the physical properties of oxynitrides.

Transpiration experiments on rare earth tellurides and selenides will be made to determine, in addition to the various phases present in these systems, the partial pressure of the nonmetal in equilibrium with the various condensed phases. Present data indicate that in the lanthanum selenium system, some of the x-ray d spaces are erroneously assigned.

Both Knudsen effusion and cursory mass spectrometric studies of the gaseous species in equilibrium with thorium dicarbide will be continued. Mass spectrometric studies of equilibrium existing between the gaseous europium carbides and condensed phases will be undertaken to elucidate the thermodynamics of these systems.
Transference numbers in fused salt systems have been a subject of extensive discussion in the scientific literature. In order to clarify certain questions in this regard a technique for the determination of the motion of the liquid electrolyte within an electrolytic cell has been devised. The method, which is based on a cell suspended from a balance and which was originally proposed by Kellogg and Duby, will be used on a series of one and two component fused salt systems.

Electron paramagnetic resonance measurements are now being carried out in a number of fused salt systems with a temperature range up to 1000°C. This work is now being extended to include a detailed study of the effect on the line width and line shape of varying the environment of the paramagnetic ion.

Solutions of alkali metals in fused salt systems continue to offer very interesting challenges to extant theories of solutions. In order to characterize further these systems a program of measuring the optical absorption spectrum of several alkali metals in their fused halides is to be carried out.
CROSS SECTIONS FOR ELECTRON IMPACT IONIZATION

Energy transfer probabilities as a function of excess energy for electron impact ionization are to be determined. A crossed beam technique will be used to study any of a number of refractory elements or simple diatomic gases. The detector is a high resolution, high mass range, 60° sector single focusing mass spectrometer.

Experimental design is aimed at permitting data obtained to be related to other fundamental properties of the atom or molecule.
EMF measurements on cells with fused salt solvents are being made with the objective of learning more about the relation of activity to concentration in molten salt solutions. With potassium thiocyanate as solvent, metal electrodes become sulfide coated. Although interesting as chemistry of thiocyanate, these cells do not seem promising in the provision of good thermodynamic data because of rapid electrode polarization. Ammonium bisulfate (m.p. 147°C) has been employed as solvent with satisfactory results. These experiments will be extended.

The solubility of thallous bromide in fused KNO₃, NaNO₃, LiNO₃ and various mixtures of these solvents has been measured as well as the solubility of silver chloride in NaNO₃. Over a range of 300° to 400°C, it has been found that solubilities in satisfactory agreement with the measured values can be calculated from the thermodynamic properties of the individual components. The measurements and calculations will be extended to systems where part of solvent is a salt with an ion in common with the solute.

Time permitting, the principal investigator hopes to extend some earlier observations on chemical reactions in fused sodium hydroxide. These reactions are oxidation-reduction and water displacement reactions.
ELECTROCHEMISTRY AND THERMOCHEMISTRY IN FUSED SALTS

Thermochemical titrations and polarographic studies will be pursued in molten nitrate and chloride solvents, in a range of temperatures between 150 and 500°C. The prevalence of a poly-sulfate equilibrium of the type

$$xSO_4^{2-} \rightleftharpoons (SO_4^2)^{-2x}$$

(analogous to the formation of similar polychromate and polynitrate species) will be explored. Current-voltage curves will be investigated at dropping mercury and rotated platinum disk electrodes. Electrooxidation of carbonate and anodic "depolarization waves" of halide and cyanide ions will be studied. Information will be obtained regarding the detailed nature of "entropy compounds" (solvates, ion pairs, etc.). Limiting currents corresponding to the processes

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
$$4OH^- \rightarrow 4e^- + O_2 + 2H_2O$$

will be used to elucidate the kinetics of hydrolytic reactions of the type

$$LiNO_3 + H_2O \rightarrow HNO_3 (\dagger) + LiOH,$$

and to devise a method for the quantitative determination of trace quantities of water in molten salts. In chloride melts, the remarkable endothermic process:

$$Cr^{+++} + 8 NO_3^- \rightarrow CrO_4^{2-} + \text{gaseous products}$$

will be investigated. Substantiation will be sought of the interesting possibility that a nitrate dimer may function as a one-electron-transfer oxidizing agent and as a "single-oxide-ion-donor" (i.e. as a univalent Lux-Flood base).
STRUCTURE OF MOLTEN SALTS

By means of the measurement of the diffusion coefficients ("into-the-capillary" method) of component ions in mixtures of molten salts at various temperatures, the dependence of the energy of activation ($\Delta E$) for diffusion on either the melting point of mixtures or on ionic radii in solution is sought. Since non-dependence of the energy of activation on concentration would substantiate a certain form of the hole model of ionic liquids, these experiments are of great theoretical interest.

The diffusion coefficients of alkali metal ions, Li, Na, K, Rb, Cs, in dilute concentration in sodium chloride have been measured, with results showing that all activation energies are about 7 kcal/mole with the possible exception of Cs for which $\Delta E = 8.6$ kcal/mol. Diffusion coefficients of Na and I in mixtures of NaI-KCl are being measured in the temperature range 570°-829°C to determine the dependence of $\Delta E$ upon concentration.

Self-diffusion coefficients have been determined over wide temperature intervals for group IIA chlorides (Ca, Sr, Ba). Refinement of the capillary technique with regard to hydrodynamic correction factors and prevention of corrosion of apparatus has been performed to investigate any possible deviations from constancy of $\Delta E$ with temperature, especially for BaCl$_2$. The objective of this work is to give information on the constituent ions in pure molten chlorides of the IIA and IIB metals.

Evaluation of the heat of activation for diffusion at constant volume has been initiated with the recent acquisition, installation and testing of a high pressure (2000 atmosphere) apparatus and associated equipment designed by the Project Team. These studies will allow a breakdown of the total activation energy in constant pressure diffusion to the component parts of the energy necessary for hole formation and jumping.

A continued program of Raman work of the system CdCl$_2$-KCl has verified the shift frequencies previously obtained, indicating that pyramidal CdCl$_3^-$ ion is the predominant complex ion. Modifications of the Raman apparatus will be made in order to permit high temperature studies in NaF-AlF$_3$ systems.
The overall aim of this program is to carry out a detailed study of the thermodynamics and kinetics of gas-solid phase and gas-phase reactions, particularly as they pertain to the vaporization process.

The initial phase of this work, as proposed, was the construction of a high temperature mass spectrometer. During the last year the electronic components of the mass spectrometer have been completed. In addition, many major mechanical components have been redesigned and fabricated. These modifications of the original University of Chicago design were deemed necessary to permit greater experimental flexibility. One of the larger changes, a completely redesigned magnet mount, is currently nearing completion. It is anticipated that the remaining components of the vacuum envelope will be completed within a few months.

Following completion of the mass spectrometer thermodynamics of vaporization studies are planned. These investigations could be carried out on single, binary, or ternary component systems. The only change of schedule which is being considered relates to the proposed research on the kinetics of vaporization. It is now proposed to speed up exploratory research in this area. It is expected that a dual kinetics and thermodynamics program can be initiated in the forthcoming year.
AN INVESTIGATION OF COMPLEX IONS IN FUSED SALT MEDIA

Initially an electrochemical study of the behavior of a number of reactive metals in molten chloride solvents at high temperatures will be undertaken. The behavior of titanium will be first studied then the investigation will be extended to such metals as zirconium, hafnium and thorium. The experimental techniques employed will include potentiometry, coulometry, polarography, and spectrophotometry.

If possible, studies of the determination of oxide concentrations in fused salts and related chemical reactions and of the behavior of silver halides in fused nitrates will be initiated.
This research includes studies in the physical chemistry of selected high temperature systems, with emphasis on theoretical problems and experimental spectroscopic investigations. The purpose is to augment the general foundation of theory and experimental data in high temperature chemistry. Particular systems will be selected with reference to the feasibility of comparing experimental results with theoretical treatment and with emphasis on types of systems of particular interest to the Atomic Energy program.

Spectroscopic studies will include investigations of fused salts and fused salt-metal systems using reflection and transmission spectroscopic techniques. Theoretical studies will include interpretation of these systems and quantum mechanical calculations from first principles of the rates of very simple chemical reactions.
The subject of this contract is a fundamental investigation of the physical properties of fused salts with particular emphasis on the study of surface tension, viscosity, and Raman spectra. Surface tension and viscosity measurements will be made to accumulate accurate data for these properties and to indicate the existence of complex ions in fused mixtures of salts. The possibility of correlating changes in viscosity with the nature of the complexes present will be investigated and supplementary studies will be made as needed in an attempt to identify specific complexes; in particular, Raman spectroscopy will be used.
This research is directed in general towards furthering our understanding of the nature of ionic liquids. One area of study is the thermodynamics of solution of metal-salt systems. The thermodynamic properties of such solutions have been studied by measuring vapor-liquid equilibria and from phase diagrams (solid-liquid equilibria). Another area under study concerns the nature of the vapor species in equilibrium with fused salts. In particular, measurements of the vapor pressure and vapor density over a fused salt are analyzed to determine the degree of polymerization of the molecules in the vapor phase. These experimental investigations are complemented by semi-empirical calculations of the energies of formation of ionic gaseous species. A third area includes studies of the properties of ionic salts in the region of their critical points. The critical temperatures of two fused salts have been measured.
Previously, the densities of liquid U, UF₄ and ThF₄ were determined; extensive preliminary surface tension studies were carried out and construction of a viscometer was begun. A simple empirical relation between the energy of activation and the melting point of a metal was discovered. The chemistry of the liquid uranium carbide system was studied.

Density measurements on liquid U, Th and uranium carbide are being continued. Surface tension and viscosity studies on UF₄, ThF₄, U and Th are being initiated.

The recently developed "liquid crucible" technique will be used in connection with the plasma jet centrifugal furnace to study the high temperature reactions of U, Th and their compounds. Some of the systems to be studied are:

1. Liquid ThO₂ crucibles and Liquid UO₂ crucibles
   a. With less dense metals as Zr, Fe, Ni
   b. With denser metals (in powder form) as W, U, Th
   c. With U and Th using alloys to lower their densities
   d. With ThB₄

2. Graphite crucibles
   a. For solubility of graphite in thorium carbide and uranium carbide above 3000°K.
   b. For reactivity with borides

3. TaC crucibles
   a. To evaluate TaC crucibles for containment of U, Th and their compounds
   b. To extend range of reaction studies in solid crucible using TaC.
A SURVEY OF FIRST TRANSITION METAL COMPLEXES IN FUSED SALTS

The purpose of this project is to investigate complex ions of the first transition metals in low melting fused salts. The methods chosen involve a study of the electrical conductivity and density and the e.m.f. of chemical and/or concentration cells. These properties are being studied as a function of concentration and temperature. To date, the cobalt(II) ion has been studied very extensively in the presence of chloride, bromide and fluoride ions, in three different solvents. The solvents have been Li-K nitrate eutectic, Na-K nitrate eutectic and pure KNO₃. Conductivity and density studies have shown that in the Na-K nitrate eutectic complexing occurs with chloride and bromide. Sharp conductivity breaks occur at Co:X⁻ ratios of 1:4, 1:5, and 1:6. Similar breaks are not observed in Li-K nitrate eutectic. In this solvent, however, a salt of a mixed complex precipitates when chloride is added. It has been shown that the precipitate has the empirical formula Li₄CoCl₂(NO₃)₄. This blue crystalline precipitate does not occur in the absence of lithium ion and does not have any of the expected properties of a simple solid solution or mixture of CoCl₂ in LiNO₃. It does not, for example, turn pink in moist air or display any hygroscopic properties at all. Unlike the chloride and bromide, the fluoride does not show any evidence for complexing. It is interesting however, that in each case the overall behavior depends on whether the excess halide is added as NaX or KX. Similar studies have just begun on the nickel(II) ion.

It has been discovered the chromate-dichromate equilibrium can exist in Li-K nitrate eutectic. This and other chromium(III) solutions are being investigated using a reversible chromium electrode. This electrode is a silver-chromium alloy which obeys the Nernst equation for chromium solutions in molten KSCN.
This research is aimed at resolving difficult experimental problems involved in investigating behavior of elements and compounds in high temperature environments. Special interest is directed toward measuring the vapor pressures, heat contents, surface tensions, heats of fusion, and electrical and diffusion phenomena, and improving the techniques used for their measurement. The following specific investigations are under way or are planned:

1. sublimation of alkaline earth difluorides
2. sublimation and decomposition of SnO₂
3. dissociation energies of diatomic alkaline earth halides
4. high temperature heat contents of inorganic compounds and refractories
5. reaction of BrF₃, KBrF₄ and related systems with oxygen and nitrogen-containing compounds
6. diffusion of O in TiO and SnO₂
7. surface tensions of liquid metals and of molten inorganic compounds by the drop-weight method
8. detection of velocity-selected atomic beams, especially with hot-wire detectors for beams of K, Rb or Cs-atoms
9. nature of condensation and evaporation coefficients
10. nuclear magnetic resonance and electron spin resonance properties of refractories
11. various theoretical approaches for calculating thermodynamic properties of solids at high temperatures
12. radiation phenomena involving high temperature solids, liquids and gases.
### COORDINATION CHEMISTRY (CC)

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See also: Section 7, Page I-12
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*Summary not available*
A THERMODYNAMIC STUDY OF THE REACTION IN AQUEOUS SOLUTION OF FISSION
PRODUCT METAL IONS WITH SELECTED LIGANDS OVER THE TEMPERATURE
RANGE 10 TO 40°C

Two metal ligand systems are presently being studied. In each system
thermodynamic equilibrium constant, enthalpy, and entropy data are
obtained as a function of temperature and used in subsequent inter-
pretation of the nature of the particular system.

1. Metal-Halide Study. A procedure making use of a membrane
electrode has been developed to determine the concentration of
chloride ion released to the solution during a potentiometric
titration of aqueous HgCl₂-HL systems where L is a neutral
ligand, e.g. ammonia, ethylenediamine, etc. This technique will
make possible the measurement of previously unobtainable equili-
brium constants for the replacement of chloride ions from
HgCl₂ by these ligands. Furthermore, the method should be
generally applicable and it is planned to use it in similar
studies with the halides of the platinum group elements where
few equilibrium constant data now exist. Enthalpy changes
for the HgCl₂-HL systems are determined calorimetrically by
a thermometric titration procedure.

2. Metal-Cyanide Study. Equilibrium constant and enthalpy
change data are being obtained at 10, 25 and 40°C for the
interaction of CN⁻ with Ni²⁺, Zn²⁺, Cd²⁺, and Hg²⁺. The
particular interest in this research is to study the manner
in which ΔH° and ΔS° vary with temperature in this series in
order to be able to determine possible reasons for the step-
wise behavior of CN⁻ toward Zn²⁺, Cd²⁺, and Hg²⁺, but not
toward Ni²⁺.
The following subjects are being studied:
1. mercury (II) and silver (I) complexes of purines and pyrimidines;
2. electrophoretic mobility of a complex ion; and
3. mercury (II) complexes of aniline.

It has been discovered that adenosine and related compounds bind mercury and silver ions, and the equilibrium association constants have been measured. The surprising and unexpected result is that upon addition of Hg$^{++}$ (at pH2) or Ag$^+$ (at pH7) to neutral adenosine a proton is liberated. This implies either the loss of a proton from the amino group to form an imino group or the addition of the metal ion as -M-OH.

The electrophoretic work was undertaken to develop an improved method for determining the charge on a complex ion.

In a series of structurally similar complexes of Hg$^{++}$ with purines, the mobilities have served to indicate that some of them have charges of +1 and others of +2.

Mercury (II) interacts with aniline not only to form a complex with the electron pair of the nitrogen atom, but also to form carbon-mercury bonds.
COMPLEX ION CHEMISTRY

Investigations of the properties and reactions of inorganic complex ions, with special emphasis on the thermodynamics, reaction mechanisms and stereochemistry of reactions involving transition-metal complexes are under way. Current studies include aquation, base hydrolysis and isomerization reactions of cis- and trans-Cr(en)₂Cl₂⁺, cis- and trans-Cr(en)₂(OH)Cl⁺, cis-Cr(en)₂Br₂⁺, cis-Cr(en)₂(OH₂)Br⁺, cis-Cr(en)₂(NCS)Cl⁺, cis- and trans-Cr(en)₂(NCS)₂⁺, trans-Cr(pn)₂(NCS)₂⁺, trans-Cr(ibt)₂(NCS)⁺, cis-Cr(pn)₂Cl₂⁺, cis-Cr(pn)₂(OH₂)Cl⁺, Ir(OH₂)Cl₅⁻, IrCl₆⁻², OsCl₆⁻², NiNH₂⁺. Syntheses of new chromium(III) complexes and studies of their UV and visible absorption spectra are also being undertaken.

NOTE: (en) represents ethylene diamine
(pn) represents propylene diamine
(ibt) represents isobutylene diamine
This project is concerned with the structure and the chemical behavior in solution of various metal chelates. Infrared spectroscopy and nuclear magnetic resonance spectroscopy are being used to establish the type of bonding and the structure for several metal-EDTA complexes. The solution properties of several metal-gluconate chelates are being investigated by polarography, spectroscopy, and potentiometric titrations. Such studies are expected to permit determination of the formulas and the stability constants for the complexes. Some of the metal ions under consideration are uranium(VI), osmium(VI,IV,III), cerium(IV) and ruthenium(III). The solution properties of other metal-chelate systems are under consideration also.

A second major area of investigation is the gas chromatography of volatile mixtures of metal chelates. Both the acetylacetonates and oximes appear promising in terms of stability and volatility. The best chromatographic conditions are being sought to permit rapid and efficient separation of mixtures of metal chelates. Such factors as liquid phase, loading, and column temperature are being investigated. Idealization of conditions should provide a convenient method of analyses and may allow the separation of isomeric mixtures of chelates.
It is proposed to study extensively the extraction behavior of dinonyl naphthalene sulfonic acid as a liquid cation-exchanger and use this to investigate the nature of the cationic metal complexes of imidazole and various substituted imidazoles. This compound forms micelles in moist heptane, and the degree of aggregation is not known. For this reason, it is planned to determine the molecular weights of the species under widely different sets of conditions, using a vapor pressure osmometer. It is also planned to use the nuclear magnetic resonance technique to study the extent of hydrogen bonding in this acid.

Thenoyltrifluoroacetone is important in solvent extraction of metal ions. Nuclear magnetic resonance will be used to measure the keto-enol tautomerism as well as the rate and equilibrium in the first complex formation between this compound and aqueous metal ions. When this compound is used in conjunction with a neutral organic phosphorous ester, the extraction property is greatly enhanced. The nuclear magnetic resonance method will be used to study the interaction between thenoyltrifluoroacetone, organic phosphorous ester and metal ions under various conditions, with the hope that a reasonable explanation can be made as to the nature of the "synergic" action.
SYNTHESIS OF NEW ORGANOMETALLIC COMPOUNDS OF THE LANTHANIDE AND ACTINIDE SERIES

The purpose of this project is to prepare new organometallic complexes (hopefully stable and volatile) of the lanthanide and actinide elements, thereby extending the chemistry of these elements. Research will be concentrated on the cyclopentadienyl derivatives of the lanthanides and actinides, as chemical intermediates for new complexes.

The initial approach in the lanthanide series will be a complete investigation of the reactions of a recently discovered class of compounds, the cyclopentadienyl metal dihalides. Halogen displacement reactions will be studied initially, followed by reactions of the dihalides with unsaturates, such as butadiene, ethylene and benzene.

In the actinide area, it is planned to evaluate tetracyclopentadienyl uranium and tetracyclopentadienyl thorium as reaction intermediates. Here, initial investigation will involve the interaction of these materials with carbon monoxide and nitric oxide. In addition, such reactions as hydride reduction and complexing with other pi-donors such as acetylene and butadiene will be explored. Also, efforts will be made to displace halogen from such complexes as tricyclopentadienyl uranium chloride.

Finally, an evaluation of all new complexes with regard to physical properties will be undertaken.
Thermodynamic data is being collected on the kojic acid and acetylacetone complexes of the lanthanide elements to assess the effect of ring size. Similar studies are in progress on the simple aliphatic carboxylate ligands such as acetate and butyrate, on the alpha hydroxy substituted carboxylate ligands, on the alpha-thio substituted carboxylate ligands and on the protonated alpha-amino carboxylate ligands with the lanthanide ions. Potentiometric and calorimetric titration techniques are used for this work. The pattern for the stability constants as a function of lanthanide atomic number is quite different for the alpha-hydroxy substituted ligands compared to the other ligands. This has led to the suggestion that the alpha-thio carboxylate ligands are not chelated. The stability constants of the alpha-hydroxy ligands with the trivalent actinide ions are being measured by solvent extraction techniques. The chloride, bromide and iodide complexing of the lanthanide ions, determined in the same fashion, was found to be very ionic with the enthalphy and entropy both quite small.

The fission of $^{238}_{92}$U and $^{232}_{90}$Th induced by protons and deuterons of 3 to 12 MeV is being investigated. The excitation function, ratio of symmetric to asymmetric fission and angular dependence has been determined. Mass yield and charge distribution studies are in progress.
The present research is a continuation of previously reported studies on the structure of metal coordination compounds and consists of:

1. Preparation and study of transition metal complexes of the positive-ion ligands

\[
\left[\left(\text{CH}_3\right)_3\text{NCH}_2\text{CH}_2\text{NH}_2\right]\text{ClO}_4^-, \quad \text{and} \quad \left[\left(\text{CH}_3\right)_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}\right]\text{ClO}_4^-.
\]

The structures of the metal complexes are being investigated by conductivity and magnetism measurements and by infrared, visible and ultraviolet spectroscopy. The investigation will be extended to zwitter-ions and related positive-ion ligands of the amino acids. This last type of ligand is specially interesting as it contains both an amino acid (zwitter-ion) coordinating system and a non-coordinating positive-ion group.

2. Preparation and study of tetrahedral complexes of nickel (II) with N-donor ligands: The complexes of various isomeric substituted pyridines are being investigated in an attempt to rationalize the formation of tetrahedral, square planar and octahedral complexes containing nitrogen-to-nickel (II) bonds. Previous to those reported by the Principal Investigator, no complexes with tetrahedral nitrogen-to-nickel (II) bonds in the solid state had been reported, and this investigation will help to elucidate a little known aspect of nickel (II) stereochemistry.

Together with the conductivity, magnetism and infrared measurements, a detailed spectrophotometric study (in the visible region) of the species present in the solutions of these complexes is also in progress. The investigation will be extended to other aromatic type N-donor ligands and to the corresponding N-oxides.
The program anticipated for the period June 1, 1962 to May 31, 1963 is as follows:

1. Continuation of kinetic studies of metal ions with $\beta$-diketones in order to obtain data on reversibility of reaction, order of reaction, heats and entropy of activation, and mechanism of the reaction.

2. Continuation of studies of metal ions with $\beta$-diketones in mixed solvents with a view to obtaining complementary thermodynamic data.

3. Continuation of efforts to obtain thermodynamic data of metal-urea complexes, via vapor pressure studies, using effusion method.

4. Continuation of studies of uranyl nitrate in mixed solvents.
This study is concerned with the nature of the processes which occur when an oxygen atom is replaced in an oxyion by another atom. One system of interest is the reaction of $\text{Cr(NH}_3)_5\text{H}_2\text{O}^{3+}$ with nucleophilic species in aqueous solution. A kinetic study of the attack of chloride ion and of other species on this ion will be continued. Other substrate species will also be investigated. Equilibrium constants for both inner and outer sphere complexes will be measured as appropriate.

Factors which influence lability of oxyions will be explored by $^{18}O$ tracer experiments on the exchange of water between various oxyanions and solvent water. Study of lability of chromate, tellurate and periodate species will be continued. These studies show promise of elucidating the role of coordination number change in oxyanion reactions.
CHELATION AND OLA TION REACTIONS OF METAL IONS IN AQUEOUS SOLUTION

The purpose of this research project is to investigate the formation and reactions in aqueous solution of the chelate compounds of metal ions of relatively high charge (+3 or +4) and of a number of oxo metal ions. Specifically the scope of the project is considered to include reactions of Th(IV), U(IV), Np(IV), Zr(IV), Hf(IV), Fe(III), the lanthanide ions, UO$_2$(VI), and VO(IV), with a wide variety of polydentate chelating agents such as aminopolycarboxylic acids, aliphatic hydroxy acids, and aromatic phenolic acids and polyphenols.

The research work emphasized is a study of the reactions of the complex compounds formed from these metal ions and chelating agents, under conditions whereby a given ligand does not completely satisfy the coordination requirements of the metal ion. Such reactions include the formation of "mixed" chelate compounds containing two different ligands bound to a metal ion, hydrolysis of the metal chelate by the formation of hydroxo chelate compounds, hydrolysis of the metal chelate compound by disproportionation to a more stable chelate and the solid metal hydroxide, and the polymerization of the mononuclear chelate initially formed to polynuclear species in solution.

Two types of polymerization are being studied:

1. The conversion of hydrolysis intermediates to polynuclear chelate compounds in which the metal ions are bound together through hydroxide ion bridges (this process is known as "olation"); and

2. The joining of metal ions by combination with one or more different coordinating groups in the same ligand molecule or anion.

A search is also being made for new, more effective chelating agents capable of forming soluble and very stable chelates of metal ions of high ionic charge.
SOME PROBLEMS IN THE CHEMISTRY OF LOW OXIDATION STATES OF METALS

An investigation of the high temperature reaction of potassium octacyanomolybdate(IV), $K_4[Mo(CN)_8]$, with potassium cyanide will be carried out. Preliminary experiments have shown the reaction to be accompanied by copious evolution of cyanogen, indicating reduction of molybdenum in the complex. An attempt to isolate and characterize the reduction product(s) will be made. Experiments may be expected to give significant information regarding the nature of the cyano-molybdenum species stable at elevated temperatures. Moreover, it would be of considerable interest to determine whether reduction of the molybdenum is accompanied by a change in its coordination number.

A study will be made of the reduction of $K_4[Mo(CN)_8]$ by means of potassium in liquid ammonia, to see whether lower valent species can be obtained in this solvent. The lowest oxidation state of molybdenum presently known in cyano complexes is +3.

Attempts will be made to prepare and characterize anhydrous binary halides and cyanides of molybdenum and other transition metals by reaction of the appropriate mercuric compound (halide or cyanide) with the free metal. This technique has been employed successfully to prepare gallium dihalides and indium monohalides and dihalides. By varying the stoichiometry of reaction and the temperature, it is hoped that the preparation of compounds containing the metals in a variety of oxidation states can be accomplished.
ION ASSOCIATION IN POLYVALENT SYMMETRICAL ELECTROLYTES

The proposed area of research is ion association in solutions of polyvalent symmetrical electrolytes. Since it has been found that copper m-benzenedisulfonate (CuBDS) and MnBDS are essentially un-associated in aqueous solution, a baseline for discussing association in similar 2-2 and 3-3 salts has been established. Work on MnBDS will be extended to include a variety of solvent mixtures since bulk parameters such as dielectric constant are not sufficient to characterize association in solvent mixtures. The mixed solvent systems will also be investigated by high-field (Wien effect) conductance which furnishes a semi-independent way of obtaining association parameters. In an attempt to investigate the effect of ion radius on association, the series MgBDS, CaBDS, SrBDS and BaBDS will be examined. Since the BDS anion is actually a bolaform ion the effect of charge separation can be examined through the Na, K and Mn salts of the three isomeric benzene disulfonic acids. 
A viscosity correction is needed in the interpretation of conductance data and the viscosities of the 2-2 salt solutions will be measured. A transference number apparatus of the moving boundary type will be constructed. In an attempt to measure transference numbers in the concentration range where the Fuoss-Onsager theory is applicable, methods for electrical detection of the boundary movement will be developed. The apparatus will be used to examine the same systems for which conductance data are available.
THE EFFECTIVE SIZE OF THE IONS OF HEAVY TRANSITION METALS IN SOLUTION

The reactions of hydrated metal ions with surfaces will be investigated. The nature of the complex, similar to metal-ligand complex ions, will be investigated. The thermodynamic constants of the reactions of heavy metal, transition metal, and lanthanide ions with the surface of hydrated silica gel, and possibly the surfaces of alumina and silica-alumina, will be determined. These constants will be compared and used to aid the determination of the nature of the metal-surface bond and the configuration of the metal-surface complex.
The kinetics and mechanism of the thermal decomposition of the oxalato complexes of some trivalent metal ions is currently being studied.

The carbon isotope effect in these decompositions is also being studied as an aid in elucidating the mechanism. The oxalato complexes being studied have one general formula \( K_3M(C_2O_4)_3 \) where \( M = \text{Fe, Cr, Mn, Co, Al or Ge} \).

Concurrent with the mechanism studies are those of the racemization of optically active oxalato complexes induced thermally or by nuclear radiation and the optical rotatory dispersion properties of tris-oxalato and mixed oxalate-diamine complexes.
MECHANISM OF SUBSTITUTION REACTION OF INORGANIC COMPLEXES

This project on the mechanism of substitution reactions of inorganic complexes is being carried out in an attempt to better understand some of the fundamental aspects of these reactions. During the past hundred years much has been learned about the preparation, properties and stereochemistry of these materials. However, only very recently have quantitative kinetic and stereochemical studies been started in an effort to elucidate the detailed mechanisms of these reactions. It is hoped that a knowledge of mechanisms can be a useful guide to the controlled synthesis of new inorganic substances.

The results of these studies are of chief interest to the inorganic chemist because in dealing with the solution chemistry of salts he is of necessity dealing with metal complexes. However, the interest in these materials cuts across several other branches of chemistry. For example since the complexes studied contain heavy metal ions, these investigations are of interest to nuclear chemists studying the chemistry of fission products and of transuranium elements. Metal complexes are important catalysts in many biological processes so that they are of interest to the biochemist. Recent industrial interest in these materials as catalysts include the "oxo" process, homogeneous hydrogenation and air oxidation of hydrocarbons; other fields such as analytical chemistry and water treatment may also be mentioned.
SPECTROPHOTOMETRIC INVESTIGATION OF CHROMATE COMPLEXES OF Th(IV), Hf(IV), Zr(IV), and Ti(IV)

For the period October 14, 1962 through October 14, 1963:

1. The cause of the non-additivity of the absorption spectra of acidic solutions of certain metal ions and chromate ions for possible complex formation or other interaction will be investigated.

2. It is planned to extend existing thermodynamic data of chromium (VI) system to several temperatures and ionic strength and existing spectral data to as wide a range as is deemed useful in the investigation of other complex systems of Cr(VI).

3. Investigation of the Th(IV)-Cr(VI) system will be continued, as will the search for other chromate complexes of cations as well as anions to learn about the nature of chromate complexes.

The project is devoted to the thermodynamic investigation of aqueous solutions of constant ionic strength at temperatures of 25°C and its vicinity.
STUDIES OF COORDINATION COMPOUNDS
CONTAINING OLEFINS OR OLEFIN-LIKE LIGANDS

Metal complexes are being investigated for which the ligands contain a basic group (N or O) in addition to a double bond which might be involved in bonding to the metal ion. A series of pyridines, amines, and carboxylic acids containing olefinic linkages have been studied. The stabilities of silver and copper complexes of 2-butene-1, 4-dicarboxylic acid are now being investigated potentiometrically and polarographically. The work with various metal complexes of allylpyridine is still in progress.

The spectra of a series of azo-methine and azo dyes, and their copper and nickel complexes are being studied. Molecular orbital calculations are now being made to determine the electronic energy levels of the azo-methine dyes and their complexes in order to interpret their spectra.

A macrocyclic olefin, 1,2,5,6,9,10,13,14-tetrabenzocyclohexadecac-1,3,5,7,9,11,13,15-octaene, has been obtained. This olefin is being investigated as a potential ligand of a new type. The initial studies will be with palladium (II) and platinum (II) which seem best suited for the kind of bonding anticipated. The investigation will be extended to include other metals.
POLAR-NONPOLAR OR AMPHIPATHIC INORGANIC COMPOUNDS

It is the ultimate aim of this project to study inorganic amphipathic compounds. Such compounds are envisioned as molecular chains which are terminated at one or both ends by groups whose affinity for a given interface is different from that of the main body of the chain. The linear polyphosphates were chosen as the starting point for this research because they have the desired chain-like structure.

The main features investigated during the past contract year were hydrolytic degradation and interaction with cations. The degradation studies have been centered on the pentaphosphate for three reasons:

1. It can be obtained in fairly good purity,

2. It is the shortest polyphosphate chain which degrades into rings, and

3. All the degradation products can be quantitatively determined.

The interaction of polyphosphates with various cations is being studied to obtain a comparison of the effects of various ionic characteristics on the extent of binding on the molecular dimensions, electrophoretic mobility and other properties of the polyphosphate chain. All these studies are being continued.
REATIONS OF SOLVATED IONS

This program is concerned with the general problem of learning how a group such as Co(NH₃)₅⁺⁺ compares with H⁺ and CH₃⁺ (each of these regarded as a Lewis acid) in affecting the reactivity of coordinated groups. The measurements which are to be made involve comparison of oxygen exchange between solvent and Co(NH₃)₅O₂CR⁺⁺, CH₃O₂CR or HO₂CR, and comparison of these rates with the rates of hydrolysis of Co(NH₃)₅O₂CR⁺⁺ and of CH₃O₂CR as catalyzed by H⁺, OH⁻ and H₂O. Of immediate interest to us as ligands is a series such as O₂CCH₃, O₂CCl₃, O₂CCF₃, in which the electronegativity of R changes, and a series comprised, for example, by -O₂CCO₂H, -O₂CH₂CH₂CO₂H, -O₂-CH=CHCO₂H in which the effect of conjugation can be studied. To learn if specific effects of d electrons are involved, an acid such as Cr(NH₃)₅⁺⁺(dY³) can be used in place of Co(NH₃)₅⁺⁺(dY⁶).

It is planned also to continue work on fundamental aspects of electron transfer reactions with particular attention to the influence which the electronic structure of the reaction partners has on the rates and chemistry of the processes.

Work on solvation of cations in CH₃OH and CH₃OH-H₂O mixtures at low temperatures will be continued.
MOLECULAR COMPLEX FORMATION AND COORDINATION CHEMISTRY
OF THE OXIDES, SULFIDES AND SELENIDES OF THE GROUP VA ELEMENTS

The purpose of this research program is to investigate the chemistry of the derivatives of the Group V elements.

Infrared studies of the P→O and As→S stretching frequencies have been carried out and will be extended to the As→O, P→S, Sb→O and Sb→S series. A continuing effort is underway to study the efficiency of these compounds as Lewis bases, especially with regard to molecular complex formation with the halogens and coordination with metal ions. Wherever possible, the equilibria will be studied using ultraviolet spectroscopic techniques. Liquid-extraction studies on the complexes formed will be carried out. An effort to synthesize group V compounds will continue and be extended to include phosphonic acid ester analogs of the amino acids. The latter should represent a new and interesting type of coordinating agent. Efforts to grow large single crystals of phosphine sulfide-halogen complexes in the hope of bringing this type of compound into the category of semiconductors, will continue.
SOME ASPECTS OF THE STABILITIES OF COMPLEX COMPOUNDS

The stability constants of complexes of cadmium and lead over a range of temperature and the use of this data to obtain precise values of the thermodynamic changes for these processes will be determined. A differential form of Leden's potentiometric method will be used for this work.

The complex of arsenic (V) with toluene-3, 4-dithiol will be synthesized and resolved, and the hydrolysis of optically active complexes of arsenic (V) with ortho dihydroxy phenols in the presence of added asymmetric species will be studied.

Coordinate bond energies in the tervalent acetylacetonates of the first row transition elements will be determined. This will be carried out in conjunction with a study of the constancy of the Fe-O coordinate bond energies in complexes with beta diketones and a study of the thermodynamics of the solution process for inner complex salts.
USE OF THE $^{15}\text{N}$ ISOTOPE TO STUDY CERTAIN PROBLEMS IN NITROGEN CHEMISTRY

The research done under this project is mainly concerned with the kinetics and mechanisms of inorganic reactions. Various isotopic tracer techniques are being used to obtain data on exchange reactions of metal ion complexes.

In liquid NH$_3$ as solvent we are studying $^{15}\text{N}_3\text{H}_3$ exchange between Cr(NH$_3$)$_6^{3+}$ and solvent. The effects of ion-pairing are receiving the major amount of attention. The exchange reaction is faster when ClO$_4^-$ anion only is present than when NO$_3^-$ is used. Mass spectrometric techniques are employed in these tracer studies. The exchange reaction of Ni(NH$_3$)$_6^{2+}$ in liquid NH$_3$ is also being investigated. The reaction is rapid and flow as well as NMR line broadening techniques are used. It is hoped that comparisons among several metal ion-ammonia complexes will shed more light on the fundamental processes involved.

In aqueous solution several exchange studies are under way. One of these involves the Ni(NH$_3$)$_6^{2+}$-NH$_3$ exchange in aqueous medium to compare effects of solvent change from liquid NH$_3$ to aqueous NH$_3$. The change produces fairly small effects it appears. NMR methods are used in this work. Another study concerns NCS$^-$ complexes of metal ions to compare different metal ions as well as different ligands. NCS$^-$ exchange is faster than NH$_3$ exchange in the cases studied. Research on the interesting ions Fe(CN)$_5$NO$_2^-$ and Fe(CN)$_5$H$_2$O$_2^-$ involves $^{15}\text{N}$ and $^{18}\text{O}$ tracer use to look for NO and/or H$_2$O exchange. Salt effects in the Co$^{2+}$-Co$^{3+}$ electron transfer reaction are also being studied.
STUDIES OF RATES AND EQUILIBRIA IN INORGANIC REACTIONS IN SOLUTION

Work during the coming year will deal with reactions of chromium (III) in mixed solvents, in particular mixtures of methanol and water. These studies include determination of the composition of the first coordination shell around chromium (III) as a function of solvent composition. These data allow evaluation of equilibrium quotients for the reactions:

\[ \text{Cr(OH}_2\text{)}^{7-n}\text{(OHMe)}_n\text{H}^{3+} + \text{MeOH} = \text{Cr(OH}_2\text{)}^{6-n}\text{(OHMe)}_n\text{H}^2\text{O} \]

for \( n = 1, 2, 3; \ldots \)

The equilibrium represented in the conventional way as

\[ \text{Cr}^{3+} + \text{Cl}^- = \text{CrCl}^{2+} \]

is a composite of reactions in methanol-water solution in which \( \text{Cr}^{3+} \) stands for \( \text{Cr(OH}_2\text{)}^{6-n}\text{(OHMe)}_n\text{H}^{3+} \) (\( n = 0, 1, 2, \ldots \)), and \( \text{CrCl}^{2+} \) stands for \( \text{Cr(OH}_2\text{)}^{5-n}\text{(OHMe)}_n\text{Cl}^{2+} \) (\( n = 0, 1, 2, \ldots \)). The effect of varying solvent composition upon the conventional equilibrium quotient

\[ Q = \frac{[\text{CrCl}^{2+}]}{[\text{Cr}^{3+}] [\text{Cl}^-]} \]

will be resolved into specific effects due to the varying composition of the first coordination shell and medium effects due to the changing composition of the solvent outside of the first coordination shell.
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* Summary not available
THE PHYSICAL, CHEMICAL STUDIES OF RARE EARTH OXIDES

The objective of this project is to obtain precise and detailed information on specific systems to learn about solid state reactions.

The rare earth oxide systems constitute an extensive group related to each other in such a way as to serve as an important source of information in understanding the more subtle aspects of reactions in the solid state.

Specifically the rare earths all exhibit stable (III) oxides of one or more of three polymorphic forms A, B and C. In addition Ce, Pr and Tb are known to form many stable higher oxides of composition between $M_01.5$-$M_02.0$. Oxides of intermediate composition are also known. Perhaps all the rare earths will form oxides with average oxidation state less than (III). Some are already known for samarium, europium, and ytterbium.

This project seeks to delineate the structures, equilibrium phase relationships, kinetics and hysteresis of interaction, electrical properties, physical properties, diffusion properties and thermodynamic values of these oxide systems. These studies utilize the techniques of X-ray and neutron diffraction analysis, high temperature heat treatment and melting, mass spectrometry, high vacuum, electrochemistry, single crystal growing, etc.

A similar fundamental study of compounds containing hydrogen is also being undertaken. These studies will involve examples of all the different ways hydrogen is combined with emphasis placed on factors determining hydrogen mobility.
THE CHEMISTRY OF METAL CHELATES
IN NONHYDROXYLIC, ORGANIC SOLVENTS

The general objective is understanding of the chemistry of metal chelate compounds under conditions such that they are not involved in solvolytic equilibria. Emphasis has been placed upon chelates in which the ligands are the anions derived from $\beta$-diketones since such compounds have very high oil-solubility.

Although substitution reactions and ligand exchange reactions are still of interest to us, we have recently emphasized study of the photochemistry of the compounds. In particular, we have made an extensive study of the relative efficiencies of various chelates in deactivation of the excited states of benzophenone. All evidence indicates that the process involves transfer of excitation energy to the chelate compounds. Transfer of triplet excitation is usually involved but we have found two compounds that are apparently capable of deactivating excited singlet states of the donor. The efficiency of the latter process must be very much greater than would have been predicted by existing theories.

Theoretical calculations indicate that the efficiency of energy transfer depends strongly on the availability of low energy transitions localized largely in orbitals of the ligands. Apparently, transfer with consequent excitation of ligand field transitions of the chelates are relatively inefficient.
STABLE ISOTOPE TRACER STUDIES

An investigation of various inorganic reaction mechanisms by the use of stable isotope tracer studies will be undertaken.

The kinetics of the reaction between $\text{UO}_2^{++}$ and $\text{H}_2\text{O}$ will be studied both as a function of species present in solution and temperature in an attempt to determine the mechanism of the exchange reaction and the thermodynamic quantities of activation.

Spectrophotometric and oxygen-18 tracer studies will be used to further elucidate the mechanism of the reaction between $\text{UO}_2^{++}$ and $\text{Cr}^{++}$ and a careful study of the U(IV) spectra in the presence of ligands such as CNS$^-$ will be undertaken.

The near infrared studies of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ in the presence of various dissolved species will be studied as a function of concentration and temperature and a complete assignment of the observed absorption bands will be made. A study of the role of water in the mechanism of the reaction of metal ions with oxygen-containing oxidizing agents by use of $\text{H}_2\text{O}^{18}$ tracer will be carried out.

The rates of fast redox reactions using $\text{Cr}^{++}$ and $\text{V}^{++}$ as reducing agents and oxygen substitution lability of VO$^{++}$ will be studied by rapid flow techniques.
The long range goal of the research program is to obtain and consider evidence concerning the mechanisms of electron transfer in inorganic oxidation-reduction reactions.

In the past year the sulfate catalyzed Fe(II) $\leftrightarrow$ *Fe(III) isotope exchange was studied in aqueous media preparatory to its study in water + dimethylsulfoxide (DMSO) mixtures and in anhydrous DMSO. A previous study, by other investigators, of this exchange in water was not successful in either determining rate constants or elucidating the mechanism of the exchange. Considerable progress has been made on this research program in solving the problems which have prevented the precision of measurement required for detection of the various possible exchange paths. At present some precise results have been obtained and, in the coming year, the same techniques and procedures should be applicable in obtaining all the data necessary for a complete, quantitative investigation of the mechanism. Upon completion of the investigation in purely aqueous media, the effect of increasing DMSO content and decreasing water content on the various reaction paths will be studied. It will be of particular interest to observe the effect of DMSO on the exchange paths which do not involve sulfate or bisulfate ion, that is, those exchange paths involving the solvated ions, e.g., Fe(HS)$_6^{2-}$ and Fe(HS)$_6^{3+}$, and solvolyzed ions, e.g., Fe(HS)$_6$(S)$^+$+Fe(HS)$_5$(S)$^{+2}$, only. Since DMSO is virtually aprotic in its behavior, the exchange by paths involving solvolyzed ions such as Fe(HS)$_5$(S)$^{+2}$, where S$^-$ is an anion of the solvent molecule HS, are not expected to be found. If these exchange paths are found to be absent, then it is likely that H-atom transfer can be eliminated as a possible mechanism of electron transfer.
REATIONS IN NON-AQUEOUS SOLVENTS

The purpose of this project is to study the reaction: \( \text{Me} + x \text{AgNO}_3 \rightarrow \text{Me(NO}_3)_x + x \text{Ag} \), where Me is a metal, in methanol solution. The stoichiometry of the reactions will be determined, using polarographic and spectrophotometric methods where possible and efforts will be made to isolate and identify the reaction products. By studying a series of metals it will be possible to construct an electrochemical displacement series. The reaction could be used for preparation of complex fluorides, and may be extended to reactions with silver nitrite, leading perhaps to a new synthesis of metal nitrites.

Further work will be done on the complex tin fluorides obtained from methanol solution, particularly with the decomposition intermediates.

A computer program for determining unit cell data from powder x-ray patterns will be tested with various fluorides, previously prepared or being prepared in the other phases of this research.
Radioactive tracers are being used as an aid in the investigation of various rate and equilibrium phenomena in non-aqueous ionizing or supposedly ionizing solvents, the phenomena so studied being primarily of a generalized acid-base character. These investigations will in general be implemented by studying the rates of isotopic exchange reactions in such media, exchange reactions between solutes and solvents and those between separate solutes in a particular solvent. The work will involve both exploratory exchange experiments, and also, where they are feasible and appear inviting, intensive studies of the exchange kinetics in selected systems. The results should provide information regarding ionization equilibria, complex formation processes, and mechanisms of acid- and base-catalyzed reactions. Solvents to be studied, as opportunity allows, will include, for example, liquid sulfur dioxide, thionyl chloride, sulfonyl chloride, liquid hydrogen sulfide, phosphorus oxychloride, concentrated sulfuric acid and others not previously examined in this work. An effort will be made to correlate the phenomena being studied with the properties of the solvent and, where possible, the same process, a particular exchange reaction for example, will be investigated in a series of solvents. Such experiments will include inert as well as exchange-participating solvents.
CHEMISTRY OF POLYVALENT METAL HALIDES

The polyvalent metal halides and hydrides are characterized by strong acceptor properties. They interact strongly with many donor molecules, even substances not normally considered to be bases. The study of these interactions has provided a powerful tool for the investigation of chemical bonding, the factors influencing the strengths of acids and bases, the mechanism of Friedel-Crafts reactions, and the influence of chemical behavior on structure.

It is proposed to study by calorimetric methods the heats of reaction of a number of representative Lewis acids with selected bases in order to test the proposal that the secondary isotope effect of deuterium is largely steric. The interaction of diborane with borohydride ion and amine-boranes will be examined as a means of obtaining further information on "single bridges." The structure of carbonium ions will be explored to test the proposal that these have non-classical bonding. Finally, the interaction of diborane with other substances will be explored in the hope of defining the interesting new chemistry of this substance.
The purpose of this work is to gain quantitative information on the nature of solutions in liquid hydrogen fluoride. The techniques employed include determinations of the solubilities of solids as a function of pH and ionic strength, solubilities of gases (e.g., HCl, HI) as a function of pH and pressure, action of complexing agents, potentiometry, polarography, visible and infrared spectroscopy and nuclear magnetic resonance. Thermodynamic constants for solubility products, acidity and basicity, complex ion formation, and electrode reactions (all with their attendant activity coefficients) are being determined. The nuclear magnetic resonance studies and (in the future) the infrared and Raman studies provide information on the structure of substances dissolved in HF. As soon as preliminary studies on the nature of Fe(CO)$_5$ and HCl solutions in hydrogen fluoride are completed, the kinetics of the HCl-catalyzed decomposition of Fe(CO)$_5$ in HF will be studied. Calorimetric studies are planned to support the above areas of work.
DISPLACEMENT REACTIONS ON SULFUR ATOMS: RADIO-EXCHANGE OF THIOSULFATE IN AQUEOUS SOLUTION

The displacement reaction has proved to be a powerful model for studies of the influence of chemical structure on reaction rates and mechanisms. In classical studies, done in the 1930's, attack by bases at a carbon atom was examined. Our present program extends studies using radiotracers, of the displacement reaction to two lesser known areas:

1. Displacement reaction by bases at atoms other than carbon: Reactions on sulfur are the first example of displacements on non-carbon atoms which will be studied. Sulfur is of particular interest since it is very similar to carbon, and it provides a potential bridge between the vast knowledge of organic reactions and lesser known inorganic reactions. In particular, displacements on thiosulfate will be studied using sulfur-35 and oxygen-18.

2. Displacement reactions by free radicals: Attack by free radicals on organic materials occurs in flames, radiation damage, etc. Displacement reactions by radicals on peroxides and disulfides are currently being examined.
Three different projects have been undertaken as part of this study. One involves the use of anhydrous acetonitrile as a medium for inorganic reactions such as the reaction of uranium and thorium with chlorine, bromine, and nitrosyl chloride. The solvated halides obtained as products of these reactions have been isolated and analyzed. Another type of reaction investigated is the reaction of uranium with auric chloride dissolved in the nitrile. The product of this displacement reaction is believed to be U (V).

The second project can be described as an attempt to degrade the CaSi$_2$ lattice to produce two-dimensional nets of silicon. Anhydrous acetonitrile appears to be a promising medium for the necessary oxidation reaction.

The third project has to do with the first stage of the reaction of carbon monoxide gas with molten K-metal or with K-metal in the form of NaK alloy. It has been known for some time that this reaction goes in at least two stages, resulting finally in the product (KCO)$_x$. In new experiments with NaK alloy and CO gas at low pressure it appears that, in the first stage of the reaction, CO dissolves to form a metallic solution of low surface tension which has a strong tendency to "wet" glass.
UNUSUAL OXIDATION STATES OF TRANSITIONAL ELEMENTS

This program is primarily concerned with the synthesis, characterization, and structure of coordination compounds produced by reduction of salts of the type $(ML_n)_y^x$ where $M$ is a transitional metal in oxidation state $y$, $L$ is a mono, di, or polyfunctional ligand, and $n$ depends upon the functionality of the ligand and the symmetry of the complex. Specifically, for example, reduction of $(Os(NH_3)_6)^3Br_3$ with potassium in liquid ammonia provides $(Os(NH_3)_6)^Br$ and $(Os(NH_3)_6)^0$. Potentiometric titration and other data are used to elucidate the mechanism of formation; magnetic susceptibility, X-ray, NMR, and infrared spectral data are used in structural studies. Closely related species are produced by starting with metal complexes representing different oxidation states of the same metal in combination with ligands such as ethylenediamine (en) and diethylenetriamine. By reaction with potassium amide in ammonia, one or more protons are removed from the ligand nitrogen atoms to produce complexes of the type $(Mn^+(en-xH)y)_{(n-yx)+}$. The magnetic properties of these species are being studied in the hope of detecting changes attributable to changes in the electrostatic field strength of the ligand; spectral data are being accumulated with a view to detecting charge transfer.
Section 8

Structural And Theoretical Chemistry (ST)

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See also: Section 9, page P-43

* Summary not available
CHEMICAL REACTIONS OF ATOMIC BEAMS AND RELATED PROBLEMS

At the Polytechnic Institute of Brooklyn an apparatus has been constructed for the investigation of reactions of energetic atoms of 200 to 1500 electron volt energy. The atoms are produced by neutralization of similarly energetic ions. For detection purposes a 90° sector mass spectrometer was built. Attached to it is an electron multiplier, fabricated to be insensitive to stray magnetic fields, and a vibrating reed electrometer. Initially, it planned to bombard hydrogen and simple gaseous organic molecules with fast moving helium atoms and to determine the identity of the ions produced as a function of the velocity of the helium atoms.

In a theoretical investigation of the lifetimes of isomerizing or dissociating energetic molecules, data on a substantial number of unimolecular reactions have been examined at this Institute. Using the RRKM theory* of unimolecular reactions, much of the data can be explained quantitatively to a reasonable degree without use of arbitrary adjustable parameters. This study was recently published in the Journal of Chemical Physics.

*Rice-Ramsperger-Kassel-Marcus
CHEMICAL REACTION CROSS-SECTIONS - A STUDY OF CHEMICAL REACTIONS
BY MEANS OF MOLECULAR BEAM TECHNIQUES

It is proposed to continue the study of elastic and inelastic scattering in crossed molecular beams with particular attention to the reactions: K + CBr₄, K + SnBr₄ (for both of which K + C(CH₃)₄ should be a suitable non-reactive analog), K + DBr and K + I. The analysis of the experiments on K + HI and K + HCl will be completed. A new apparatus will be started for the study of inelastic non-reactive scattering.

Shock wave work on the relaxation of individual vibrational states of HI and the recombination of Br atoms will be continued.
THEORETICAL INVESTIGATIONS IN THE STATISTICAL MECHANICS AND QUANTUM MECHANICS OF MANY PARTICLE SYSTEMS

The present effort of the group is devoted entirely to an attempt to formulate a very general prescription for a statistical mechanical theory of the approach to thermodynamic equilibrium. The theory is limited to small displacements from equilibrium, where transport of heat, or material diffusion, etc., will be governed by linear laws. Otherwise, however, it attempts to keep the same openness that is characteristic of classical thermodynamics, of the Gibbs equilibrium statistical mechanics, and of the Onsager formulation of linear non-equilibrium thermodynamics; namely that the formalism permits immediate extension, without change of general form, to unspecified generalized thermodynamic coordinates and forces.

This necessitates the concept of generalized thermodynamic dimensionless extensive and intensive conjugate variables which can be said to be normalized and orthogonal, in the sense that they have a one to one correspondence with an orthonormal set of functions in phase space. These variable pairs can be chosen in an infinite continuum of ways, only one of which diagonalizes the Onsager Matrix. The corresponding functions show particularly simple behavior under repeated operation by the Liouville operator.
PARMAGNETIC RESONANCE ABSORPTION

Problems to be investigated include the following:

1. Photoexcited triplets. Single crystals solutions of organic phosphors in a variety of hosts will be investigated; both fine structure and hyperfine structure data are needed in order to provide the necessary information for understanding the quantitative details of the triplet electronic states of such systems. The spectrometer for the investigation of photoexcited triplet state systems will be revised and improved.

The paramagnetic resonance spectra of single crystals of perdeutero-naphthalene containing various concentrations of light naphthalene will be investigated. These experiments will provide detailed information on triplet state exciton energy transfer in naphthalene crystals. It is hoped also to extend this type of investigation to other similar isotopically mixed crystals of a single pure organic compound.

Single host crystals containing two or more chemically different guest species will be investigated with a view toward elucidating the nature of energy transfer processes in such systems.

2. Zero-field studies. The new zero-field spectrometer now will be used to investigate a variety of single crystal systems and also randomly oriented molecules and for further investigations of transition in rare earth ions.

3. Ground State Triplet Organic Molecules. Other ground state triplet molecules oriented in single crystals will be investigated. The monophenyl methylene and the fluorenene molecules are of particular interest. Proton hyperfine structure and \(^{13}\)C hyperfine structures (anisotropic) will be investigated in these systems. The very interesting photochemistry which takes place on continued irradiation and on thermal cycling in these crystals will be investigated.

4. Electron Nuclear Double Resonance. The ENDOR spectrum of trivalent U\(^{233}\) in lanthanum trichloride single crystals and of a variety of rare earth ions will be investigated. The new ENDOR spectrometer will be used in the investigation of photoexcited triplet states in naphthalene, isotopically substituted naphthalenes and in other photoexcited triplet state systems.
THEORETICAL CHEMISTRY

This project comprises theoretical studies motivated by applicability to present or possible future experiments in the fields of electron resonance, lasers and biophysics.

Two topics are presently emphasized:

1. The behavior of atomic and molecular systems exposed to time dependent electric and magnetic fields. Usually the frequency dependent susceptibility is obtained by a perturbation theory sum over excited states. Inasmuch as little is known about the excited states the calculated results are often poor. Attempts are being made to construct a variation function which should give better results.

2. The magnetic spin-spin interaction of unpaired electrons has become of considerable interest recently because of the large number of paramagnetic resonance experiments performed on transition metal ions and on the triplet states of aromatic hydrocarbons. Extensive calculations are being made of these interactions to try to relate the unpaired electron distribution to the observed interaction constants.
COLOR CENTERS AND RELATED PHENOMENA IN ALKALI HALIDE TYPE CRYSTALS

Color centers produced by x-irradiation on zone refined KCN are being investigated. The F band occurs at 6200Å and there are M center absorptions at 8580, 5450 and 5150 Å as shown by the dichroism introduced by bleaching with polarized M light. Other absorptions at 4000Å, 10300Å and several in the U.V. are yet to be studied in detail.

A search is under way for (CN)₂⁻ centers in KBr-KCN-Pb⁺⁺ mixed crystals, x-irradiated at 70⁰K. Two absorptions (3700 and 7400Å) appear, which do not exactly correspond with those of the Br₂⁻ center. Dichroic studies and pulse annealing experiments are in progress.

The electrical conductivity of KCN is being measured by a.c. techniques. After the intrinsic and extrinsic aspects of the conductivity are better understood, the investigation will be extended to ultra pure KCN, doped KCN and samples taken from zone-refining ingots.

A characterization of color centers in NaF is also in progress using crystals from two sources. The F absorption occurs at 3330Å and the M absorption at 4975Å. Several well resolved, but previously unreported, absorptions appear in the U.V., these are being investigated by growth curve and optical bleaching techniques. The M center will also be studied, i.e. the F-M equilibrium, and the M center dichroism. Additive coloring of NaF will be attempted.

The relaxations arising from impurity: vacancy complexes in KCl-Ba are being investigated using mechanical (and dielectric) measurements as a means for the determination of mobilities of vacancies and impurity ions.
The optical properties of monocrystalline cuprous oxide in the infrared region will be measured and interpreted. The effect of irradiation of cuprous oxide by slow neutrons on the defect structure of the crystal will be studied.

Single crystals of nickel oxide will be studied with respect to their optical, electrical, and magnetic properties, with correlation of the defect centers and excess oxygen content of the crystals.

The optical, magnetic and electrical properties of topaze and related crystals will be studied. Diffusion of fluorine and oxygen in topaze will be measured by tracer techniques. An attempt will be made to grow single crystals of synthetic topaze.

Diffusion of helium will be measured in silicon, germanium, and diamond, and an attempt will be made to understand the diffusion parameters in terms of the interatomic potentials fields within the crystals.

A Siemens electron microscope laboratory is being established and work will be initiated on microscopy of thin films and reactions in solids.

Chemical reactions effected by ionic bombardment of solids with light ions in the range of kilovolt energies will be studied with ionic beam equipment previously used in our laboratory.
ROTATION AND DEBYE RELAXATION SPECTRA OF DIPOLAR COMPOUNDS IN THE MICROWAVE REGION

The dielectric constant measurements during liquid-solid phase transitions at the remaining unexamined wavelengths, viz., 3 and 10 cms, will be completed for the following alkylamines: ethyl, n-propyl, n-butyl, n-amyl, diethyl, di-n-propyl, di-n-butyl and tri-n-propyl. Electronic and microwave equipment will then be constructed for the measurement of the dielectric properties of gases at elevated pressures. Measurement of the dielectric constant of CH₃CN, (CH₃)₃N, CH₃CF₃, and if time permits of CH₃-C≡C-CF₃ will be made at elevated pressures as dilute mixtures in ethane.

The measurements on amines should, for example, help us decide the possibility of independent and free rotation in the solid phase of the -NH₂ group in primary amines. The measurements on compressed gases should give us useful information on the dynamical behavior of gases, and in particular, the angle dependent forces responsible for molecular reorientation during collision.
VIBRATIONAL SPECTRA OF INORGANIC COMPOUNDS

This is an investigation of the infrared and Raman spectra of interesting inorganic molecules and ions, with the object of establishing their structures, determining their fundamental frequencies, and thereby learning more about covalent bonds involving metal atoms. Examples of substances of interest are ClC(CN)₃, TaCl₅, Si(NCS)₄, and Co(CO)₃NO.
MOLECULAR BEAM SCATTERING STUDIES

The proposed research involves the experimental and theoretical study of elastic and inelastic scattering of molecular beams. Specific investigations include:

1. differential and total elastic scattering of velocity-selected atomic beams of lithium by mercury

2. semiclassical analysis of the extrema in the velocity dependence of total elastic scattering cross sections

3. experimental study of rotational excitation and scattering of diatomic molecules.
Successful observations and interpretations of the NT₃ fundamentals have been made. As a result, further research work on tritium-substituted molecules is proposed. These compounds are provided by and the spectra jointly analyzed with, personnel of the Los Alamos Scientific Laboratory. High-resolution (with capabilities of resolving spectral lines separated by 0.02 - 0.03 cm⁻¹ in the region 1-6 μ) and precision (with capability of measuring spectral positions to an accuracy ± 0.004 cm⁻¹) have been achieved with the newly constructed Ebert-type spectrometer. These will be exploited next to study the tritium-substituted diatomic halides. Certain parts of this cooperative research program, especially those involving the T₂O molecule, are expected to be the subjects of Ph.D. dissertations in future years.

SPECTROSCOPIC PROPERTIES OF FLUOROCARBONS AND FLUORINATED HYDROCARBONS

A normal coordinate analysis, based on Urey-Bradley potential functions, will be made of CH₃-CH₂F, CH₃-CHF₂, CH₂F-CF₃. Initial values for most of the force constants will be transferred from the work on CH₃-CF₃, C₂H₆ and C₂F₆, recently completed here. A least square procedure will be used to obtain the best possible values for the force constants.

An effort will be made to revise the assignment of vibrational fundamentals for the "trans" rotational isomer of CH₂F-CH₂F and to complete normal coordinate analyses, based on quite general quadratic potential functions, of this isomer and of "trans" CHF₂-CHF₂. At the same time, new normal coordinate analyses, based on Urey-Bradley potential functions, will be made of these molecules.

If time permits, the work will be extended to other halogenated ethanes.
A complete single crystal x-ray laboratory has been set up and several programs for x-ray data processing have been written for the IBM 704 and are in use. Complete single-crystal three-dimensional x-ray intensity data have been obtained for aluminum isopropoxide.

Scope and objectives for the coming year include solution of the aluminum isopropoxide crystal structure; preparation of single crystals of aluminum sesquichloride \((\text{Al}_2\text{Cl}_3(\text{CH}_3)_3)\) and collection of intensity data for the solution of this structure, and preparation of single crystals of the aluminum hydride-trimethyl amine complex suitable for single crystal x-ray analysis.
ION MOBILITY IN FUSED SALTS

Transference measurements are being carried out to determine relative mobilities of the two cationic species in LiCl-KCl mixtures over the entire range of concentration. The effect of temperature on these results is also being studied. Experiments of this type will shortly be extended to include AgNO$_3$-KNO$_3$ and PbCl$_2$-NaCl mixtures. Subsequently other systems, particularly alkali halides, will be added. A recheck of published conductivity data for the system LiCl-KCl is being carried out before extending careful conductance and density measurements to other alkali halide mixtures. Diffusion experiments of the type recently completed in molten nitrates will shortly be undertaken in the same alkali halide systems, as well as in other systems of interest. Both ordinary and tracer diffusion coefficients will be measured. Theoretical efforts are concentrated on developing the phenomenological approach to transport processes by the methods of irreversible thermodynamics. The purpose of this research is to gain an understanding of the factors controlling ionic mobility in fused salt systems and to seek correlations with other properties of such systems on both microscopic and macroscopic levels. Thus, sufficient experimental data will eventually be obtained to make possible the calculation of all six interionic friction coefficients as functions of composition in a number of simple binary molten salt mixtures.
STUDIES IN MOLECULAR SPECTROSCOPY

The broad objective of this work is to study chemical bonding via spectroscopy and to develop methods for this purpose. The current work has three main phases: the study of the vibrational spectra of metal carbonyls and their derivatives, the development of the "localized mode" method of treating molecular vibrations, and the study of the species involved in the reaction of Fe(CO)$_5$ and amines.

A molecular orbital view of the bonding in metal carbonyls and derivatives has proved fruitful. A study of the infrared and Raman spectra of a number of neutral and ionic species is underway. A quantitative treatment of the bonding is in progress.

The development of an automated, normal mode, digital computation for the molecular vibrations of smaller molecules based on the "localized mode" approach has been completed. It is now being extended to the treatment of larger molecules.

The reaction between Fe(CO)$_5$ and amines has proved to be complex. An attempt is being made to determine the intermediate species using spectroscopic and conductimetric methods.
Mechanical and statistical mechanical models, with wall forces explicitly taken into account, are being examined for the purpose of characterizing the effect of walls on trajectories and on the approach to equilibrium in an irreversible process. An attempt will be made to describe trajectories in a classical three-body system in which the wall is the third body; thus the problem is one of solving a particular type of coupled, non-linear differential equations. Similar systems are to be considered quantum mechanically in which case the problem is one of solving a set of linear equations with periodic coefficients, to obtain the time-dependence of the wave function. The Liouville equation with wall forces explicit will be used in an effort to determine whether or not the presence of walls alters the roles of various assumptions which have been used to introduce irreversibility into ensemble behavior. Perturbation solutions of the Liouville and Pauli equations will be sought in which wall effects are included in zero order. For the effect of walls on transport properties, the Boltzmann equation would be used with a term added to take into account the reflection of velocities at a rigid wall.
STUDIES IN NUCLEAR AND RADIOCHEMISTRY

This project concerns itself with three areas of nuclear and radiochemistry: isotopic exchange kinetics, chemical effects of nuclear transformations, and resonant gamma ray absorption. A study of halogen exchange reactions of $\text{BCl}_3$ with $\text{HCl}$ and $(\text{HNBCl})_3$ and of the latter with $\text{POCl}_3$ and $\text{SnCl}_4$ are currently under way. The chemical effects of k-capture in $\text{Co}^{57}$ labelled metal organic compounds have recently been studied using the resonant absorption of gamma radiation (Mössbauer effect) as an analytical method. Additional studies of the chemical effects of k-capture in cobaltous ($\text{Co}^{57}$) iodide and of the isomeric transition in a variety of tin ($\text{Sn}^{119m}$) compounds are presently being pursued. A large number of metal-organic compounds have been studied using the Mössbauer effect in an effort to elucidate molecular architecture and solid state (vibrational) related parameters. This work is being pursued further using both iron and tin metal organic compounds as absorbers in gamma ray resonance studies.
This research has as its objective the acquisition of additional knowledge concerning molecular structure and chemical reactivity through study of the behavior of molecules under electron bombardment. Recent calculations have indicated that the use of a reasonably exact method for counting states in the quasi-equilibrium theory rate expression permits the calculation for propane of parent-ion breakdown curves and the mass spectral dependence on electron voltage in good agreement with experiment. Such calculations will be extended to larger hydrocarbons and to substituted ethanes isoelectronic with propane. The reconstruction of a Nier-type mass spectrometer so as to incorporate a monoenergetic electron source is progressing rapidly. The instrument will be used for the detailed study of ionization efficiency curves for fragment ions near threshold. Semi-quantitative evidence has been obtained using a time-of-flight mass spectrometer that unimolecular decompositions of ions in the ion source continue for at least 40 microseconds after ionization. This work will be continued in an endeavor to obtain quantitative information on the rates of the ion dissociation reactions as a function of delay time between ionization and mass analysis.
THE VIBRATIONAL SPECTRA, FORCE CONSTANTS AND THERMODYNAMIC PROPERTIES OF FLUORINE COMPOUNDS

The purpose of the work under this contract is to contribute to the knowledge of the physical and chemical properties of fluorine compounds by spectroscopic studies. One objective of the research is to interpret the rotation-vibration spectra of the fluorine molecules and when possible to calculate the thermodynamic properties and force constants from the spectroscopic data. The pentafluorides formed from elements in the fifth column of the periodic table are under investigation. These studies include the low resolution prism work, high resolution grating studies in the 2-40 micron region, and investigations of the Raman spectra. Practically no data are available on the long wave infrared absorption studies of volatile fluorine compounds and these data are being taken. Such data would be helpful in the elucidation of the molecular structure, and the evaluation of many physical properties such as dielectric constants and indices of refraction. It is also proposed to investigate the new fluorine compounds which result from the irradiation of fluorinated ethylenes with low energy x-rays and the gamma rays from cobalt-60.
Current effort is aimed at removing some of the uncertainty from semi-empirical theories of the spectra of aromatic molecules, such as the Pariser, Parr, and Pople theory. In these theories, the one center two electron repulsion integral over $2p_{\pi}$ orbitals is commonly estimated empirically by taking it to be equal to the experimental ionization potential of carbon minus the electron affinity of carbon. This work is designed to obtain a fairly simple but flexible basis set which will account for the spectra of aromatic systems through fixed parameters in the wave function, rather than the usual use of the integral parameters. The basis set it is hoped to attain will still be determined in an arbitrary but hopefully more reasonable manner than is presently in use.
This is a study of the syntheses and structures of new compounds of niobium and other transition metal complexes of particular interest. The structural investigations use single-crystal X-ray diffraction and infrared and NMR spectroscopy when applicable. Synthetic work on compounds containing strong $\pi$-bonding ligands and niobium in lower oxidation states is underway, and two new niobium iodide complexes already have been prepared. Characterization of four complexes of niobium and two of vanadium and technetium are in progress in order to obtain a better understanding of their chemical and physical behavior as well as an insight into their nature of bonding.
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See also: Section 1, pages N-7, N-13, N-14, N-21
Section 2, page G-11

* Summary not available
Emission from a number of Cr(III) complexes has been observed. The position of the emission band ($^2D \rightarrow ^2A_2$) varies with the ligand, but for complexes with ligands possessing extensive $\pi$-delocalized systems the energy of the transition is always considerably lower than for other complexes. The lifetime of the radiating state varies from 70-500 $\mu$sec (compared to 3700 $\mu$sec for ruby) at 77°K. Quantum yield measurements are now in progress.

In contrast to the cases of dibenzoylmethane and oxine, the acetylacetone ligand does not luminesce appreciably, nor do any of the acetylacetonate complexes other than chromium.

A study of covalency parameters for chromium complexes is being initiated.
OXIDATION-REDUCTION REACTIONS OF NEPTUNIUM, URANIUM AND OTHER IONS, AND OTHER PHENOMENA IN PURE AND MIXED SOLVENTS

The proposed work includes the kinetic studies of electron exchange reactions and other reactions in pure and mixed solvents. For example, the kinetics of the reduction of neptunium (V) with uranium (IV) is being investigated.

The polarography of U(V) and other ions in pure and mixed solvents is planned. The work includes complex formation and the effect of solvent on diffusion currents and half-wave potentials.

Complexes of uranyl, neptunium and other ions are to be investigated spectrophotometrically and, if feasible, otherwise.

Conductance studies in mixed solvents of uranium and other salts will be made. These studies may make evident the degree and nature of protolyses of the ions in solution.

Transference numbers and solvation of the ions of various electrolytes in pure and mixed solvents are to be investigated. Evidence for selective solvation will be sought.

Electromotive force phenomena of electrolytes in pure and mixed solvents will be explored. These investigations may make evident the nature and extent of ionization of the electrolytes.

As is evident from the above, much of the research involves the chemistry of neptunium and uranium, although the project is in no wise limited to the chemistry of these elements. The work, in general, involves the chemistry of electrolytes in solvation.
INVESTIGATION OF BINDING OF IONS TO POLYELECTROLYTES IN DILUTE SOLUTION AND THE INVESTIGATION OF RADIOCOLLOIDAL BARIUM SULFATE

The binding of strontium to polystyrene sulfonic acid in dilute solution will be investigated further by suitable electrode measurements, to see whether the binding is a function of the strontium-hydrogen ion or the strontium-sodium ion ratios. Indicator studies involving weak simple indicators like the various nitro-anilines will be made at various strontium-hydrogen ratios to investigate the same problem.

The solubility of barium sulfate in the presence of excess barium and excess sulfate ions, and (as a control) the solubility of strontium sulfate in similar solutions will be determined in connection with the radiocolloidal BaSO₄. The technique employed is displacement of a radioactive tracer from a loaded exchange resin by the ions in the saturated solution.

Diffusion studies of trace barium and radium in sulfuric acid will be made at the same time as the solubility studies.

Acid-base studies in benzene will be made at various concentration levels, with 2,4-dinitrophenol and di-n-butylamine. Piperidine will also be examined. The purpose of this work is to measure ion-pair formation constants in very dilute solutions, and attempt to quantitatively estimate higher aggregate formation in more concentrated solutions.
This project has been concerned with two types of inorganic oxygen compounds, the oxyanions and the peroxides. In general, the aspects being investigated are the structures, the aqueous chemistries (ionization constants and spectra), the oxidation-reduction reactions, and the mechanisms of the various reactions.

Some of the things under investigation in the area of oxyanions are the mechanism of the nitrosation reaction, the deuterium isotope effect on rate and equilibrium constants and the structure of solid borate compounds.

In the area of peroxide chemistry, the structure of Caro's acid (H₂SO₅) is being investigated by x-ray methods. The solvent effect on rates of oxidation by hydrogen peroxide, the decomposition mechanisms for a variety of monosubstituted peroxides, the aqueous chemistry of several peroxides, the rates of nucleophilic attack on peroxide oxygen, the ultraviolet spectra of peroxides, and trace metal catalysis of peroxide reactions are all under investigation.

Among the results obtained in the past year are the following:

1. The product of one of the reactions investigated has been found to be thioxane oxide:

   \[
   \text{CH}_2\text{CH}_2\overset{\text{0-S-0}}{\text{CH}_2\text{CH}_2}
   \]

   this has found to be an excellent complexing agent for a variety of cations.

2. A peroxide recently prepared in these studies has been shown to be ClCH₂COOH: this is a new peroxide which is a powerful oxidizing agent.

3. The monosubstituted peroxides all decompose by a common type of mechanism which is second order in peroxide, is base-catalyzed, and apparently is a true, spontaneous, non-radical path.

4. There is a characteristic ultraviolet absorption pattern for all peroxide molecules.
PROPERTIES OF ELECTROLYTES IN SOLVENT MIXTURES

Conductances and transference numbers of LiCl in methanol, acetone-water and dioxane-water are being measured by methods developed in this laboratory. The electrophoretic effect will be obtained from the concentration dependence of the transference numbers leaving only the relaxation effect and association to account for the concentration dependence of the equivalent conductance. The results will be compared to the predictions of the Fuoss-Onsager theory and should verify the presence or absence of association in the dielectric constant range above 20. Measurements will also be carried out in a solvent of lower dielectric constant where the interionic effects become exceedingly large.

Conductances, dielectric increments and dielectric dispersion and absorption measurements are being made on quaternary and tri-substituted ammonium picrates and chlorides in benzene solutions. Existing data on these systems cover a rather restricted frequency and concentration range but indicate large differences exist in the nature of the dissolved species depending on the properties of both anion and cation.
A major research now nearly ready to be written up for publication will present data on the solubility, entropy of solution, and partial molal volumes of CF$_4$ and SF$_6$ in a series of selected solvents. They show considerable departures from regularities exhibited by other gases having nearly the same force-constants. The solubilities of both fall off steeply in the series of solvents CCl$_4$, C$_6$H$_5$CH$_3$, C$_6$H$_6$, CS$_2$. The results confirm other evidences published under this contract showing the abnormally low attractive forces between non-polar fluorides and molecules of other types. They show also the close relation between partial molal volumes and solubility. The partial molal volumes of these two gases show the same zig-zag variation against solubility parameters as do the solubilities in the plot.

A paper in press (J. Phys. Chem.) gives a comparison of the solubility relations of the two isomeric trichlorotrifluoroethanes, and also a plot of the solubility of iodine against the square of the differences between the solubility parameters of iodine and of 22 solvents. This plot presents a striking picture of the status of regular solution theory, the departures due to complexing, and the wide departure of paraffin chain molecules from spherical symmetry.

Future projects include a spectroscopic study of interactions between molecules of different species in solution.
Our research on fluorocarbon solutions, supported by the AEC since 1953, is continuing. A completely satisfactory explanation of the anomalously low mutual solubilities of fluorocarbons has yet to be found, but new experimental data are giving a fuller picture of the problem. Our recent research includes:

1. Calorimetric measurements of the heats of mixing (at several temperatures) of C\(_7\)F\(_{15}\)H + acetone, C\(_7\)F\(_{16}\) + C\(_7\)F\(_{15}\)H, C\(_7\)F\(_{16}\) + H(CF\(_2\))\(_4\)H, C\(_7\)F\(_{15}\)H + CCl\(_4\), C\(_7\)F\(_{15}\)H + CHCl\(_3\), C\(_7\)F\(_{16}\) + H(CF\(_2\))\(_2\)CH\(_2\)OH.

2. Vapor pressure and liquid-liquid phase equilibrium in fluorocarbon solutions at low temperatures: C\(_3\)H\(_8\) + C\(_3\)F\(_8\), C\(_2\)H\(_6\) + C\(_3\)F\(_8\), n-C\(_4\)H\(_{10}\) + C\(_3\)F\(_8\), N\(_2\)O + C\(_3\)F\(_8\).

3. The effect of pressure (1 to 100 atm.) on upper and lower critical solution temperatures: C\(_7\)F\(_{16}\) + isooctane, C\(_7\)F\(_{16}\) + acetone, C\(_7\)F\(_{16}\) + CCl\(_4\), C\(_7\)F\(_{15}\)H + benzene, C\(_7\)F\(_{15}\)H + CCl\(_4\), C\(_7\)F\(_{15}\)H + dioxane.

Research in all these directions is continuing. In addition, an apparatus for precise measurements of second virial coefficients of gases and gas mixtures has been constructed; from this we expect to obtain information concerning intermolecular potential energy functions. Future measurements contemplated include measurements of gas solubilities and chromatographic studies.
SPECIFIC ATTRACTIONS IN ION EXCHANGE

The main purpose of the research under this contract is the investigation of the chemical forces governing ion exchange equilibrium in order to provide a better understanding of the basic chemistry involved in the ion exchange phenomena.

Present concern is with the exchange of amines with the ammonia of metal-ammonia cations absorbed on ion exchange resins and with co-ion uptake and electrolyte diffusion out of ion-exchange resin beads.

The displacement of ammonia by amines, and vice versa, as ligands on cations held in cation exchange resins is called ligand exchange. Particularly interesting results have been obtained with diamines, and it is planned to investigate diamines and polyamines further. An attempt will be made to correlate exchange equilibria with structural parameters as well as stability constants of metal-amine complexes, and to explore the possibilities of ligand exchange as a method for elution chromatography of mixtures of amines.

Using Cl\textsuperscript{36}, a study is being made of the diffusion of sodium chloride out of beads of cation-exchange resin that have been equilibrated with solutions of sodium chloride. Water is passed through a shallow layer of resin, and the radioactivity of the effluent solution is measured. Information is gained regarding the diffusion rate of the imbibed electrolyte and the electrolyte content of the resin. The simple Donnan relation is not obeyed. Results can be interpreted by supposing the concentration of fixed ionic groups to be non-uniform within the beads, but there are inconsistencies which further experimental work may resolve. Professor Walton seeks to relate co-ion uptake with the nature of the counter-ion and the water content of the resin, and to find out whether ion-pairing exists.
The vapor pressure and activity coefficients of uranyl nitrate solutions when graphed as a function of concentration show a slight anomaly between 0.9 and 1.3 molal at 0°C. This anomaly is not observable at 25°C. If it is real, it should manifest itself in other measurable properties of these solutions. These phenomena are probably to be associated with the degree of hydrolysis and polymerization of the uranyl ion. In the future, heats of mixing of these solutions will be measured and a calculation of the entropy changes will be made with a calorimeter utilizing Peltier cooling. It operates essentially isothermally and heat energy is removed electrically. It currently has an accuracy of about 2%. It is hoped to improve this to less than 1% and to use the instrument to follow the rates of nitration reactions.
ION EXCHANGE IN POLAR NON-AQUEOUS SOLVENTS

This research is aimed at the development of a thermodynamic interpretation of ion-exchange in non-aqueous solvents and the theoretical interpretation of the general phenomenon of ion exchange.

Current research plans include quantitative equilibrium studies of ion exchange in polar non-aqueous systems and also in mixed systems where water is present. Studies in single solvents are desirable to simplify interpretation. Concentration equilibrium quotients and resin swelling data will be determined for the systems. Particular attention will be given to the solvent composition of the resin phase. The pairs of ions to be exchanged and the solvent medium will be selected to furnish detailed information of the role of the dielectric constant, degree of local order in the solvent, size of the solvent molecules, and inherent acidity in the ion exchange process.
The relationship of the manner of preparation and physical properties of active thorium oxide to its behavior as a catalyst is being studied. Conditions of precipitation of the hydroxide from which the oxide is derived, such as temperature, pH, and concentration, are varied to determine the effect on catalytic activity. The reactions of alcohols, including ethyl and isopropyl alcohol, over the thorium oxide are being followed, in order to establish a relation between pore size and relative dehydration and dehydrogenation activity of the catalyst. These reactions are carried out in a continuous flow reaction system and also in a micro-scale batch reactor, and the products are quantitatively determined by vapor phase chromatography. Activity of the thoria as a catalyst in the reactions of amines is also being investigated. The reaction course is different from that found previously with alumina as catalyst, and it is hoped to relate the reaction course and kinetics to the nature of the amine being used. For these reactions also, product separation is achieved by chromatography as well as by distillation and other techniques.

Concurrently with the catalytic studies, investigation of adsorption on the active thoria is being carried out by nuclear magnetic resonance. Relaxation times of protons in adsorbed water and alcohol molecules will be measured as functions of temperature and surface coverage on several samples of thoria to ascertain whether the NMR results can be related to the structure of the surface.
THERMODYNAMICS OF LIQUID SURFACES

Work at this laboratory in the past year has produced the following results:

(1) The interfacial free energy between liquid gallium and mercury, at 30°C, was found to be 39.7 ergs/cm^2. The interfacial entropy is 0.25 ergs/cm^2/degree, and the total interfacial energy is 118 ergs/cm^2.

(2) The Hg-Ga results, item 1, show that a theory of interfacial energies, (previously developed by the senior investigator), in the form $\gamma = \gamma_r + \gamma_s - 2\phi \gamma_r \gamma_s$ (where $\phi$ is very close to unity) is applicable to liquid metals.

(3) Measurements were made of the interfacial tension between CCl₄ and perfluorotributylamine, to test the theory referred to above. The preliminary result was 3.6 ergs/cm^2 at 20°C.

(4) The relative wetting of glass by mercury vs gallium (the metals being mutually saturated) was studied. This work required some new developments in the "double capillary" method of measuring contact angles. On glass previously exposed to a (moderately humid) laboratory atmosphere, the equilibrium contact angle (measured through the mercury) is approximately 70 - 90°. On the glass that had been evacuated and flamed, the contact angle through the mercury is zero.

(5) A theoretical study showed that, for the adhesion between water and organic liquids, the constant $\phi$ in the equation given above is strongly dependent on the dipole moment and ionization energy of the organic compound. The theoretical curve which was developed, for $\phi$ vs $\mu$, was found to be in accord with experimental data.

(6) The theory of interfacial energies (see the equation in item 2, above) was applied to certain interfaces between liquid metals and solid metals. It was found that a contribution could be made to the theory of fracture and embrittlement of metals by liquid metals: the magnitudes of the liquid-solid interfacial tensions, calculated by the theory, were in excellent agreement with those calculated from fracture data by theories due to Petch and Stroh.
This research is concerned with non-aqueous solvent behavior. Recently¹, a new model for non-aqueous solvent behavior was proposed which indicated that basicity and dielectric constant of the solvent are the most important properties. The structure and concentration of various species present in non-aqueous solutions of various solutes, (for example, iron (III) chloride) are being determined and the equilibria is being correlated with solvent basicity and dielectric constant.

Basicity of the solvent is measured by evaluating heats of formation of adducts of various solvents with iodine, phenol, iodine monochloride, etc. The magnitude of the interaction with a metal ion is estimated from this basicity data and the spectrochemical parameter Dq. It is hoped that a model can be developed that allows prediction of the nature of the species encountered in solutions of various non-aqueous solvents.

This project concerns fundamental and practical aspects of electrochemistry and thermodynamics in anhydrous solvent systems, principally amines. It seeks to investigate the chemical and electrochemical behaviors of solutes in these solvents and to explain these behaviors on the basis of the electronic structures and chemical properties of the solute and solvent species and in terms of the modern theory of solutions. Several different experimental research techniques are being employed, including conductance and transference number measurements, polarographic and electrode potential studies, cryoscopic and vapor pressure measurements, and calorimetric measurements. Radioactive tracers are being used in an effort to extend the measurements to concentrations low enough to approach solute ideality.

It is a goal of this research to be able to make precise calculations of ionic activities and of equilibrium constants in nonaqueous solvent systems. Demonstration of good agreement between calculated and experimental results over wide ranges of concentration is proof that all important factors are known, understood and correctly evaluated. Outside of aqueous solutions such demonstrations are virtually unknown, especially for solvents very unlike water in their physical properties. Particular attention is being given to theoretical calculation and experimental evaluation of ion-pair association constants, activity coefficients and liquid junction potentials in solvents of low dielectric constant.

Another goal of these studies is to be able to understand, to correlate and even to predict with reasonable accuracy numerical values of electrode potentials and equilibrium constants for non-aqueous systems utilizing the vast amount of data already available for aqueous systems and a minimum amount of interconnecting thermodynamic data. The principles involved should apply regardless of type of solvent medium employed, i.e., mixed aqueous, organic or even fused salt.
This is part of a systematic study of thermodynamic properties of solutions of typical strong electrolytes over a wide range of concentration, to test current theories of such solutions and to provide the basic information which will allow their extension.

A new FM ultrasonic interferometer to measure the velocity of sound in liquids to about ± 0.002% has been developed. Solutions of NaCl, NaBr, KCl, RbCl, CsCl, and CsBr over a wide range of concentration at 25°C have already been studied. These data, together with the densities of the solutions, yield the adiabatic compressibilities from which the apparent molal compressibilities are calculated. The other halides of these alkalies and of lithium to complete the picture of this property for 1-1 electrolytes will be studied.

Development of a new ultrasonic interferometer with a sensitivity of 1 ppm will be continued. This will be used, together with a magnetic density float, to study more dilute solutions.

We have also determined specific heats of solutions of NaCl, NaBr, and KCl over the temperature range from 5 to 85°C.
THE KINETICS OF METAL DISSOLUTION IN AQUEOUS ACIDS

The project is concerned with the kinetics of reactions occurring at the interface between a solid and a fluid flowing past the surface. Available mathematical and experimental techniques for the description and study of such reactions have been reviewed. Both have been improved for the purposes of this work. The Iodine/I⁻ reaction has been studied and this work is now complete. Although there is no intrinsic interest in this particular reaction, it was chosen as a representative and simple system with which to test the techniques developed for more interesting but more complicated cases. The project will continue with the study of the kinetics of aluminum dissolution in alkaline media. The effect of impurities and the metallographic state of the metal surface, as well as the usual parameters which are of importance in a kinetic study, will be investigated. It is expected that the result from this work will add to our knowledge of the true surface - chemical - kinetics of the process without the confusion which often results from the intrusion of diffusional effects.
When an electrode, placed in a solution containing a photoreducible material, is irradiated a change in the potential of the electrode with time occurs. This change has been interpreted to arise from the presence of free radicals, produced in the photochemical reaction, at the electrode surface. Although several preliminary investigations of the kinetics of photopotential production have been attempted, no conclusive results have been attained.

Photopotential-time curves will be studied with a fast response instrument in an effort to obtain valid kinetic data about the process giving rise to photopotentials. Systems will be studied where the lifetime of the electroactive contribution of diffusion the decay of photopotentials.

Kinetics of photopotential production will be compared for irradiation on the $n \rightarrow \pi^*$ absorption band of a compound and on the $\pi \rightarrow \pi^*$ absorption band. This will help determine whether or not the same photochemically active state is produced by both excitation processes.

In addition to the potentiometric studies described, investigations will be made by irradiation of electrodes at which mass transfer is occurring. These will consist of irradiating the working electrode in chronopotentiometry and observing changes in potential-time curves produced.
TRACER APPLICATIONS AND EPR STUDIES OF ORGANIC ELECTROCHEMICAL REACTIONS

The mechanisms of organic electrode reactions are under investigation using a variety of electroanalytical and supporting techniques. Included among the techniques are: rapid sweep and cyclic voltammetry, rotated disk electrodes, tritium tracer identification of products, and in situ electron paramagnetic resonance studies. These techniques have been applied successfully to the elucidation of the oxidation pathways of aromatic amines and diamines. Considerable work is in progress on the reduction of aromatic and aliphatic nitro compounds, especially with regard to free radical intermediates. Diffusion coefficients are being measured by tritium tracer techniques. Rotated disk electrodes are being used to measure heterogeneous rate constants of electrode reactions as a function of the electrochemical systems, supporting electrolyte and electrode material.

In the EPR studies, electro-generations of stable radical ions are being examined for the purpose of preparing radical ions and examining their EPR, visible, and uv spectra. In addition, studies of solvent effects on hyperfine coupling constants and chemical reactions of the radical anions and cations are under investigation.
PROPERTIES OF SOLVENTS HAVING HIGH DIELECTRIC CONSTANTS

With stable hydrogen and silver-silver chloride electrodes in N-methylacetamide at hand, studies of the changes in electromotive force with changes in temperature will be continued. These data will be used in determining the thermodynamic properties of the system. In addition, attempts will be made to develop other stable reversible metal-metal ion electrodes in N-methylacetamide.

Solubilities and characteristic reactions of various inorganic and organic compounds in N-methylacetamide will be investigated.

Insofar as time and available personnel will permit, studies will be made of selected reactions in N-methylacetamide and in solvents related to it.
The chemisorption of molecules on evaporated metallic and metallic oxide films will be studied using infrared techniques. The objectives are to identify the molecular species absorbed on metallic and metallic oxide surfaces; to determine the factors governing the type and amount of the molecular species absorbed and how the metallic phase is affected by the adsorbed species; and to learn how the distribution of products is governed by the adsorbed species when a chemical reaction occurs.

The following experiments are being performed to obtain the above information: Obtain the infrared spectra of the molecular species adsorbed on the surface of evaporated metal films; determine the change in reflectivity of the adsorbing surface under the conditions of the experiment; measure surface areas and surface characteristics under the conditions of the experiment; analyze the gas phase during the infrared studies and obtain kinetic data. Initial work will be carried out with deuterium, hydrogen and ethylene over evaporated films of rhodium and nickel.

Computer programs will be written for the analysis, correlation and plotting of the data.

Since this represents a long range program covering many man-months of experimentation, studies will first be made with deuterium over rhodium films and with the preparation of computer programs. The interpretation of the hydrogen and of the deuterium spectra over rhodium will be attempted.
SYNTHESIS AND PROPERTIES OF ION EXCHANGE RESINS

Ion exchange resins show a variety of kinetic and thermodynamic characteristics which are attributable to heterogeneity of exchange site. Such heterogeneity appears to be inherent in ion exchange resins as presently produced commercially because the introduction of the exchange group is difficult to control and the commonly used styrene-divinyl benzene copolymer lattice is prepared in an unnecessarily heterogeneous copolymerization. In theory both of these complications can be eliminated to give materials more uniform in preparation, structure, and behavior. The objective of this project is to develop significant experimental data which will enable others working with ion exchange resins, especially those whose interests are primarily practical, to appreciate the significance and potentiality in careful consideration of these factors.

It has been shown, in studies to date (J. Polymer Sci. 42, 491), that the molecular structure of styrene-divinyl cross-linked copolymers can be varied. The kinetics of the copolymerization, using C-14 labeled styrene assay, of pure meta- \( r_1 = 0.59; r_2 = 0.57 \) and pure para \( r_1 = 0.1, r_2 = 0.5 \) divinyl benzene with styrene vary significantly. For these studies new techniques for the syntheses of these pure divinyl benzenes have been achieved. These rate data, with data obtained in copolymerization studies with other monomers (J. Polymer Sci., in press), demonstrate that at least three of four theoretically possible structural networks can be obtained and that there are two other variants of much interest. Data on the performance characteristics of exchange materials prepared with divinyl monomers of varying \( r_2 \) values indicate significant differences but further study is necessary. It has also been shown, by the use of selected mono- and di-vinyl compounds that materials can be prepared so as to avoid the usual lattice-destroying reactions encountered in the introduction of exchange sites.

The objective of this research in the immediate future is to utilize the data now available from our studies to prepare exchange materials with the widest possible variations in molecular network structure and to correlate the data about their preparation and physical characteristics through key tests.
This project is centered on a study of the interfaces of mineral solids with gases and liquids.

One study is of the adsorption of sodium hexadecyl sulfonate at the three interfaces formed when hematite, an aqueous solution and an organic liquid, di-isobutyl ketone made contact. The adsorption density depends strongly on the salt distribution in the bulk phases and the pH.

A second study is of the simultaneous adsorption of mixed vapors of water and butyl amine on hematite. Measurements are made with a chromatographic conductivity detector sensitive to changes in gas composition.

A third study is of the mechanical behavior of kaolin suspensions under the influence of polyelectrolytes. The polyelectrolyte molecules are very long and offer a limited number of points of attachment to the mineral. Under suitable operating conditions clay pellets or balls are formed under water.

In a fourth study application is being made of a flame spectrophotometer to the measurement of the concentration of ions in flotation pulps. Flotation depends on controlled adsorption of organic and inorganic ions at mineral surfaces, and this in turn depends on the approach to saturation of various ion products.
A PHYSICO-CHEMICAL STUDY OF INTERHALOGEN COMPOUNDS

This project is devoted principally to a study of inorganic and organic fluorine compounds by physico-chemical methods. Fluorine compounds have been prepared and such properties as dielectric constants, dipole moments, electrical conductivities, viscosities, surface tensions, vapor pressures and spectra have been studied. At present, emphasis is on nuclear and electron resonance spectroscopy. Nuclear-magnetic resonance spectroscopy is being applied to fluorine chemistry and other problems including the analysis of NMR spectra and the interpretation of chemical shifts and spin-spin coupling constants. Electron spin resonance spectra of radiation damaged solids are being investigated to determine the structures and stabilities of the free radicals, particularly those containing fluorine, produced on irradiation. Studies of molecular complexes of the interhalogen compounds are planned.
ELECTROCHEMISTRY AND SPECTRA OF METAL-AMMONIA AND METAL-AMINE SOLUTIONS

Continue measurements of transference numbers in metal-ammonia solutions by the moving-boundary method as well as conductances and e.m.f. of cells with transference. Measurement of the conductance of K in ND₃.

Examination of the electron spin resonance spectra of concentrated metal-ammonia solutions, frozen solutions, and solutions in amines (methyl-amine and ethylenediamine).

Rate of reaction of species in ethylenediamine, (followed by absorption spectra) with reactants also in ethylenediamine. For this purpose, the stopped-flow technique will be employed. Construction of temperature-jump equipment for use in non-aqueous media for determination of the relaxation times for reactions occurring in these media.

Study of the spectra, solubilities and conductances of solutions of metals in ethylenediamine and related amines.
EFFECTS OF POLYFUNCTIONAL ANIONS ON ELECTRON TRANSFER BETWEEN METAL IONS IN SOLUTIONS

Evidence has shown that a variety of polyfunctional anions (or acids) catalyze electron transfer processes. This research is for a quantitative evaluation of the effects of such potential bridge formers as are found to act as such catalysts. Both one- and two-electron transfers, e.g., U(IV)-UO_2(II), U(IV)-Tl(III) and Fe(II)-Fe(III), are being tested and current interest in these systems is centered around maleic, fumaric, malic, and tartaric acids.

Additional studies on the role of chloride (or HCl) in catalysis of PCl_3-PCl_5 and SbCl_3-SbCl_5 exchanges are planned and photochemical acceleration of the Sn(II)-Sn(IV) exchange in H_2SO_4 is to be investigated.

ESR and NMR studies of polynuclear, bridged complexes and in the heteropoly cobalt (II and III) tungstates will be included as added methods for elucidating the nature of bridging groups, capable of facilitating electron transfer.
POLAROGRAPHIC BEHAVIOR OF ORGANIC COMPOUNDS

The project involves an experimental and theoretical study of the electrochemical, in particular, polarographic and voltammetric behavior of organic compounds with stress on the elucidation of the reaction mechanisms involved, evaluation of the fundamental factors influencing electrochemical behavior and the nature of irreversible organic electrode processes, correlation of such behavior with structure and reactivity, and development of analytical procedures.

The major areas in which work will be pursued during the coming year are:

1. Oxidation of uric acid and related purine derivatives, and of tetraphenylborate,
2. Improvement of the graphite electrode and its further application,
3. Reductive fission of the pyridine ring,
4. Measurement of the electrode kinetics for carbonyl group reduction and carbon-halogen bond fission, and
5. Elucidation of the observed patterns of $E_1-pH$ behavior.

In addition, studies are being continued on the mechanisms of other types of electrochemical bond fission, the effects of experimental conditions, structure and substitution on the ease of bond fission, the development and applicability to the foregoing problems of electrometric techniques, and the design of analytical methods based on the experimental results obtained and their interpretation.
The immediate objectives of this investigation involve the study of low-temperature thermal properties which are either inherently interesting or relevant to the evaluation of chemical thermodynamic functions. Properties which exist as a consequence of hydrogen bonds or structural anisotropy, or phenomena such as molecular freedom in crystals, transition and higher-order transformation thermal effects, magnetic and electrical phenomena (especially antiferromagnetism and antiferroelectricity), and third law discrepancies are of special concern to the chemical thermodynamicist and the solid-state physicist. Important facets of the work involve:

1. An intensive survey of heat capacities of certain materials to temperatures from below 1 to 20 K;
2. A test of the spin wave theory of the magnetic contributions to the heat capacity considerably below the Neel temperature;
3. Studies of transitions in molecular lattices of reasonably symmetrical molecular species and the attempt to correlate the transitional entropy increment thereof in a quantitative statistical manner;
4. The attempt to evaluate heat capacities of isostructural crystalline substances in terms of simple parameters; and
5. The definitive resolution of lattice and magnetic contributions to the thermal properties. A long-term goal involves the attempt to achieve more accurate semi-empirical estimates of absolute entropies.
The Chemical Behavior of Carrier-Free Iodine-131 is being studied to determine the rate of reduction of carrier-free iodate in aqueous solutions. The reduction products will be characterized by observing their behavior regarding coprecipitation, isotopic exchange with carrier iodine, distillation, solvent extraction, migration in an electric field, and adsorption by ion-exchange resins. Eventually, the controlled anodic oxidation of carrier-free iodine in various media will be studied with regard to possible formation of the anomalous iodine fractions.

The Kinetics of Isotopic Exchange Reactions and Solvent Effects are being investigated to determine the kinetics of exchange between p-nitrobenzyl iodide and tetrabutylammonium iodide in carbon tetrachloride - nitrobenzene mixtures. An attempt will be made to correlate the rate of this reaction with the dielectric constant of the medium. Eventually, this reaction will be studied in other solvent pairs with regard to the dielectric constant of the medium and specific solvent interactions with the reacting species.
STUDIES IN SOLUTION AND NUCLEAR CHEMISTRY

Research with different ion-exchange, electrolyte systems is being carried out to
1. Study the solution chemistry of the alkali metals, the alkaline earths, the transition elements and the rare earth elements, and
2. To elucidate the ion exchange phenomenon.

Studies are being made with both resin and zeolite ion exchangers and with both aqueous and molten salt systems. Among the specific systems being studied are trivalent rare earth carbonate complexes and Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$ ions in nitric acid and chelates formed with Dowex A-1 resin.

Studies in nuclear chemistry related to the fission process have been initiated. Particular concern is with short-lived Mo and Tc isotopes, and their unique identification. Experiments to obtain accurate fission-yield values for these nuclides to facilitate their mass assignment are also contemplated.
Abstraction of hydrogen atoms by methyl radicals from aromatic compounds has been studied in the liquid phase in this laboratory using acetyl peroxide. Relative rate constants of hydrogen abstractions were determined and it was shown that many structural factors influenced the rate. It is planned to determine the activation energies for hydrogen abstraction by using, wherever possible, the photolysis of azomethane which will permit the studies to be made over the temperature range of 0°C to 100°C. Methyl radicals will be generated in a solution of tritiated toluene and the hydrocarbon under study and the ratio of CH₃T to CH₄ will be measured. In this manner, it is hoped that the activation energy of the hydrogen abstraction from the aromatic solvent can be determined with enough accuracy so that the influence of the ring structure on the reactivity of the relevant C-H's can be determined for compounds such as ethyl benzene, indan and tetralin. It would be interesting to know, for example, why the secondary hydrogen atoms in an aromatic system like ethyl benzene are much less reactive than similar hydrogens located in a ring system such as indan and tetralin, how much of this change in reactivity is due to variations in activation energy, and how much is due to changes in entropy of activation.
STUDY OF NUCLEATION PROCESSES

The nucleation process is being studied in gas phase and solution using electron microscopic techniques, spectrophotometric measurements and nuclear magnetic resonance. The gas phase work consists of determining the formation of nuclei of a liquid on surfaces and detecting and characterizing the same by the nature of the magnetic resonance curve obtained. The specific system of interest has been the condensation of water on the surface and in the pores of porous Vycor glass.

The liquid phase work has three aspects. The first is an electron microscope study of nucleation that leads to plate-like particles of gold, platinum and palladium. The rate of formation of these particles and electron microscopic observation of their shape permits one to elucidate the mechanism of formation. Radiation from radioactive sources is used to induce nucleation in solution. In another aspect of the work spectrophotometric methods are used to characterize the processes whereby nuclei are formed in metallic systems. The data obtained are correlated with electron microscopic work and interpreted in terms of ligand theory. Work is also carried out in the mechanism of slow coagulation of uniform gold particles which produce secondary nuclei for crystals.
The purpose of this investigation is to study polarographic problems using non-aqueous solvents. Both fused salts and organic liquids have been used in investigations under this contract.

Future plans call for a study of electrochemical reactions of both inorganic and organic compounds in stearyl-trimethyl-ammonium chloride (Aliquat-7, General Mills) as solvent which was found to be an excellent non-aqueous material for this purpose. Since this is the first time this compound, 50% solution in isopropanol, is to be used for polarographic study, part of the time must be devoted to a survey of its possibilities, and then further study restricted to an intensive study of the reduction of aldehydes, ketones and nitro-compounds.

Some work has been done in our laboratory using fused salts as polarographic solvents. It is our purpose to use the techniques of anode stripping, similar to the hanging drop technique used in aqueous solutions, for the determination of trace amounts of metals in fused salts. At present it appears that tungsten microelectrodes function better than platinum for this purpose.
THERMODYNAMICS AND CONDUCTANCE OF SIMPLE ELECTROLYTES IN POLAR ORGANIC SOLVENTS

The studies of the thermodynamics and conductance of simple electrolytes in polar organic solvents will be extended in the coming year in accord with the following guidelines. Acetonitrile and benzonitrile are illustrative of the non-aqueous solvents: AgNO₃, CoCl₂, hydrogen halides are examples of solutes. Electrolyte diffusion data are non-existent; the stirred diaphragm cell technique will be modified for non-aqueous studies and exploratory studies with AgNO₃ in CH₃CN will be undertaken in this area. Electrolytic transport studies, and measurements of conductance, viscosity, and density over the temperature range 15°-45°C are foreseen to evaluate the ion-solvent interaction schemes and the marked temperature dependence of these in non-aqueous systems, as required in light of current theoretical concepts.
The proposed work involves a continuation of the investigation of the properties of soluble "model" compounds which are similar in structure to the monomeric units of a sulfonated styrene-divinylbenzene cation exchanger. The selectivity of a cation exchanger for singly charged ions has been expressed algebraically by Boyd and others by the equation:

\[ \log k = P \left( \frac{\bar{v}_B - \bar{v}_A}{2.3 RT} \right) + \log \left( \frac{\gamma_B^+/\gamma_A^+}{\text{resin}} \right) - \log \left( \frac{\gamma_B^+/\gamma_A^+}{\text{sol}} \right) \]

The ratio of the activity coefficients in the resin phase makes the largest contribution of the three terms. In order to calculate activity coefficient data from the results of completed studies of concentrated solutions of model compounds and thus compare the results with ion exchange equilibrium data, it is necessary to extend these measurements to dilute solutions. An attempt will be made to do this by means of osmotic pressure measurements and measurements of the potentials of concentration cells. Certain incomplete investigations in concentrated solutions will also be continued. The work will therefore fall into three classifications:

1. Continued isopiestic measurements on concentrated solutions of "model" compounds
2. Calculation of osmotic coefficients in dilute solutions of the compounds from osmotic pressure measurements
3. Calculation of activity coefficients from the potentials of concentration cells containing the model compounds.

AQUEOUS CHEMISTRY OF FREE RADICALS AND OTHER INORGANIC REACTIVE INTERMEDIATES

Studies are being made of the chain reaction of carbon monoxide and hydrogen peroxide, with the two links in the chain being given by equations 1 and 2, and the overall reaction products being \( \text{CO}_2 \) and \( \text{H}_2\text{O} \).

\[
\text{CO} + \text{OH} \xrightarrow{k_1} \text{CO}_2\text{H} \tag{1}
\]

\[
\text{CO}_2\text{H} + \text{H}_2\text{O}_2 \xrightarrow{k_2} \text{CO}_2 + \text{H}_2\text{O} + \text{OH} \tag{2}
\]

The hydroxyl radicals consumed in reaction 1 are generated by photolysis of \( \text{H}_2\text{O}_2 \).

Our current results yield a value for \( k_1/k_3 = 13 \), the rate constants being defined by the symbol above the arrows in the equations.

\[
\text{H}_2\text{O}_2 + \text{OH} \xrightarrow{k_3} \text{HO}_2 + \text{H}_2\text{O} \tag{3}
\]

This work also yields the value \( k_2/(k_4)^{1/3} = 170 \).

\[
2 \text{CO}_2\text{H} \xrightarrow{k_4} \text{H}_2\text{C}_2\text{O}_4 \tag{4}
\]

Future work will involve studies of various aspects of the chemistry of the sulfate radical formed by reaction 5:

\[
\text{SO}_4^{2-} + \text{OH} + \text{H} \rightarrow \text{H}_2\text{O} + \text{SO}_4^{2-} \tag{5}
\]

An attempt will also be made to evaluate the acidity of the \( \text{CO}_2\text{H} \) radical and the possible existence of the isomeric form \( \text{HCO}_2 \) with the \( \text{H} \) bonded to carbon instead of oxygen.

In a second project an extension is being made of a study of the mechanism of substitution of the water in \( \text{Co(CN)}_5\text{OH}_2^{2-} \) by various nucleophiles. The system is of considerable interest in that it seems to represent the first well-established case of substitution in a charged octahedral complex by a limiting type of \( S_N^1 \) mechanism, the rate-determining step being given by equation 6:

\[
\text{Co(CN)}_5\text{OH}_2^{2-} \xrightarrow{k_6} \text{Co(CN)}_5^{2-} + \text{H}_2\text{O} \tag{6}
\]
Currently, this project is concerned with a study of the gas phase, kinetic and thermodynamic properties of free radicals and of the relation between these properties and chemical structure. For these purposes, the thermal and photochemical reactions occurring in systems containing organic iodides, HI and I₂, have been selected for examination.

From these studies, reliable heats of formation for CH₃, C₂H₅, CH₃CO and most recently t-butyl radicals have been obtained. Also, accurate ΔHᵢ and ΔSᵢ for organic iodides have been obtained. From equilibrium studies of the systems:

\[ \text{RH} + \text{I}_2 \rightarrow 2 \text{HI} + \text{olefin (all positional isomers)} \]

very precise (± 0.05 Kcal) ΔF⁰ and ΔH⁰ (± 0.1 Kcal) and ΔS⁰ (±0.2 e.u.) values have been obtained for the isomeric olefins relative to the parent alkanes. Kinetic studies have yielded values of the allylic resonance energy (12 ± 1 Kcal).

A study of the molecular addition of HI to olefins has given the first clean-cut kinetic data on 4-center molecular reactions. They show that the kinetics are dominated by the electrical properties of the reacting molecules indicating an acid-base type of interaction in the transition state. Generalizations of this result indicate that in all chemical reactions, the activation energy is determined by the acid-base properties of the reacting pair. This result seems to hold true for ionic reactions, molecular reactions and radical reactions.
The aim of the project is to study the validity and implications of a model, the hydroxo-complex model, of oxide surfaces immersed in aqueous solutions. A quantitative relationship between the pH of the zero point of charge (ZPC) and aqueous hydroxo-complex formation constants of the parent cation has been the key subject of investigation.

Three sub-projects have developed:

1. Accumulation, through literature searches, of electrokinetic and appropriate thermodynamic data useful in comparison of observed and predicted ZPC.

2. Experimental determination of new ZPC and attempts to interpret trends observed in the relationship of ZPC to the ionic potential (ratio of cation charge to radius). Electrophoretic methods are anticipated.

3. Precision determination of the variation of ZPC and $H^+$, $OH^-$ adsorption behavior among oxides and hydroxides of aluminum. Adsorption measurements will be made by potentiometric titration.

In each project, particular attention is being paid to clarifying the effects of substrate hydration and the mechanism of electrolyte adsorption.
STUDY OF SURFACE CHEMISTRY PHENOMENA

Four separate projects are involved in the proposed study for the period, February 1, 1963, through January 31, 1964. These are:

1. Surface reactions of nickel containing internal hydrogen. The hydrogen is cathodically introduced, and is discharged from the lattice by vacuum annealing. The half-cell potential of nickel with varying amounts of contained hydrogen is measured in a variety of electrolytes and the data theoretically interpreted.

2. The adsorption of mercaptans and organic sulfides on platinum is being studied by observing the depolarization of hydrogen from a platinum cathode which has adsorbed mercaptans and organic sulfides thereon.

3. The corrosion of zirconium and zircaloy-2 alloy in fused salt systems is being studied to determine the corrosion product, the nature of the corrosion film, and the rate of film formation.

4. A quantum mechanical study is being made to learn how to calculate the bond strength of various adsorbents on the surface of various metals. The recently developed "molecular orbital theory" furnishes the approach being used to make these calculations.
This is a comparative study of the thermodynamic properties of electrolytes at various temperatures in aqueous and in non-aqueous solutions. Thermodynamic values calculated and taken from data in the literature will be supplemented by additional measurements on key electrolytes to find the heats and free energies of formation of the solvated species. In order to determine these quantities a solution calorimeter and thermostat will be constructed which will be used to measure the heats of solution of these electrolytes in water and in non-aqueous solvents at several temperatures. In addition the silver-silver chloride electrode's behavior will be studied as a function of temperature in non-aqueous solvents. From these data ionic entropies and heat capacities will be evaluated and an attempt will be made to correlate these quantities as a function of temperature and solvent type. This should be of use in estimating thermodynamic functions for solvated electrolytes for which there are no experimental data. The temperature dependence of ionic entropies and heat capacities will be used to elucidate ion-solvent interactions, both aqueous and non-aqueous.
Swollen volume measurement of ion exchange resin spheres are made with highly accurate photomicrographic methods. The variation of swollen volume with aqueous electrolyte concentration has been studied with a few, strong electrolyte type, ion exchange resins. The methods are being applied to a study of cross-linking correlations, and inter-particle homogeneity. A study of retention errors is to be made; the basis is the absence of retention error in the single particle volume determinations.

The objective is to sharpen the intercomparison of electrolyte specificities measurements in ion exchange systems.
The low-temperature calorimetric investigations of simple fluorine-containing gases which have now been completed with silicon tetrafluoride ($\text{SiF}_4$) and tribluorophosphine ($\text{PF}_3$) are being continued with thionyl fluoride ($\text{SOF}_2$), sulfur tetrafluoride ($\text{SF}_4$) and carbonyl fluoride ($\text{COF}_2$). For thionyl fluoride, the experimental measurements have been completed and the final correlation of the experimental entropy with that computed from structural parameters will be made. For sulfur tetrafluoride and carbonyl fluoride, the work will continue with the formidable problem of increasing the purity of these very reactive compounds from 95 percent available in raw samples to more than 99 percent required for calorimetric samples. Accomplishing this, the calorimetric measurement of heat capacity of the condensed phases and heats of transition from 10 to 250 K necessary for the evaluation of an experimental entropy of the gas will be carried out. Finally, a correlation of the experimental entropy with a statistical entropy based on molecular parameters will be of interest because of the question of randomness in solid in the case of carbonyl fluoride versus carbonyl chloride and because of structural similarities existing between sulfur tetrafluoride and thionyl fluoride and sulfuryl fluoride.

As time allows, research is being pursued in two directions which are supplementary in purpose to the low-temperature calorimetry. One of these involves the design, construction and use of Raman low-temperature liquid cells and multipass gas cells for the observation of Raman spectra, and the other, the instrumentation necessary for the direct measurement of the heat capacity of gaseous compounds.
ISOTOPE EXCHANGE AND ISOTOPE EFFECTS IN THE REACTIONS OF ORGANOLITHIUM COMPOUNDS

Problems to be investigated include:

1. Studies of the structure and bonding in organolithium compounds by proton and lithium-7 nuclear magnetic resonance. Research will include studies of the temperature dependence of the proton nmr spectrum to determine rates of exchange of alkyl groups bonded to lithium.

2. Generation of organometallic free radicals by ultraviolet irradiation and study of these species by electron spin resonance spectroscopy. The first compounds to be investigated will be organosilyl iodides (R₃SiI), but later the problem will be extended to include many other 4th and 5th group organometallic compounds.

3. Study of the intermediates obtained in the decomposition of organometallic azides. These compounds decompose photolytically with formation of nitrogen. Initial studies will attempt to determine whether the reaction proceeds through a triplet state nitrene intermediate or by some other path. The reaction will be followed using electron spin resonance spectroscopy.
THE RELATIONSHIP BETWEEN OXIDE FILMS AND ELECTRODE POTENTIALS

Measurements of the effect of oxide films upon electrode potentials of aluminum is to be extended to include alkaline solutions. The potential of oxide free surfaces in the alkaline solutions will be used to study the electrode reactions in the alkaline solutions. The technique for measuring the effects of oxide films and then obtaining the potentials for oxide free surfaces will be extended as time permits to include other metals.

The study of the kinetics of oxidation of aluminum by means of elliptically polarized light will continue and when the results are satisfactory they will be compared to the observations on change of electrode potential with time of oxidation in order more precisely to determine how the oxide film affects the electrode potential.
ELECTROLYTE STUDIES UTILIZING HIGH FIELD CONDUCTANCE AND BOILING-POINT RISE MEASUREMENTS

The association of electrolytes is under study through boiling-point rise and high field conductance measurements. The principal work has centered on the latter technique to study the behavior of uranyl ion solutions; in these the interaction between the ion and its hydrolysis products, at concentrations in the order of $10^{-4}$ molar, causes the conductance to decrease upon the application of a high electrical field. To show experimentally that this behavior is not limited to uranyl nitrate and perchlorate, coordination compounds of iron and cobalt are under study. In the case of freshly prepared solutions of cobalt(III)pentammonoaquo perchlorate, no high field conductance change is displayed, as is the case with solutions of the uranyl salts named at 25° and over a wide range of fields. Deviations are also noted at low fields in the conductances of these two uranyl salts, and work is under way to study the low field conductance more carefully than has been done heretofore, and at lower concentrations. In addition to studies on uranyl ions, solutions of the alkaline earth chlorides, nitrates and sulfates are being studied, and mixtures of these and uni-univalent salts are being studied to explore the range of validity of the Onsager-Kim theories for the low and high field conductance of ions and mixtures of ions.
# Section 10

## PHYSICAL-ORGANIC CHEMISTRY

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See also: Section 4, Page IE-1

*Summary not available*
The purpose of the present work is to study isotope effects during reactions of allyl carbanion which is labeled with carbon-$^{14}$ at a single terminal methylene group and to use carbon-$^{14}$ as a tracer to study the mechanism of some reactions which may proceed by way of an allyl carbanion.

In previous years the following allyl-$^1$-$^{14}$ compounds were cleaved by alkali metals in liquid ammonia solution: $\text{CH}_2 = \text{CHCH}_2\text{N(CH}_3\text{)}_3\text{Cl}$, $\text{CH}_2 = \text{CHCH}_2\text{Cl}$, $\text{CH}_2 = \text{CHCH}_2\text{OH}$, and $\text{CH}_2 = \text{CHCH}_2\text{SC}_6\text{H}_4\text{-p-CH}_3$. These cleavages when run in liquid ammonia solution containing excess ammonium chloride or methanol gave propylene with only $5.2 \pm 1.5\%$ excess carbon-$^{14}$ at position-1. Since cleavage of allyltrimethylammonium chloride containing carbon-$^{14}$ distributed equally at C-1 and C-3 gave propylene having $4.9 \pm 1.5\%$ excess carbon-$^{14}$ at position-1, it is concluded that cleavage of the present allyl compounds gives a symmetrical intermediate, probably an allyl carbanion, which undergoes protonation slightly more rapidly at C-12 than at C-14 (i.e., the isotope effect $= k_{12}/k_{14} = 1.052 \pm 0.015$).

The present year's work will consist chiefly of a study of the possible isomerization of allyl-$^1$-$^{14}$ trimethylammonium chloride (and/or any of the compounds listed above) with alkali metal amide in liquid ammonia; a study of the nature of the products formed from reaction of biallyl with strong bases; a study of the distribution of carbon-$^{14}$ in biallyl formed from reaction of allyl chloride-$^1$-$^{14}$ with sodium in liquid ammonia; and a study of the product composition from reaction of 3-chloropropyltrimethylammonium chloride, allyltrimethylammonium chloride, and cyclopropyltrimethylammonium chloride with sodium in liquid ammonia.
AROMATIC HYDROGEN EXCHANGE

The purpose of this research is to elucidate the mechanism of aromatic hydrogen exchange and then to use this reaction as a tool in investigations concerning physical and organic chemistry. Specifically, the reaction will be used to study electrophilic aromatic substitution, phenomena in concentrated acids, low energy intermediates (π-complexes) in chemical reactions, isotope effects, and slow proton transfer reactions.

General acid catalysis is being studied and measurement of activation parameters along a series of aromatics of decreasing reactivity are being made. General acid catalysis has already been demonstrated and established as the mechanism for the most reactive substance in the series, 1,3,5-trimethoxybenzene. Activation parameters for the next member of the series, 1,3-dimethoxybenzene indicate that this material very probably reacts by the same mechanism as trimethoxybenzene.
The work proposed under this contract is a three-fold approach to elucidate the mechanism or mechanisms involved in the addition and substitution of tritium in compounds containing a carbon-carbon double bond under the conditions of the Wilzbach method.

First, the mechanism of the radiation-induced addition and substitution of tritium in unsaturated systems will be studied further. This will involve the kinetic investigation of the reaction between cyclohexene and tritium gas in the absence and presence of scavengers, the analysis of the labeling pattern in tritiated cyclohexene-1-C^{14} to determine whether or not the double bond in cyclohexene shifts under the conditions of the Wilzbach reaction, and the study of the substitution process which occurs in the tritiation of cyclohexene.

Second, the tritiation of a representative group of allylic bromides will be investigated as a possible route to labeled olefinic compounds.

Third, the kinetics of the reaction between cyclohexene and tritium gas at pressures of 5 mm. of mercury or less will be examined to determine if an excited species of cyclohexene is formed which undergoes unimolecular breakdown.
Radioactive propylene and heptene-1 have been used to show the extensive secondary participation of these two gases in the catalytic cracking of cetane over silica-alumina catalysts; saturated hydrocarbon such as propane, normal butane and heptane have been shown not to participate appreciably.

Methylene labelled radioactive ketene added to a hydrogen-carbon monoxide mixture and passed at 250°C over an iron catalyst rapidly transfers its radioactive CH₂ group to the catalyst and nucleates the formation of higher hydrocarbons. The C₂ to C₆ hydrocarbon present 15% of the way through the catalyst bed have molar radioactivities equal to or greater than that of the added ketene.

During the coming year the cracking of cetane will be further studied by the use of radioactive tracers including ethylene, pentene, benzene, toluene and decane. The mechanism of formation of aromatics during catalytic cracking will be especially studied.

Our final experiment will be made in the series that have been made in elucidating the mechanism of the catalytic synthesis of hydrocarbon over iron catalysts. It will involve the addition of a small amount of radioactive propylene to the synthesis gas and the analysis of the hydrocarbon products for radioactivity.

In one other tracer experiment, H₂O¹⁸ will be used to measure by exchange the amount of oxygen left in an iron catalyst during reduction and also the surface concentration of oxide promoters in metallic iron catalysts.
Quantitative Study of Stereoselective Reactions

Isotope dilution techniques are being used to obtain quantitative data describing the diastereoisomeric ratios resulting from the stereoselective addition of organometallic reagents to diketones and ketols to yield cyclohexyl glycols. Variation of solvent and temperature will be examined for combinations of reactants leading to 2,3-diphenyl-2,3-butanediol.

Research to be undertaken will include studies on combinations of reactants leading to 2,3-di(2-pyridyl)-2,3-butanediol, combinations of reactants leading to either 2,3-di-o-tolyl-2,3-butanediol or 2,3-di(α or β)-naphthyl-2,3-butanediol, and combinations of reactants leading to 2,4-diphenyl-2,4-pentanediol and 2,5-diphenyl-2,5-hexanediol.

These problems will all be studied by isotope dilution techniques, involving proof of relative configuration of the diastereoisomeric forms, and either labelled reactants and non-labelled dilution materials or vice versa.
STUDIES OF PHYSICAL-ORGANIC CHEMISTRY PROBLEMS BY USE OF ISOTOPES

The proposed work consists of three projects:

1. **Spin-Spin Coupling Between C\textsuperscript{13} and Proton:** Studies of J\textsubscript{C\textsuperscript{13}H} as a function of the hybridization of C\textsuperscript{13} atomic orbitals, the number of bonds separating the two nuclei, and molecular conformations are contemplated in order to understand better the general problem of spin-spin coupling. Cyclic and acyclic compounds suitably labeled with C\textsuperscript{13} will be examined.

2. **Wagner-Meerwein 1,3-shifts in Open Chain Systems:** Wagner-Meerwein 1,3-shifts in open chain systems have not been demonstrated unambiguously, because of the difficulty in distinguishing 1,3-shifts from successive 1,2-shifts. Studies with suitably chosen systems, such as 1,1,2,2-tetraduero-1-propyl amine under diazotization conditions, are expected to either prove or disprove the occurrence of 1,3-shifts.

3. **Stereochmical Studies of Carbonyl Derivatives by Proton N.M.R.:** Proton n.m.r. has been applied successfully in elucidating problems of structural isomerism involving restricted rotation. From studies of chemical shifts and long-range spin-spin coupling of various carbonyl compounds and their derivatives, the favored molecular conformations of these compounds have been determined. These studies are being extended.
DEUTERATION OF AROMATIC HYDROCARBONS

Triphenylene will be investigated and the relative rates of deuterium-hydrogen exchange determined.

1,3,5-Triphenylbenzene will be studied. Previously, biphenyl and 4-methylbiphenyl were studied; an attempt will be made to correlate the partial rate factors.

It is believed that compound I, below, is more reactive than o-xylene. It is possible that in the case of I, unlike II, a charge transfer from one ring to the other takes place. A sample of compound I has been prepared.

The following series is being studied:

The partial rate factors for toluene have been determined. They are 250 for the ortho position, 4 for the meta position and 420 for the para position. If the effect of a methyl group is additive, it should be possible to calculate the ratio of exchanges in compounds III, IV and V, depicted above. Deviation from this calculated value for V, if it occurs, might be due to steric factors.
This research is concerned with the chemistry of organometallic derivatives of bicyclo(2,2,1) heptene. Of current interest are certain compounds in which the metal is a group IVb metal, such as silicon or tin. These compounds are being prepared via hydrometallation of bicyclo(2,2,1) heptadiene and Diels-Alder reactions of vinylmetallics with cyclopentadiene. The stereochemistry of the compounds is to be investigated as a prelude to study of the course and mechanisms of reactions with electrophilic reagents such as protonic acids, halogens, and metallic salts, particularly those which might lead to formation of nortricyclenes.
In the dehydrogenation of butane-1 tagged with radioactive beta-emitting C$^{14}$ in the 1-position, it was found that cold butane and radioactive butadiene were produced:

$$\begin{align*}
\text{C*} & \quad \text{C*} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C*} & \quad \text{C*}
\end{align*}$$

$$1100^\circ F$$

Butadiene (active) + Butane (cold)

If this observation is correct, it would rule out the case of single site mechanism and favor dual site mechanism, that requires adjacent activated molecules.

It is the purpose of this proposal to study further this unexpected observation using the radioactive butane tagged with C$^{14}$ in the 1 or 2 position as the starting material, and further, to determine the position of the radioactive C$^{14}$ atom in the butadiene produced.
USE OF ISOTOPES IN THE STUDY OF ORGANIC REACTION MECHANISMS

This contract is concerned with the determination of kinetic isotope effects and isotopic exchange reactions and their correlation with organic reaction mechanisms. The systems that will be studied include:

1. The determination of the kinetic isotope effects encountered in hydrolytic reactions carried out in deuterium oxide;
2. The determination of the kinetic isotope effects encountered in solvolytic reactions carried out in ethanol-d; and
3. The determination of isotopic oxygen exchange which accompanies the hydrolysis of a number of organic compounds.

The most interesting investigation contemplated at the moment is the combination of 1 and 3 above, that is, the determination of deuterium oxide solvent effects in reactions that involve isotopic oxygen exchange. It is hoped that in these latter investigations important proton transfers occurring in the unstable intermediate of the reaction will be reflected in deuterium oxide isotope effects.
The aromatization studies of n-alkanes over chromia-alumina catalysts led to the belief that cycloheptane and/or cyclooctane adsorbed species may be involved in the transition state. In the case of aromatization of branched alkanes, such as 2,2,4-, 2,2,3- and 2,3,4-trimethylpentane, it was concluded that the reaction proceeds via cyclopropane- and cyclobutane-adsorbed species. It is the purpose of the projected study, using C-14-labeled alkanes, to determine the relative contribution of the various adsorbed species to the formation of aromatic hydrocarbons.

Recent studies carried out in this laboratory with alumina as a catalyst and support led to the conclusion that certain catalytic reactions occur not on the alumina surfaces but within the alumina channels. This conclusion was based on the study of dehydration reactions using various steroisomeric alcohols such as endo- and exo-norbornanols and bornanols, menthol and neomenthol and cis- and trans-cyclohexanediols. For a more thorough understanding of this phenomenon, which invalidates many proposed catalytic theories, it is intended to synthesize and study the dehydration of C-14 and tritium labeled alcohols.
THE ISOTOPE EFFECT IN THE STUDY OF CHEMICAL REACTIONS

The purpose of this work is to study the mechanisms of reactions of organic compounds by means of isotope effects, particularly of tritium and of carbon-14.

The following reactions will be studied as time permits:

1. Reduction of vicinal halides with lithium aluminum hydride, using DL- and meso-2,3-dibromobutane; the stereochemistry of the reaction will be investigated.

2. Electrophilic substitution of aromatic compounds by tritium; compounds such as toluene and chlorobenzene in the presence of benzene will be contacted with tritio acids, the products separated and assayed by means of gas chromatography.

3. Free-radical arylation of benzene-t; Aryl radicals will be generated by photolysis of p-iodotoluene and the ratios of all three reaction rate constants will be sought.

4. Equilibrium between benzophenone-carbonyl-C\(^{14}\) and benzhydrol (catalyzed with aluminum tert.-butoxide); kinetics of the reaction and the equilibrium isotope effect will be studied.

5. Free-radical bromination of 2-methyl-2-t-propane; primary and secondary isotope effects will be determined.
Section 11

ANALYTICAL CHEMISTRY (A)

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See also:  Section 1, Pages N-5, N-10
           Section 2, Page G-12
           Section 12, Page CS-13
SENSITIVITY OF INCREMENTAL DERIVATIVE POLAROGRAPHY

Two of the limitations in the sensitivity of polarographic analysis are the effect of capacitative charging current and electrical "noise" generated in the capillary dropping mercury electrode. The purpose of this research is to find new methods of compensating the charging current in the incremental method of derivative polarography. These are "second increment" methods, which can lead to an instrument response from which the charging current response has been subtracted. The reduction of capillary noise will be approached by fabrication of plastic or metal capillaries. These will have surface properties opposing the entry of solutions into the capillary, which is believed to be the cause of capillary noise.
The purpose of this project is to develop a coulometric method of analysis for rare-earth elements at controlled potential. Europium and ytterbium have been successfully determined, and the extension of the method to other rare-earth elements is being investigated.

Polarographic studies of samarium and neodymium in acetonitrile solvent with tetraethylammonium perchlorate as the supporting electrolyte have provided information which will be used in the development of methods for coulometrically determining these elements. This solvent system will then be used to study the polarographic and coulometric reduction of thulium.

A direct-reading wide-range coulometer has been developed to facilitate constant-potential coulometric titrations.

The rate of reaction of a reducible rare-earth species at a microelectrode is being studied by precisely measuring the time required to achieve electrical stability at the microelectrode surface following an abrupt change in the potential of the electrode with respect to the solution.
DEVELOPMENT AND TESTING OF ORGANIC REAGENTS FOR USE IN INORGANIC ANALYSIS

The purpose and scope of the proposed research may be summarized as follows:

1. To synthesize, evaluate, and develop organic chelating agents for application to analytical separations and determinations of the rare earth and other less familiar metals.

2. To study the theoretical aspects of chelate formation in order to uncover more fundamental relationships between the thermodynamic and kinetic parameters of chelation and structural parameters of both reagents and metal ions.

3. To investigate both physical and chemical properties of metal chelates that are of a special interest in their analytical applications. These will include:
   a. Intrinsic solubility in both water and organic solvents,
   b. Distribution coefficients, $K_D$.
   c. Absorption spectra both in the infrared and ultra-violet regions,
   d. Determination of dipole moments,
   e. Crystal structure determination by x-ray techniques and
   f. Alteration of redox properties of metal ions via chelation.

4. To investigate the use of metal complexing agents in analytical separations processes including solvent extraction, precipitation, and ion exchange.
A STUDY OF COLLOIDAL PARTICLES BY LIGHT SCATTERING AND ELECTRON MICROSCOPY

This research effort is concerned with the extension and refinement of light scattering as a quantitative analytical method; both experimental and theoretical studies are being performed. Determination by light scattering methods of molecular weights of the basic units of heteropoly acids, such as 12-tungstophosphoric or 12-tungstosilicic acid, continues to be a prime goal under this contract.

Extensive physical chemistry data has been obtained on heteropoly acids in order to permit meaningful correlations and interpretation of light scattering data on these compounds. Activity data has been obtained in aqueous-acid systems by isopiestic methods and by light scattering techniques and results by both methods are in good agreement.

Light scattering experiments with heteropoly acids will be extended to nonaqueous solvents, especially at high concentrations. In addition, light scattering in mixed solvents will be studied with parallel determinations of activity by other methods.

Theoretical work on computation and analysis of light scattering functions will be continued and both computational and experimental work on scattering of electromagnetic radiation by cylinders will be performed.

Problems completed under this contract have related mainly to the characterization of the heteropoly acids and a number of papers on "Heteropoly Compounds" have been published in the Journal of Physical Chemistry and the Journal of Chemical and Engineering Data. Papers on "Correlation of Turbidity and Activity Data" and papers on "Detection of Metal Ion Hydrolysis by Coagulation" have been published in the Journal of Physical Chemistry.
The analysis by electrochemical titration for very low concentrations of cyanide, nitrite and other anions is being investigated; major concern is being given to methods of eliminating interferences and study of suitable reference electrodes. Currently, the following specific studies are being carried out or are planned:

1. The amperometric titration at solid electrodes of low concentrations of nitrite.

2. The solubility of mercuric chloride, lithium chloride, and mixtures of these in ethylenediamine and in ethylenediamine-water systems. Potentiometric reference electrodes for use in ethylenediamine systems.

3. Improvements to a simple potentiometric autotitrator.

4. The synthesis, polarography, and possible uses in amperometric titration of various disubstituted quinoline derivatives.

5. The determination of microgram quantities of chloride by polarographic stripping analysis.

6. Miscellaneous, such as the microdetermination of acetate in the presence of a high concentration of inorganic acids and biamperometric and related titrations with mercury and other electrodes.
STUDIES ON CHELATE COMPLEXES AND INSTRUMENTATION IN ANALYTICAL CHEMISTRY

This project involves two main divisions. In one, the crystal structures of organic compounds which form chelate complexes with inorganic ions and the complexes themselves are being determined by means of X-ray diffraction methods. Compounds and complexes which are of interest to analytical chemists are of primary, but not sole interest. Compounds under investigation are: p-arsanilic acid, silver, rhodanine, dimethylglyoxime, 8-hydroxyquinoline and derivatives of it.

In part two, improvements and applications of existing instruments and development of new instrumental methods of analysis are being studied. In particular, applications of controlled-potential coulometry to preparation of standard solutions, stripping methods and precipitation methods are being studied. Attempts are being made to go down to very small quantities of material. Also it is proposed to investigate photometric titrations using infrared detection of endpoints. An automatic, electrical balance has been developed and its performance will be further studied.
It is proposed to obtain fairly complete kinetic data on the oxidative destruction of metal complexes with ethylenediamine tetraacetic acid by ammoniacal hydrogen peroxide, on the reaction of hydroxylamine with biacetyl to form dimethylglyoxime, and on a few other reactions which can be used as the slow reaction in precipitation reactions from homogeneous solution. Similar data are already available on the hydrolysis of thioacetamide to hydrogen sulfide, the hydrolysis of sulfamic acid to sulfate ion and the hydrolysis of urea to ammonia.

Each of these slow reactions will be used in the presence of other appropriate ions for the precipitation of various substances from homogeneous solution. At selected intervals during the reaction, including some times within the first one-thousandth of the total reaction time, aliquots will be withdrawn for particle counts and for other observation in the electron microscope. In some experiments, the reaction medium will be filtered through millipore filters; further nucleation will thus be forced as the reaction continues in the filtrate.
Additional work has been done on the separation of trimetaphosphate from the linear polyphosphates with four or more phosphorous atoms per molecule by the precipitation of the latter as barium salts.

Separation of the condensed phosphates with 13 or less phosphorus atoms per molecule has been studied by anion-exchange chromatography. An unexpected compound was found in phosphate glasses having an average degree of polymerization of six to ten. This compound has been isolated and studied. End-group titrations and paper chromatography prove it to be a cyclic compound distinct from the well-known trimetaphosphate and tetrametaphosphate. It is probably either pentametaphosphate or the boat form of tetrametaphosphate, but the experiments have not progressed sufficiently to decide between these possibilities. A method of anion-exchange chromatography has been developed by which all constituents can be isolated from a mixture of the first 13 linear polymers, trimetaphosphate, tetrametaphosphate and the unknown cyclic, except that trimetaphosphate and hexaphosphate overlap. These can be separated by precipitation with barium.

Work during 1962 included attempts to identify the unknown cyclic, to extend the separation by anion-exchange chromatography beyond tridecaphosphate and to prove the identity of the higher linear compounds by end-group titration.
USE OF RADIOTRACERS IN CONTINUOUS ANALYSIS

The main purpose of the current research is to devise or develop methods for measuring traces of specific substances continuously in flowing streams, in the presence of other similar substances.

In the early part of the work, now under way, primary emphasis is on the development of equipment and techniques that will permit analytical operations to be performed continuously and with little holdup. Examples of such equipment are:

1. A metering pump for non-aqueous solutions. Pumping rate, up to 4 ml/min; holdup, 0.1 ml.
2. A liquid-liquid extractor. Throughput, up to 3 ml/min for each phase, with 2 ml holdup.
3. An electrochromatographic column. 9 ft. long, 1 mm x 2 mm in cross section, with 1 mm interelectrode spacing.
4. A tubular platinum electrode (0.020" i.d. x 0.5 cm long), for measuring the concentration of an anodically oxidizable substance in a flowing stream.

When development is completed, the equipment will be applied to existing methods of analysis, to test the equipment and to improve the methods. After testing, the equipment and techniques will be used to work out analytical methods that are not feasible with present techniques.
KINETIC AND MASS TRANSFER PROCESSES IN ELECTROCHEMISTRY:
APPLICATION TO ANALYTICAL METHODS

The proposed work involves the extension of the technique and theory of stripping analysis, and at the same time, further development of the hanging mercury drop electrode for applications in analysis and electrochemical kinetics. Stripping analysis will be used to study the electrochemistry of tin and selenium in order to extend the applicability and sensitivity of the analyses, and at the same time, to investigate the specific electrode reactions involved. In further work with the hanging mercury drop electrode, both voltammetry with linearly varying potential and potentiostatic methods will be used. This stationary electrode is of particular value in that the products of the electrode reaction can be accumulated around the electrode surface, and thus are available for further study. In this connection, diffusion processes of dilute amalgams formed within the hanging mercury drop electrode will be studied. In addition, the electrode will be especially useful in those kinetic cases where the product of an electrode reaction undergoes further chemical reaction, and the rates and mechanism of certain organic electrode reactions will be investigated as examples of such processes.
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See also: Section 2, page G-14
Section 6, page CC-7
The proposed work is a continuation of a study concerning precipitation from homogeneous solutions of mixed solvents. A portion of this study will be devoted to investigating the characteristics of the precipitates formed when various cations and precipitants are reacted in the presence of large amounts of organic solvents. Earlier work has shown that improvements in crystal size, precipitate purity and the filtering characteristics of the precipitates could be obtained by this technique. The proposed work will study these characteristics for some systems not previously investigated.

A second portion of the work will be designed to yield a better understanding of the nucleation and crystal growth reactions as they occur when large and variable amounts of organic solvents are present. The aim of this portion of the work will be to gain, through a study of nucleation and crystal growth rates, an insight into the reasons for the observed changes of crystal habit and size. Also it is expected that X-ray diffraction studies will be performed to determine whether the changed crystal habit is the result of a change in the structure of the unit cell or results entirely from a modification of the growth rate of the various crystal faces.
NUCLEATION AND COPRECIPITATION FROM HOMOGENEOUS SOLUTION

This investigation is primarily concerned with coprecipitation phenomena under near-equilibrium conditions. Near-equilibrium conditions are achieved through controlled precipitation of metal ions by precipitants slowly generated in the homogeneous solutions under study.

Currently, studies are on four interrelated subjects. These are mechanism of nucleation, pre-nucleation kinetics, coprecipitation, and new precipitation methods.

Nucleation studies are directed toward characterization of the initial stable nucleus and the effect of the initial nucleation process upon coprecipitation. Pre-nucleation kinetics studies are aimed at identifying the preliminary processes and species involved in the nucleation process. Coprecipitation studies are directed toward elucidation of the mechanism by which various precipitates entrain or "carry down" ions present in trace quantities and are also directed toward clarification of the nature of the distribution coefficient. The development of new precipitation methods is limited to studies on precipitation of metal organic chelates from homogeneous solution.

All of these subjects are being studied using the same or similar chemical systems. Precipitants being studied are formed in situ. Precipitants used include dimethylglyoxime formed by the biacetyl-hydroxylamine reaction, 8-acetoxyquinoline and dimethyl oxalate. Major metal ions studied include those of U, Th, Ni, Al, and Mg. Trace ions studied in coprecipitation include those of Nb, Ta, and Pd.
The purpose of this research is to develop generalized design correlations for packed columns. Current effort is concerned with the problem of absorption from a gas phase into a liquid phase accompanied by chemical reaction.

Absorption accompanied by chemical reaction in a packed column will be studied in an attempt to develop methods for predicting the transient behavior of packed columns and the effects of gas concentration and liquid concentration on the gas-phase mass transfer coefficient. Measurements will be made to determine operating holdups, static holdups, rates of water vaporization, rates of ammonia absorption in water and rates of ammonia absorption in acidic solutions in one packed column. Transient and equilibrium operation will be studied.

Problems completed under this contract have been concerned with mass transfer without chemical reaction and successful design correlations have been developed and are published in the AIChE Journal.
A FUNDAMENTAL STUDY OF HEAT AND MASS TRANSFER IN THE
CONDENSATION OF MULTICOMPONENT SYSTEMS

It is the purpose of this study to experimentally observe and quantita-
tively evaluate the effect of molecular weight differences upon the
mass transfer coefficient associated with a vapor stream in turbulent
motion. This effect has been theoretically described in the literature
by Bedingfield and Drew.

The experimental method chosen provides the means for effecting
extreme changes in the major variables (rates of mass transfer and
differences in molecular weights). It consists mainly of a cooled,
horizontal, porous plate upon which condensation of a multicomponent
vapor takes place and through which the condensate is continuously
removed. This technique eliminates the complicating fluid mechanical
phenomena which are present when flow occurs parallel to the area of
mass transfer.

An associated phenomenon which also must be studied during this
investigation is the effect of mass transfer upon the mass transfer
coefficient. After perfecting this technique and evaluating the
described phenomena, it will be possible to expand the investigation
to systems containing more than two components being transferred.
This work was initiated in April, 1961.
SOLVENT EXTRACTION AND SPECTROGRAPHIC ANALYSIS OF RARE EARTHS

The purpose of this research is to study the fundamental factors influencing the formation of the various solvates of the chelates of transition and rare earth elements, and to study the effect of these factors on the extraction of systems containing two chelating agents.

The study of the halo-methane solvates, currently underway, will be extended to include the halo-ethane solvates. Nuclear magnetic resonance measurements will be employed to obtain evidence for the type of bonding of the solvate molecules as well as stability and number of solvate molecules. The strength of solvate bonds will also be investigated by calorimetric methods. Attempts will be made to prepare the anhydrous rare earth acetylacetonates.

Studies of the characteristics of the rare earth thenoyltrifluoroacetonates will be performed, including structures by x-ray diffraction, formation of solvates by vapor pressure-composition diagrams, calorimetry and solubility determinations. Attempts will be made to obtain data for calculating theoretical extraction curves in the presence of two chelating agents.
SOLVENT EXTRACTION STUDIES

The study of the extraction potential of long chain alkyl amines for the anionic complexes of the Group VIII metals will be continued. During the proposed contract period chief emphasis will be on the extraction of the Ru, Rh and Pd triad from chloride and sulfate media and on the extraction of the oxalato and cyano complexes of these metals. It is also planned to continue evaluation of some high molecular weight benzyl amines as liquid extractors on the Ru, Rh and Pd triad as well as the Fe, Co and Ni triad. In addition, the study of temperature effects in these extraction systems will be continued. By proper evaluation of the data obtained it is hoped to enlarge the basic chemical knowledge of these lesser known elements, to work out good, practical analytical techniques for these metals, and to propose possible solvent extraction type separation procedures for these elements.
THERMAL DIFFUSION IN GASES

Investigation will be continued on forces between unlike molecules from measurements on thermal diffusion and the rate of approach to the steady state in binary gas mixtures. Corollary studies will be made of ordinary diffusion under non-isothermal conditions and of the theory of transport phenomena in gases.

A summary of the program includes:

1. Completion and checking of measurements on CO₂-CO₂, Kr-Kr, and the start of measurements on new systems.
2. Theoretical interpretation of the experimental results and theoretical work on transport phenomena in gases.
3. Other pertinent problems of interest which may arise in the course of the work.
The ultimate objective of this investigation is to develop an efficient and practical catalyst for the exchange reaction between liquid water and hydrogen gas dissolved under pressure. To this end, the rate of the exchange reaction

\[ \text{HDO} + \text{H}_2 \rightarrow \text{HD} + \text{H}_2\text{O} \]

is to be measured as a function of temperature, pressure and catalyst content. Various volatile organic bases are to be investigated as possible catalysts. Apparatus built for this research consists of a stirred autoclave to serve as a batch reaction vessel, a constant temperature bath capable of operation at temperatures up to 250°C, equipment for charging measured quantities of hydrogen, water and catalyst at pressures up to 100 atm., and means for sampling and discharging gas and liquid phases. The rate of exchange is to be determined from the rate of change in isotopic content of hydrogen in the gas phase, inferred from the voltage output of a thermal conductivity cell and bridge, calibrated with hydrogen samples of known deuterium content.
THE SEPARATION OF SOME OF THE RADIOACTIVE FISSION PRODUCTS BY ELECTRODIALYSIS

The purpose of the proposed research is:

1. To investigate methods for the separation of radioactive fission elements from aqueous solutions by electrodialysis.
2. To study equipment design, power efficiency and economics for separating radioactive materials by electrodialytic methods developed at the University of Missouri, School of Mines and Metallurgy.
3. To investigate the separation of radioactive fission elements by solvent extraction.

The work on electrodialysis will be an extension of a study for the separation of radioactive elements by use of ion transfer membranes. A study of the effect of aminopolycarboxylic acids on the properties of metallic ions will be made. The feasibility of using electrodialysis equipment for industrial separations of fission products will be studied. Investigations of liquid extraction methods will include studies of the extraction of metal ions with alkyl orthophosphoric acids in the presence of aminopolycarboxylic acids as suppressing agents.

Requisite data will be sought to determine the degree of separation of radioactive elements in the presence of an aminopolycarboxylic acid and a mixture of these acids by electrodialysis. Data will be obtained on construction materials, operating variables, optimum equipment design, and economics of the electrodialytic process. Distribution coefficients for the extraction of metallic ions will be determined. Alkyl orthophosphoric acids will be used as extractants and chelating agents will be used to suppress the extraction of undesirable ions.
THE TEMPERATURE OF SOLID PARTICLES IN A FLUIDIZED SYSTEM

The transfer of heat between the gas and solid particle within a fluidized bed is of importance in estimating the temperature of a solid catalyst from the measured temperature of the gas stream. This information is essential for a kinetic analysis of a chemical reaction in a fluid bed system.

In all work to date using steady state conditions, it has been impossible to measure the temperature of the solid directly, and consequently there has been a number of assumptions to establish this temperature. Different opinions exist whether a thermocouple in a fluidized bed indicates the temperature of the fluid, solid, or some intermediate temperatures.

The unsteady state method has also been used and given heat transfer coefficients one to two orders of magnitude lower than the steady state method. This procedure does not require knowledge of the solid temperature.

The work proposed is directed toward obtaining heat transfer coefficients by a frequency response method and, in addition, is directed toward obtaining direct measurements of the temperature of the solid particles within the fluidized bed. A comparison of these two results will demonstrate that the heat transfer coefficients obtained are reliable.
A STUDY OF MASS TRANSFER KINETICS OF URANIUM COMPLEXES

The rates of transfer of uranyl nitrate between aqueous solutions and 30% tributyl phosphate-Amsco odorless mineral spirits is being investigated. Fick diffusion coefficients for uranyl nitrate in aqueous solution and in 30% tributyl phosphate-Amsco are being determined using the capillary cell technique in concentrated solutions and a birefringent interferometer in dilute solutions. The effect of uranyl nitrate concentration and the effect of simultaneously diffusing multivalent cations will be determined.

Interfacial mass transfer rates of uranyl nitrate are being investigated using a stirred extraction cell. The effect of concentration level and concentration gradient across the interface on transfer rates will be determined for uranyl nitrate transferring from aqueous solution to 30% tributyl phosphate-Amsco and in the reverse direction. The effect of the simultaneous transfer of nitric acid, aluminum nitrate and typical fission products will be investigated.

Similar investigations of the transfer kinetics of uranyl nitrate in aqueous-tri-n-octylamine solutions will be initiated.
A STUDY OF FACTORS AFFECTING THE LIQUID-LIQUID EXTRACTION AND SEPARATION OF SALTS

The purpose of this research is to study the factors affecting the distribution of salts of the transition metals of the iron family between aqueous solutions and oxygenated solvents; e.g., alcohols, ketones, and ethers. Particular concern is with salting-out or salting-in action of added electrolytes upon extraction and thermodynamic equilibrium relations in each phase.

The hydration of such salts as the chlorides, nitrates, and perchlorates in the hydrous butyl alcohols will be investigated. Three methods will be used: measurement of the enthalpy of the hydration reaction by titration calorimetry, determination of the average number of bound waters per metal atom by absorption spectrophotometry, and determination of the hydration of charge carriers by Hittorf transference measurements.

A second part of the proposed work is a study of the effect of non-extracted anions upon the extraction of transition metals. It is planned to measure the activities of all three solution components in mixed anion systems of the type $\text{MSO}_4\text{-HCl-H}_2\text{O}$ by the gas-transpiration method and to correlate the results with distribution measurements on the systems. $\text{CuSO}_4\text{-HCl-H}_2\text{O}$ is being studied first.
FUNDAMENTAL STUDIES OF SEPARATION PROCESSES

One goal is to examine the effects of porosity and liquid loading on chromatographic separations using specially prepared molecular sieves. Partial dehydration of crystals of pure salts has already been shown to be a feasible preparative method, so it will be used to prepare a variety of sieves for selectivity studies involving volatile substances. Later, impregnation of the sieves with small amounts of non-volatile partitioning liquid will be examined for effects of plugging of holes and adsorption on the surface of the liquid. Adsorption by the surfaces of solids may also be examined briefly in attempting to clarify the roles of the support.

A second goal is to examine the fractionation of solutes in foam. The interrelationships between reflux and drainage will be examined at low concentration levels using radio-carbon or radio-sulfur compounds.

A third goal is to examine the effect of the non-aqueous solvent on the nature of the species found in liquid-liquid extractions, particularly their redox behavior. Complexes and chelates of transition metals will be studied first.
Studies are being carried out on mass transfer in the methyl isobutyl ketone-acetic acid-water system in a circulating tank extractor. Measurements have been made with both phases at chemical and physical equilibrium, and with stirring, for the transfer of acetic acid from water to ketone and from ketone to water. This work showed that the mass transfer rate constant was concentration dependent.

A series of experiments under unsteady state conditions in the same system has demonstrated that the concentration dependence of the rate constant is indeed significant, and, moreover, no simple relationship exists between the constant and the bulk properties of the fluids.

Additional work is being performed using radioactive acetic acid to detect the effect of transfer of tracer in a direction opposite to the transfer of non-tracer in the same experimental set-up as used for the above studies. This work will be carried out under unsteady-state conditions. The tracer analyses will be performed by liquid scintillation counting, and the data collected will be analyzed by previously developed statistical techniques.
INFLUENCE OF KINETIC PROCESSES ON RESOLUTION OF CHROMATOGRAPHY AND RELATED PROCESSES

The objective of this work is to improve the usefulness of chromatography through a study of the fundamental processes which are responsible for chromatographic separation. One part of this work involves the prediction of optimum parameters for either maximum separability or minimum analysis time. The other part involves the study of the basic processes which must be understood before meaningful optimums can be obtained. The experimental vehicle will be gas chromatography although the results will be generalized to include all column techniques.

The specific areas which are to be investigated with the above methods and objectives in mind are:

1. The study of preparative scale operation,
2. Investigation of optimum parameters,
3. Basic chromatographic processes, and
4. Temperature and temperature programming.
Exchange between solid salts and their saturated solutions closely follows a modified form of the exponential exchange law. The distribution of isotopes throughout the interior of the crystal is rapid compared to the rate determining step in exchange between the surface and the interior of the crystal. Exchange studies are being continued using solid silver chromate in contact with its saturated solution. The nature of the exchanging species can be determined from combined data on cationic and anionic exchange.

The exchange between surface oxidized silver powder and solutions containing silver ion showed a number of free energy states of oriented silver oxide on the metal. Solubility measurements by potentiometric methods indicate free energy states of oriented silver oxide of about 6 Kcal/mole below the free energy state in the bulk form. Decomposition temperatures of oxide on single crystals of silver will be studied in order to connect the various free energy states with specific orientations on the silver metal. These data should be of importance in evaluating conditions at which protective oxide layers are formed on metals, and the chemical stability of the layers can be estimated.
SEPARATION EFFICIENCIES OF PULSED EXTRACTION COLUMNS

Experimental and theoretical studies of the factors affecting the separation efficiency of pulsed solvent extraction columns will be continued.

Longitudinal mixing studies in dispersed phases using a radioactive tracer soluble only in an organic phase will be completed during 1962.

Simulation of the steady and unsteady state behavior of a pulsed column using both digital and analog computers is currently in progress.

The interferometric study of the transfer of sulfur across a nitromethane-n-heptane interface will be completed in 1962. If time permits, the interfacial transfer of sulfur in the aniline methyl-cyclohexane system will also be studied.
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