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CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

FOR PERIOD ENDING JUNE 20, 1959

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CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

for Period Ending June 20, 1959

E. H. Taylor, Director
M. A. Bredig, Associate Director

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CHEMISTRY DIVISION ANNUAL PROGRESS REPORT

SUMMARY

NUCLEAR CHEMISTRY

Soon after the first demonstration of nonconservation of parity, the longitudinal polarization of P^{32} beta rays was measured in cooperation with members of the Physics Division. The polarization was found to be $-v/c$, as predicted by the new beta-decay theory, within the experimental error of ±2%.

From measurements of the radiations of Dy^{159}, an electron-capture decay scheme was proposed, and the disintegration energy was deduced. The 8-min Ga^{74} was separated from the fission products of U^{235}, and its fission yield was found to be 3.4×10^{-4}%. This is believed to be the first observation of mass 74 in the fission process. The energies of the two principal gamma rays in the decay of Y^{88} were measured as 0.899 ± 0.004 and 1.832 ± 0.006 Mev by using a 3 × 3 in. NaI scintillation spectrometer. A method is described for measuring the sum spectra from gamma-scintillation spectrometers.

Iodine-136, an 83-sec activity, was studied with scintillation techniques. An energy level scheme in Xe^{136} was proposed on the basis of the single-crystal and coincidence measurements. A decay scheme was postulated for I^{134} based on both single-crystal and coincidence measurements. This scheme involves first and second excited levels in Xe^{134} at 0.85 and 1.74 Mev, respectively, and shows an I^{134}-Xe^{134} ground state energy separation of 4.15 Mev.

Specific activity measurements were performed on long-lived technetium isolated from the uranium fission products and from neutron-irradiated molybdenum using 4π beta counting techniques. The half-life values derived from these measurements on technetium formed by different nuclear processes were the same within experimental errors. An average value of $(2.17 \pm 0.05) \times 10^5$ years for Tc^{99g} was obtained.

New observations on the radiations emitted by molybdenum bombarded with thermal neutrons to an nvt of 5×10^{20} confirmed the presence of niobium x rays in the decay of long-lived Mo^{93g} and further revealed the occurrence of a low-intensity (~55 kev) gamma ray. A half life of $\sim 10^4$ years was estimated for Mo^{93g}.

Values of 1450 ± 100 and 400 ± 100 barns, respectively, were obtained for the thermal neutron cross section and the resonance integral of the 23-min Th^{233} with the use of cadmium ratio techniques. Resonance integrals of 85 ± 8 and 75 ± 5 barns were determined for Th^{232} and Co^{59}, respectively.

Effective cadmium cutoff energies were calculated for infinitely small $1/v$ samples at the centers of spherical and cylindrical cadmium shells. Shell thicknesses of 40 mils are recommended in cadmium ratio work in order that the cutoff energies be insensitive to Maxwellian flux parameters.

ISOLATION AND CHEMICAL PROPERTIES OF SYNTHETIC ELEMENTS

Two different species of Tc(V) stable in concentrated hydrochloric acid were observed. The existence of at least two differing oxygenated Tc(IV) species was indicated by reductions of pertechnetate ion in dilute hydrochloric acid solutions with $SnCl_2$.

In survey measurements of the solvent extraction of pentavalent and tetravalent technetium from acid aqueous solutions both oxidation states were extracted efficiently by dilute solutions of trioctylphosphine oxide and trioctylamine in nonpolar organic solvents. Neither Tc(V) in 12 *N* HCl nor Tc(IV) present as $TcCl_6^{--}$ in 3 *N* HCl was extracted by diethyl ether.

A partial fractionation of the nuclear isomers of Tc^{95} was effected with anion exchange chromatography used to separate TcO_4^- ion containing the 20-hr ground state, Tc^{95g}, from $TcCl_6^{--}$ ion containing the parent 60-day metastable state, Tc^{95m}.

A determination by x-ray diffraction of the lattice constants, a_0, for K_2TcCl_6 and K_2ReCl_6 (K_2PtCl_6 structure) gave values of 9.90 ± 0.01 and 9.839 ± 0.005 Å, respectively, in agreement with previous measurements in this Laboratory.

Semiquantitative data were obtained for the rate of electrodeposition of technetium from 0.5 *m* H_2SO_4 solutions at 25 and 80°C.

Data are presented from a series of experiments designed to observe the oxidation rate and release of fission products from highly irradiated metallic uranium. Irradiated metal at 1000 and 1200°C burns in air approximately twice as fast as unirradiated metal.

CHEMICAL SEPARATION OF ISOTOPES

Considerable quantities of D_2 and D_2O of low tritium content were produced. A study was made of the variation of the single-stage separation factor α for lithium isotopes in an ion exchange system as a function of the eluting cation and anion. The variation of the lithium ion exchange α with the composition of a methanol-water solvent mixture was measured.

Vapor pressure and α measurements were made at various temperatures for systems involving the BF_3 addition compounds of methyl and ethyl sulfide. Several systems for enriching C^{13} utilizing the exchange of CO gas with carbonyls and CO complexes were studied.

An investigation of the feasibility of enriching nitrogen and oxygen isotopes by distilling NO was begun. A nitrogen α value of 1.024 was measured at −152°C. The oxygen α value between SO_2 gas and H_2O liquid was determined. Oxygen and carbon α values were obtained for the distillation of several amine carbamates. Sulfur and oxygen isotopic fractionations were measured for the distillation of SO_3. The sulfur α value between H_2SO_3 and HSO_3^- on Dowex 2 resin was determined. Isotopic fractionation data were obtained for the system CS_2, S^{--}, CS_3^{--}.

The infrared spectra of the normal and N^{15} forms of N_2O_4, NO_3^-, and NOCl were examined. Raman studies were made of $Zn(ND_3)_4^{++}$ as well as the N^{14} and N^{15} forms of N_2O_4 and NO_3^-.

RADIATION CHEMISTRY

Very marked increases in catalytic activity for H_2-D_2 exchange were induced in silica gel by both gamma rays and neutrons. The formation by radiation of new adsorption sites was demonstrated, and adsorption of hydrogen on them was correlated with the disappearance of the amethyst color produced by the irradiation.

Infrared analysis of the polymer cuprene, produced by irradiation of acetylene, indicates that it is a network of aromatic rings. The polymer from benzene radiolysis consists of aliphatic chains with pendant aromatic rings, the spectrum resembling that of polystyrene.

Electron irradiation of methane-oxygen gaseous mixtures containing a high proportion of oxygen produces only carbon dioxide, water, and ozone. For mixtures containing less than half oxygen, a variety of products, including methanol, formic acid, carbon monoxide, carbon dioxide, ethylene, and acetylene, are produced.

Preliminary results were obtained on radiolysis of fused nitrates and nitrites.

The following studies were completed and results submitted for publication: kinetics of the radiation-induced reaction of Fe(III) and Sn(II); kinetics of the radiation-induced reduction of Ce(IV) in the presence of Ce(III), H_2, and H_2SO_4; the relation between molecular hydrogen yield and activity of nitrate; the effect of Ce(IV) on "molecular" hydrogen yield; radiation-induced reactions in the N_2-O_2-H_2O system.

ORGANIC CHEMISTRY

The Oracle was employed in the calculation of tables of isotope effect functions for homocompetitive first-order reactions.

The diphenyl-*m*-tolyl glycol system was examined radiochemically, and the results completely support a mechanism previously proposed for the pinacol rearrangement. By a combination of radiochemical and stereochemical techniques, the decomposition of D- and L-*N*-acetyl-C^{14}-*N*-nitroso-1,2,2-triphenylethyl-1-C^{14}-amine was employed to relate the configuration of (+)-1,2,2-triphenylethanol with (+)-1,2,2-triphenylethylamine. The deamination of 1,1-diphenyl-2-propylamine was studied by stereospecific labeling techniques. The presence of open carbonium-ion intermediates was demonstrated.

The mechanism of decarbonylation of formic, benzoylformic, and triphenylacetic acids was investigated with deuterium and C^{14} isotope effect measurements and C^{14} and O^{18} tracer techniques. A C^{14} tracer study showed that no Hayashi rearrangement of *o*-benzoylbenzoic acid occurs under conditions which lead to cyclization to anthraquinone.

In connection with a study of strong specific interactions between tributylphosphine oxide and aqueous solutions of electrolytes, its solubility in water and aqueous acid solutions was measured.

Preliminary investigations of a "polymer" formed during gamma-ray radiolysis of neutral phosphate esters point to the polymerization through the alkyl chains rather than by the formation of pyrophosphate (P-O-P) linkages.

Quantitative removal of alkyl groups from trialkyl phosphates was accomplished by high concentrations of aqueous HCl or HBr. Isomerization was

found in the presence of the chloride catalysts $ZnCl_2$ and $FeCl_3$, and with PCl_5.

CHEMISTRY OF AQUEOUS SYSTEMS

In an investigation of the thermodynamic properties of hydrochloric acid by emf measurements at temperatures up to 275°C, good agreement was found between experimental activity coefficients and those calculated by means of the extended Debye-Hückel equation.

Based on the solubilities in pure water and a Debye-Hückel expression for the variation in the activity coefficient of Ag_2SO_4 with ionic strength at any temperature, a calculation of solubilities of Ag_2SO_4 at various temperatures up to above 150°C in 0.1, 0.5, and 1.0 m solutions gave good agreement between observed and calculated solubilities.

In the high-temperature isopiestic apparatus the osmotic coefficients of the following salts were determined as a function of concentration at 100°C: LiCl, NaCl, KCl, CsCl, $BaCl_2$, Na_2SO_4, $MgSO_4$, and UO_2SO_4.

A second high-temperature spectrophotometric cell is being constructed which will permit rapid equilibration between solution and gases under pressure during measurements.

Additional measurements of equilibrium ionic selectivity coefficients on new preparations of variable-capacity cation and anion exchangers confirmed the generalization that as the exchange capacity (on a dry basis) increased, the selectivity for the preferred ion decreased. This inverse dependence was found also, with one exception, when the capacity was expressed in terms of the exchange site density of the wet, fully swollen exchanger in equilibrium with an aqueous electrolyte solution. It was concluded that the capacity dependence predictions of a recent statistical thermodynamic theory of ion exchangers are incorrect when an appreciable cross-linking exists.

The concentration dependence of the anion exchange absorption of microamounts of bromide ion from aqueous hydrochloric acid solutions by a liquid anion exchanger could be accounted for quantitatively when corrections were made only for the thermodynamic ionic activity coefficients in the aqueous phase. This result may be of value in the understanding of the factors governing the uptake of ions from concentrated electrolyte solutions by organic polymeric ion exchangers.

Measurements of the standard free energies and heats were completed, and standard entropies were derived for the exchange of silver with sodium ion in nominal 1, 4, 8, 16, and 24% divinylbenzene cross-linked Dowex 50 cation exchangers. Positive ΔH^0 and ΔS^0 values were observed, in contrast with the exchanges of H^+, Li^+, K^+, and Cs^+ ions with the sodium form of the exchanger, where heat was evolved and the entropy change was always negative. Interestingly, the observed differential heats, $\Delta\bar{H}$, of exchange were negative (i.e., heat evolved) when the equivalent fraction of silver in the exchanger was below 0.15; above this "loading," heat was absorbed and $\Delta\bar{H}$ was almost independent of the fraction of silver.

Some theoretical calculations on the influence of electrostatic interactions on ion exchanger selectivity are briefly discussed.

Experiments directed toward elucidation of the properties of an ion exchange resin were continued. An attempt was made to correlate kinetic and equilibrium properties of quaternary amine salt solutions with properties of cross-linked anion exchange resins.

The investigation of the adsorptive properties of zirconium phosphate precipitates was extended. The behavior of oxides of Zr(IV), Ti(IV), Sn(IV), Nb(V), and Ta(V) in acidic and basic media was investigated with a pressurized column at 200°C.

A program was written for the Oracle which computes the concentration distribution of a charged polymeric solute at equilibrium during ultracentrifugation.

The degree of polymerization N of UO_2Cl_2, obtained from equilibrium ultracentrifugation, was studied as a function of the hydroxyl number n.

CHEMISTRY OF CORROSION

Further studies on the action of inhibitors were made with agents which cannot by themselves produce passivity. Polarization was measured on iron electrodes in both the active and the passive states in the study of the effect of inhibitors on the partial electrochemical reactions related to corrosion. The kinetics of the anodic oxidation of crystal-bar zirconium in oxygen-free sulfate solutions and of reduction of oxygen, hydrogen peroxide, and copper(II) ions at a zirconium electrode were determined. The reduction of uranyl ions and copper(II) ions at electrodes of stainless steel was also investigated, along with the effect of complexing

upon these rates. The detailed kinetic treatment of electrode processes in galvanic couples was developed.

NONAQUEOUS SYSTEMS AT HIGH TEMPERATURES

The study of the fluorine exchange between F^{18}-labeled gaseous fluorocarbons and solid metal fluorides was extended. A correlation between exchange rate, defect structure, and catalytic properties of cesium fluoride crystals was found.

The degree of association of NaI to Na_2I_2 in the vapor was measured through the vapor density; at 1260°K, ΔE^0 is −40.2 kcal/mole and ΔS^0 is −27.0 e.u.

Measurements of the electrical conductivity of potassium metal solutions in molten potassium fluoride confirmed the strong dependence of the electronic conductance, at infinite metal dilution, on the anion, an effect believed to be connected with the polarizability of the anion.

Observations are described on the transport, in an electric field, of the color imparted by the addition of metal to its molten halide.

The entropies of fusion of the alkali halides were determined calorimetrically, and while in agreement with more recent theory were found to disagree very considerably in several cases with earlier data of the literature. Redetermination of the solubility of sodium metal in its halides near their melting points confirmed, in combination with the new reliable values of the entropies of fusion, a strong deviation from Raoult's law which is interpreted in terms of diatomic sodium molecule formation.

Vapor pressure and liquid-solid phase equilibrium measurements by others on bismuth metal–bismuth halide systems were evaluated semiquantitatively by means of the Oracle in terms of two solutes, dimeric Bi(I) ions, Bi_2^{++}, and diatomic Bi molecules, Bi_2.

CHEMICAL PHYSICS

A preliminary value for the yield of hydrogen atoms from 0.129 mole fraction sulfuric acid irradiated at 77°K with gamma rays was determined by paramagnetic resonance. It is twice the yield of hydrogen molecules obtained from similarly irradiated acid after warming ($G_{H_2} = 0.62$). This assay, along with previous relative assays on acids of various concentrations, shows a direct correspondence between the atom and molecule yields. Additional paramagnetic resonance observations were made on irradiated single crystals of calcium tungstate and calcite (calcium carbonate).

Dilute solid solutions of the stable free radical α,α-diphenyl-β-picrylhydrazyl in single crystals of the corresponding hydrazine were studied by paramagnetic resonance, and details of the anisotropic hyperfine interaction with nitrogen were observed and measured. The cell size and space group of the hydrazine were determined by x-ray diffraction.

A neutron diffraction study of the ammonium and hydronium perchlorates disclosed that the positive ions are in disordered orientation in the crystal. The crystal structure of H_2O_2 also was determined. Theoretical implications of the observed molecular geometry are considered. A neutron diffraction study of acetamide hemihydrochloride disclosed the proton position in the symmetrical and very short O–H–O bond and provided evidence that the proton site is most likely a single, ordered one.

A novel neutron diffraction installation was designed and put into operation, which permits utilizing a single beam hole for two or more diffraction units and allows for operation of one unit with a 90° primary beam scattering angle and with the neutron spectrometer operating in a vertical plane. Results obtained with this instrument indicate that a monochromatic beam of high intensity and excellent wavelength resolution has been obtained.

The least-squares method of refining crystal structure parameters is discussed, and a computer program for performing this calculation is described. An evaluation for the general case was made of the form of the polarization factor that applies to the Weissenberg goniometer technique with crystal-monochromatized x radiation.

The results of extensive studies on the diffraction of x rays (and, in some cases, of neutrons) by molten salts, especially alkali halides, and by aqueous solutions are summarized. Average coordination numbers as well as shortest and most frequent interionic distances in the molten halides are listed. The occurrence of certain complexes of bismuth and uranium in aqueous solutions, assumed on the basis of other physical-chemical measurements, was confirmed by these diffraction studies.

The liquid-helium-cooled low-temperature calorimeter was proved to be satisfactory by measurements on a standard sample of benzoic acid. The high-temperature drop calorimeter was found to give results on a standard sample of Al_2O_3 accurate to within ~0.4%.

The source of the pulses of positive ions from heated tungsten is believed to be minute cavities formed by the pinning, at a point, of many dislocations. The "anomalous flicker effect" in electron tubes is shown to be explicable by the effect of such bursts on the electron space charge.

Mass spectrometric studies of nitric oxide and nitrous oxide showed that NO^- is formed as a result of electron impact. In the case of nitrous oxide, NO^- is shown by isotopic labeling to be formed almost exclusively by cleavage of the N–N bond. The relative abundance for negative ions formed by electron impact in methane, the C_2 hydrocarbons, *n*-butane, and all the alkyl alcohols through the butyl alcohols reveals many abundant ion fragments previously unreported.

Ions induced in polyatomic gases by alpha particles were measured with the research mass spectrometer. The results indicate that the use of alpha particles to produce ions in a mass spectrometer may be useful for mass spectral analysis in addition to the obvious application to radiation chemistry studies. The alpha radiolysis of acetylene in the alpha-particle mass spectrometer shows that every ionic species is involved in ion-molecule reactions. The studies of binary mixtures of hydrocarbons in this spectrometer show that energetically possible charge-transfer reactions are not necessarily probable.

A rapid mass spectrometric method was developed to measure the deuterium isotope effect that occurs during the photochemical oxidation of formic-*d* acid, DCOOH, with chlorine. The method should be applicable to the study of deuterium isotope effects in other gas-phase reactions and is not limited to photochemical reactions.

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NUCLEAR CHEMISTRY

POLARIZATION OF P^{32} BETA RAYS

A. Galonsky[1] H. B. Willard[1]
B. H. Ketelle A. R. Brosi

Soon after the first demonstrations of nonconservation of parity, an experiment was started here to test to as high a precision as possible the new beta decay theory of Feynman and Gell-Mann. A beam of beta particles from a P^{32} source was deflected in an electric field to change the polarization from longitudinal to transverse. The transverse polarization of the beam was determined by measuring the asymmetry in single scattering from gold nuclei.

High specific activity sources containing as much as 1.5 curies of P^{32} were used to measure the asymmetry in scattering from foils as thin as 117 $\mu g/cm^2$. Corrections to the data for depolarization of the electrons by scattering in the source and in the measuring equipment were determined experimentally. Corrections for multiple scattering from the gold foil and for asymmetry of the apparatus were also determined by experiment. The sum of all correction factors amounted to only a few per cent.

The longitudinal polarization of 620-kev beta rays from P^{32} was found to be equal to $-v/c$ within the standard deviation of the data, which was 2%. This result is consistent with the beta decay theory of Feynman and Gell-Mann.

RADIOACTIVE DECAY OF Dy^{159}

B. H. Ketelle A. R. Brosi

Decay of Dy^{159} was shown to feed three excited levels in Tb^{159}. Gamma rays with energies of 58, 200, 290, and 350 kev were observed and electron-capture branching ratios were determined. Only L electron capture to the 350-kev level was detected. The half life of the 58-kev level in Tb^{159} was shown to be less than 1×10^{-9} sec. The K conversion coefficient of the 58-kev gamma ray was measured and found to be 5 ± 1.5. The disintegration energy of Dy^{159} was shown to be between 360 and 400 kev; the half life was remeasured and found to be 144.4 ± 0.2 days.

[1]Physics Division.

A NEW FISSION PRODUCT: Ga^{74}

J. A. Marinsky[2] E. Eichler

An 8-min activity observed by bombarding natural germanium with fast neutrons was tentatively assigned to Ga^{74} by Morinaga.[3] This assignment was confirmed by work at this Laboratory[4,5] and in the Netherlands[6] through irradiation of enriched Ge^{74} with 14-Mev neutrons and through subsequent chemical separation. In addition, the yield of the 8-min activity was demonstrated to be proportional to the isotopic enrichment of Ge^{74}. Since mass 74 had not yet been reported in fission, it was of interest in the present study to demonstrate the occurrence of the 8-min Ga^{74} activity in the fission process and to compare its yield with that predicted by the smooth mass–fission-yield curve[7] for U^{235}.

The separation procedure used was a composite of standard techniques.[8–11] Each separate operation, however, was performed as rapidly as possible to minimize loss by decay of the 8-min gallium activity. The gallium was separated by extraction into diisopropyl ether. Further decontamination was effected by passage through an anion exchange column, volatilization of the solution after HBr treatment, and scavenging with bismuth and molybdenum sulfides and molybdenum

[2]ORINS research participant, summer, 1958; permanent address: University of Buffalo, Buffalo, New York.

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[7]S. Katcoff, *Nucleonics* 16, 78–85 (1958).

[8]L. E. Glendenin, *Natl. Nuclear Energy Ser., Div. IV* 9, 1657–61 (1951).

[9]J. M. Siegel and L. E. Glendenin, *Natl. Nuclear Energy Ser., Div. IV* 9, 1436–39 (1951).

[10]G. E. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis*, Wiley, New York, 1938.

[11]F. Nelson, R. M. Rush, and K. A. Kraus, "Anion Exchange Studies. XXVII. Adsorbability of a Number of Elements in HCl-HF Solutions," submitted to *J. Am. Chem. Soc.*

α-benzoinoxime precipitates. The 12.8-day Ba^{140} was separated from aliquot samples of the aqueous phase to provide a fission-yield standard.

Two types of gamma-ray spectral runs were performed with the separated gallium fraction: (1) complete spectra were observed for comparison with the spectral shape obtained from (n,p)-produced Ga^{74}; (2) the decay of the intense 0.60-Mev gamma ray was observed by measuring the low-energy portion of the spectra as a function of time. The beta decay of Ga^{74} samples was followed with an end-window gas-flow proportional counter. For fission-yield determinations both the Ga^{74} and the Ba^{140} disintegration rates were obtained from gamma-ray spectra. The Ba^{140} spectra were taken soon after separation to minimize La^{140} growth.

The gamma-ray spectrum produced by the gallium sample after separation from fission products is shown in Fig. 1, while that produced by a sample of Ga^{74} resulting from $Ge^{74}(n,p)$ is given in Fig. 2. The spectrum in Fig. 1 is a composite of two spectra: the portion below ~0.80 Mev from a very pure but weak source and the portion above ~0.80 Mev from a source with more activity but somewhat contaminated with Tc^{101}, which has essentially no high-energy gamma rays. It is seen that the fission product gallium produces a spectrum in good agreement with that from Ga^{74}. The decay of the beta rays and the 0.60-Mev gamma rays from the fission-produced gallium gave half lives of 7.7 ± 0.4 and 8.3 ± 0.4 min, respectively, in agreement with the previously reported values.[4-6]

The areas under the 0.60-Mev gamma-ray peak of Ga^{74} and the 0.54-Mev gamma-ray peak of Ba^{140} were corrected for decay, for degree of saturation during irradiation, for chemical yield, and for intrinsic peak efficiency. The fission yield of Ga^{74} was then calculated relative to the absolute fission yield of Ba^{140} by means of the respective absolute gamma-ray intensities (the number of gamma rays per disintegration). Two separate determinations gave 3.42×10^{-4} and 3.35×10^{-4}%. Averaging the two results gives a yield of 3.4×10^{-4}%, with an expected error of

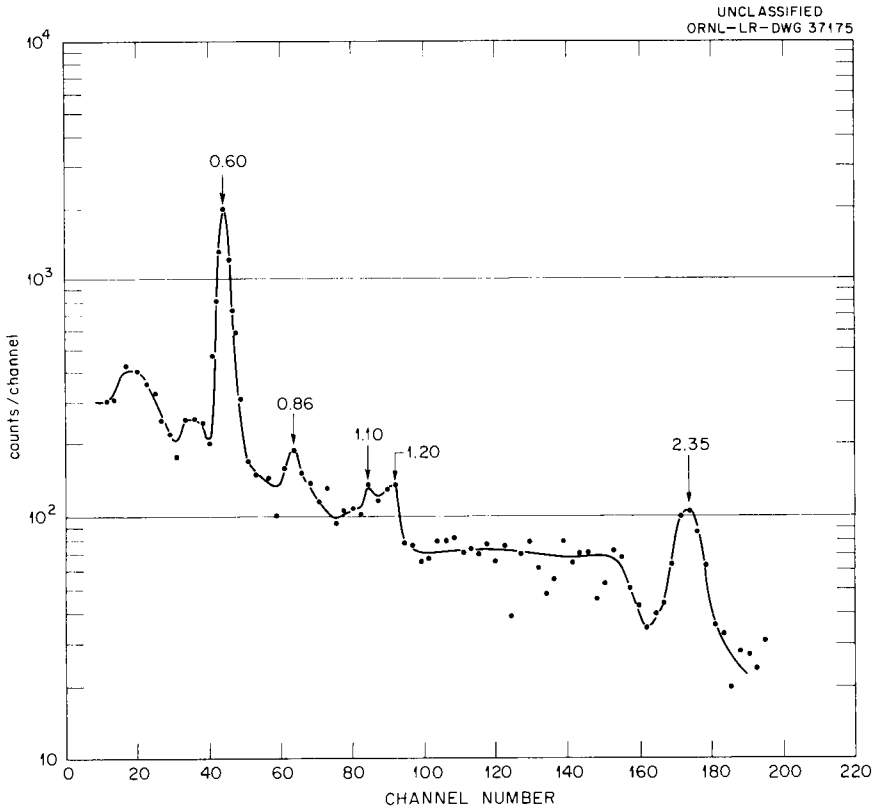

Fig. 1. Gamma-Ray Spectrum Produced by Fission Product Gallium.

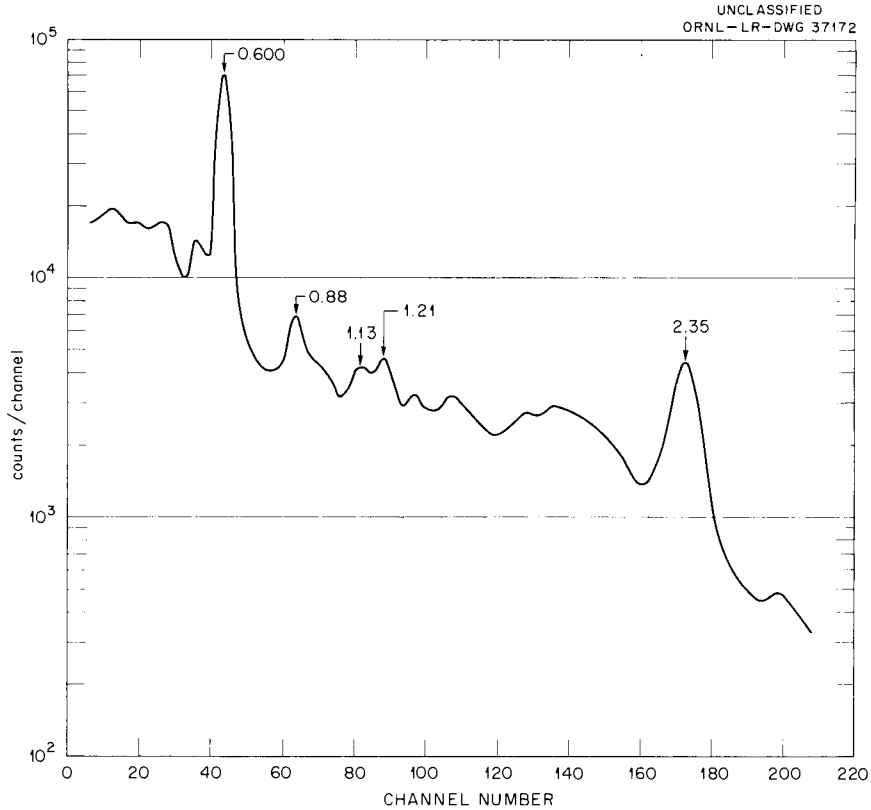

Fig. 2. Gamma-Ray Spectrum Produced by Ga^{74} from Ge^{74} (n,p).

10 to 20%; this is in good agreement with the value obtained by interpolation of the U^{235} mass-yield data.[7]

ENERGY OF THE Y^{88} GAMMA RAYS

G. D. O'Kelley N. R. Johnson
E. Eichler

The two principal gamma rays in the decay of 104-day Y^{88} are often used to determine response functions of scintillation spectrometers. Although these gamma rays would be convenient for use as energy standards, there has not been a recent determination of their energies to the necessary accuracy. The widely quoted values of 0.908 and 1.853 Mev were determined by Peacock and Jones,[12] who used a magnetic lens spectrometer to measure the internal conversion electron spectrum of a Y^{88} source. Because Peacock and Jones used a rather thick source and a spectrometer adjustment for broad line width, it was felt that their measurement should be checked with sufficient accuracy ($\leq \frac{1}{2}\%$) to permit use of the Y^{88} gamma rays as secondary standards for energy calibration of scintillation spectrometers.

A 3 × 3 in. NaI scintillation detector having a resolution of 7.4% at 0.662 Mev and a 256-channel pulse-height analyzer were used in our measurements of the Y^{88} gamma energies. To minimize effects of short-term gain shifts or of photomultiplier gain variations with counting rate, a Y^{88} source was measured simultaneously with the energy standards. The low-energy gamma ray was compared with a Bi^{207} source (0.5697 and 1.064 Mev) in some experiments and with a mixed source of Cs^{137} (0.6616 Mev) and Co^{60} (1.1728 and 1.3325 Mev) in other measurements. The average energy obtained for Y^{88} was 0.899 ± 0.004 Mev. The other prominent Y^{88} gamma ray was compared with Na^{24} (1.368 and 2.754 Mev), and a value of 1.832 ± 0.006 Mev was obtained. The errors quoted for these measurements are primarily

[12] W. C. Peacock and J. W. Jones, *Decay Scheme of Y^{88}*, AECD-1812.

conservative estimates of possible systematic errors, such as amplifier or analyzer nonlinearities, for which no corrections were made.

Two additional redeterminations of the Y^{88} gamma-ray energies have been made recently by the scintillation method and are in agreement with the above results. In a report by Heath,[13] the energies are given as 0.900 and 1.830 Mev, and measurements by Peelle and Love[14] yielded energies of 0.8988 ± 0.0012 and 1.840 ± 0.002 Mev.

GAMMA-RAY SUM SPECTRA

E. Eichler G. D. O'Kelley
N. R. Johnson

An attempt has been made to develop experimental means of subtracting the real and random summing contributions from gamma-ray scintillation spectra by utilizing a modification of the sum-coincidence circuit of Hoogenboom.[15] The coincident or "real" summing of cascade gamma rays coupled with the random summing of noncorrelated radiations produces a pulse-height distribution which complicates and distorts gamma-ray spectra.

The apparatus shown in Fig. 3 was used to produce an experimental sum spectrum. The gains of the two NaI-crystal–photomultiplier assemblies were matched and their outputs summed in the linear adder. The amplified sum pulses were then fed to an RCL 256-channel pulse-height analyzer. The photomultiplier outputs were also fed to a coincidence mixer which gated the analyzer each time a sum event occurred in the two crystals.

Tests were performed with standard sources such as Cr^{51} and Co^{60}. Single-crystal spectra were measured so that the region beyond the photopeaks might be compared with the experimental sum spectrum. It was found that the "real" summing effect due to the cascade gamma rays from Co^{60} could be rather precisely duplicated with the apparatus of Fig. 3. With a Cr^{51} source, which emits a single gamma ray and produces only random summing, the resolving time of the coincidence mixer was adjusted to about 1 μsec,

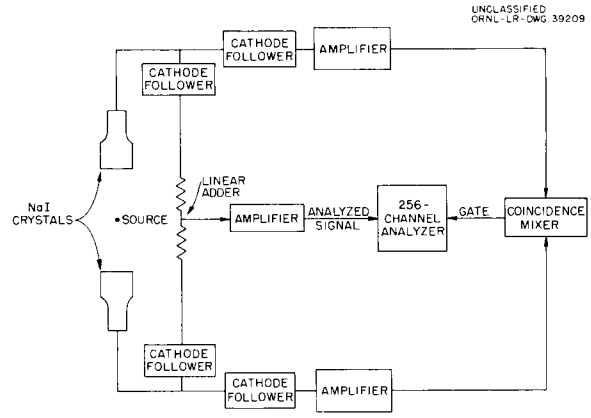

Fig. 3. Block Diagram of Gamma-Ray Sum Spectrum Apparatus.

so that the height of the sum peak matched that observed in a single-crystal spectrum. However, the region below the sum peak did not reproduce the single-crystal spectrum in that the two-crystal spectrum was much lower.

In each of the above experiments the counting time for the summing spectrum was one-half that for the single-crystal spectrum because of the doubled detector geometry. Since the "real" portion of the summing distribution predominates over the "random" part, the above procedure seems satisfactory as a way of approximately correcting for the summing contribution. It was applied to the gamma-ray spectrum of I^{134} (see "Nuclear Decay of I^{134}," this report).

DECAY PROPERTIES OF I^{136}[16]

N. R. Johnson G. D. O'Kelley

Iodine-136, an 83-sec activity produced from the slow-neutron fission of uranium, has been studied with scintillation techniques. An analysis of the gamma-ray spectrum obtained with a 3 × 3 in. NaI spectrometer was made by using Gaussian shapes for the full-energy peaks and by matching the distributions of the Compton and pair peaks with standards run under similar experimental conditions. The information from the single-crystal experiment and also the gamma-gamma coincidence results are summarized in Table 1.

[13] R. L. Heath, *Scintillation Spectrometry Gamma-Ray Spectrum Catalog*, IDO-16408 (July 1, 1957).

[14] R. W. Peelle and T. A. Love, private communication.

[15] A. M. Hoogenboom, *Nuclear Instr.* 3, 57–68 (1958).

[16] N. R. Johnson and G. D. O'Kelley, *Phys. Rev.* 114 (1959) (in press).

Table 1. Summary of I^{136} Gamma-Ray Data

Gamma-Ray Energy (Mev)	Single-Crystal Intensity Relative to 1.31-Mev Gamma Rays	Gamma-Ray Intensity* in Coincidence with		
		1.31 Mev	0.39 Mev	0.20 Mev
0.20 ± 0.01	0.13	W	VS	?
0.27 ± 0.01	0.19	?	?	?
0.39 ± 0.01	0.20	S	W	VS
0.46 ± 0.02	0.04	W	S (0.51 Mev)	?
0.52 ± 0.02		W		
0.70 ± 0.03	0.03	W	W	?
0.99 ± 0.04	0.06	W	W	?
1.307 ± 0.006	1.00**	VS	VS	VS
1.53 ± 0.04	0.04	W	?	?
1.70 ± 0.05	0.02	W	?	No
1.89 ± 0.05	0.05	S (2.0 Mev)	?	No
2.23 ± 0.07	0.07		?	No
2.37 ± 0.07	0.13		?	No
2.60 ± 0.05	0.11	No	?	No
2.81 ± 0.08	0.08	No	?	No
3.2 ± 0.1	0.05	No	?	No

*VS = very strong, S = strong, W = weak, ? = data insufficient to determine whether true coincidences are present, and No = no indications for coincidences.

**This intensity results from a cascade of two 1.31-Mev gamma rays to the ground state of Xe^{136}. The upper transition has 0.26 unit and the lower one 0.74 unit of the total.

The beta-ray spectra were measured with a $1\frac{1}{4} \times 1$ in. anthracene crystal. From the single-crystal and beta-gamma coincidence data, beta rays were found with energies of 7.00 ± 0.10, 5.62 ± 0.15, 4.23 ± 0.20, and 2.73 ± 0.20 Mev.

A decay scheme based on the experimental observations is shown in Fig. 4. The tentative spin and parity assignment of 2^- for the I^{136} ground state is consistent with the observed log ft of 8.1 for the beta group to the 0^+ ground state of Xe^{136}. Such a 2^- state could be explained by the odd $f_{7/2}$ neutron coupling with given configurations of $(g_{7/2})^3$ protons.

An interesting characteristic of the level scheme in Xe^{136} is that the ratio of the second to the first excited level is precisely 2. Also, a value of 0.74 is found for $E_1/\hbar\omega$, where E_1 is the energy of the first excited state and ω is the characteristic phonon frequency of a statically undeformed nucleus. Accordingly, when interpreted in terms of either the "free vibration" model of Scharff-Goldhaber and Weneser[17] or the "shape unstable" model of Willets and Jean,[18] there is to be expected a very nearly pure harmonic quadrupole vibration of the core, with a very small coupling contribution from the four protons beyond the closed shell.

[17] G. Scharff-Goldhaber and J. Weneser, *Phys. Rev.* 98, 212 (1955).

[18] L. Willets and M. Jean, *Phys. Rev.* 102, 788 (1956).

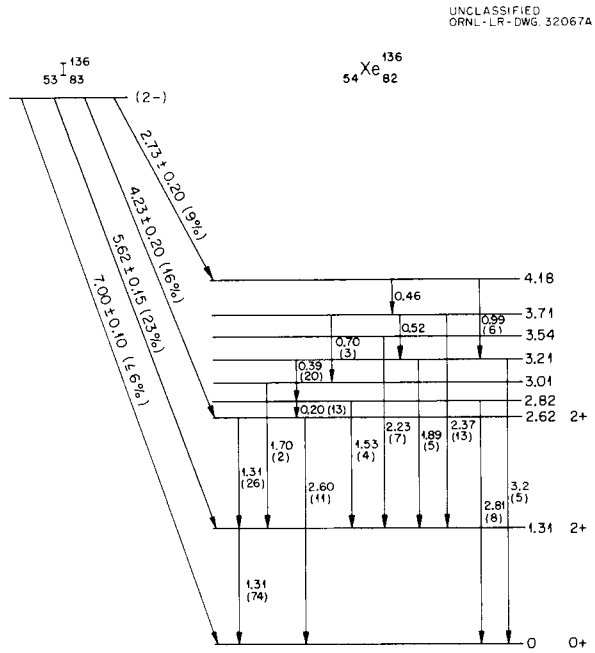

Fig. 4. Decay Scheme Proposed for I^{136}. The percentage branching for the beta rays was determined from gamma-ray intensities. Absolute intensities of only the observed beta rays are shown, whereas relative gamma-ray intensities are shown in parentheses.

NUCLEAR DECAY OF I^{134}

N. R. Johnson G. D. O'Kelley
E. Eichler J. T. Wasson[19]
J. W. Chase[20]

The gamma-ray spectrum of 53-min I^{134} was measured with a 3 × 3 in. NaI spectrometer and when analyzed showed 17 prominent photopeaks having energies of 0.12, 0.41, 0.55, 0.61, 0.69, 0.76, 0.849, 0.890, 0.98, 1.08, 1.15, 1.27, 1.34, 1.46, 1.62, 1.79, and 2.03 Mev, as well as indications for other low-intensity transitions. Also, some of the analyzed peaks appeared to be too broad, a probable indication of additional weak gamma rays. The spectrum was corrected for the effect of random plus real gamma-ray coincidence summing which represented a substantial fraction of the true spectrum. The method for making the correction is discussed in another part of this report ("Gamma-Ray Sum Spectra").

Gamma-gamma coincidence measurements have been made with the single-channel window set at the following energies: 0.41, 0.61, 0.82, 0.86, 0.91, 1.08, 1.34, 1.46, 1.62, and 1.79 Mev.

Beta-ray spectra were measured with a $1\frac{1}{4} \times 1$ in. anthracene crystal as the detector. After correcting the observed beta distribution for distortions introduced by the finite detector resolution, the Fermi plot showed beta rays at 2.41 ± 0.05, 2.07 ± 0.06, and 1.62 ± 0.07 Mev. Conventional beta-gamma coincidence experiments indicated that the 2.41-Mev group fed a level in Xe^{136} followed by the emission of 0.85- and 0.89-Mev gamma rays. This was verified by an experiment which measured the beta spectrum coincident with the sum of the two gamma rays, 1.74 Mev. For this the gains of two NaI spectrometers were matched and their outputs fed into a linear adder circuit. After amplification, the signal went to a single-channel analyzer with a narrow window set at 1.74 Mev. The single-channel output was fed into one half of a slow coincidence mixer, with the output from an anthracene detector feeding the other. A coincidence here gated the multichannel analyzer which recorded the beta spectrum.

A tentative decay scheme has been postulated on the basis of the above data. This scheme involves first and second excited levels in Xe^{134} at 0.85 and 0.89 Mev, respectively, and has a I^{134}-Xe^{134} ground state energy separation of 4.15 Mev.

SPECIFIC ACTIVITY AND HALF LIFE OF Tc^{99g}

G. E. Boyd Q. V. Larson

The increased utility of the long-lived Tc^{99g} for chemical researches has prompted us to undertake precision measurements of its half life, as up to this time there have been no independent confirmations of the value 2.12×10^5 years published by S. Fried and associates[21] in 1951. Since their work, it has been established that technetium isolated from the uranium fission products is not isotopically pure. Therefore it

[19] Summer employee from Massachusetts Institute of Technology, 1957.

[20] Summer employee from Massachusetts Institute of Technology, 1958–59.

[21] S. Fried *et al.*, *Phys. Rev.* 81, 741 (1951).

was of further interest in our work to compare the specific activity of long-lived technetium isolated from neutron-irradiated molybdenum with that from the uranium fission products. Technetium separated from molybdenum should contain only Tc^{99g} and possibly Tc^{100}, whereas that produced by fission will have Tc^{98} and possibly Tc^{100} in addition to Tc^{99g}.

In the new specific activity measurements 4π beta counting techniques were employed to minimize corrections for the absorption of the low-energy beta rays emitted by Tc^{99g}. The weight of technetium counted was accurately measured by polarography, as it has been shown[22] that the reduction of Tc(VII) to Tc(IV) is accurately proportional to the quantity of technetium in aqueous solution. The polarographic analyses were checked spectrophotometrically by measuring the optical densities of the bands in the ultraviolet absorption spectrum of TcO_4^- in aqueous solution and by measuring the absorption of the Tc(V) thiocyanate complex at 5100 Å.

Values of $(2.19 \pm 0.04) \times 10^5$ and $(2.15 \pm 0.05) \times 10^5$ years were found for the half lives of technetium isolated from the fission products and from neutron-irradiated molybdenum, respectively. These values may be taken to be the same within the experimental errors, and hence it may be concluded that the amounts of Tc^{98} and/or Tc^{100} present in technetium from either source are negligibly small (or that their half lives do not differ greatly from that for Tc^{99g}). The average value, $(2.17 \pm 0.05) \times 10^5$ years, is considered also to be in agreement with the earlier value of Fried *et al.*[21] within the experimental error ($\pm 2\%$) which they have quoted.

OBSERVATIONS ON LONG-LIVED Mo^{93g}

G. E. Boyd Q. V. Larson

A new, long-lived molybdenum isotope, presumably formed by neutron capture, was observed in 1949[23] in molybdenum metal irradiated in the ORNL Graphite Reactor for an accumulated flux, *nvt*, of 3.1×10^{19}. Exhaustive chemical purifications involving precipitating molybdenum sulfide in the presence of tartaric acid, igniting to MoO_3, dissolving in ammonium hydroxide, scavenging with $Fe(OH)_3$, precipitating molybdenum α-benzoinoxime and then igniting were conducted until MoO_3 sources of constant specific activity weighing ~150 mg were obtained. The intensities of these sources were measured with a Geiger counter for approximately five years without any indication either of decay or of growth in their relatively small (approximately 200 counts/min at 30% geometry) activities. The absorption of the radiations in aluminum indicated that niobium x rays only were emitted. This observation has been confirmed by measurements with a krypton-filled proportional x-ray spectrometer (Fig. 5).

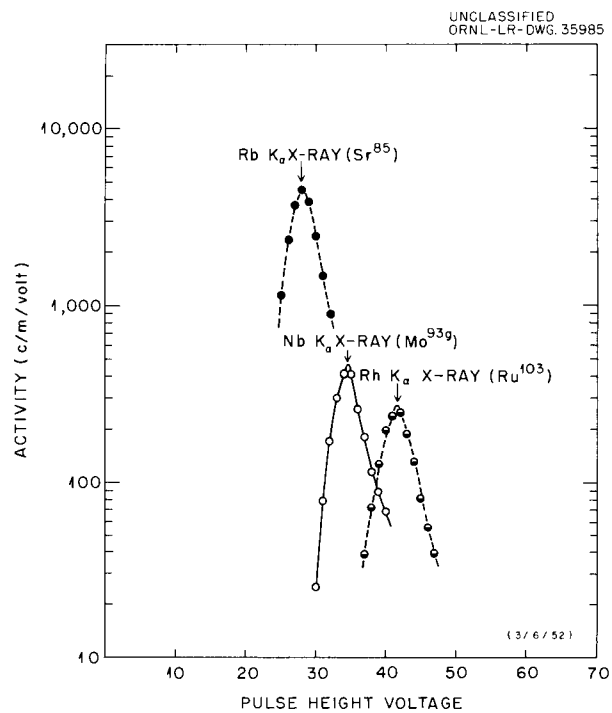

Fig. 5. Radiations from Long-Lived Mo^{93g} Measured on Krypton-Filled Proportional X-Ray Spectrometer.

An approximate half-life range estimate may be derived from the observed specific activity, the counting geometry (28.8%), and the intrinsic counting efficiency (2% for Nb x rays) if a neutron absorption cross section for Mo^{92} is assumed. The latter quantity is almost certainly less than

[22] H. H. Miller, M. T. Kelley, and P. F. Thomason, *Polarographic Studies of the Reduction of Pertechnetate Ion in Aqueous Solutions*, paper to be presented at International Congress on Polarography, Cambridge, England, Aug. 24–29, 1959.

[23] G. E. Boyd and Q. V. Larson, *Chem. Quar. Prog. Rep. Sept. 30, 1949*, ORNL-499, p 40.

0.3 barn (ref 24); if it were as small as 1 mb, the half life of Mo^{93} would be ~170 years; if it were 0.1 barn, which seems more likely, it would be $\sim 1.7 \times 10^4$ years.

A long half life for Mo^{93g} is not improbable from stability (and spin) considerations. The instability of Mo^{93g} relative to Nb^{93g} may be estimated as 0.5 ± 0.3 Mev from (p,n) threshold measurements[25] and the known total decay energy of Mo^{93m}. Confirmation is afforded by mass spectrographic measurements, which indicate that Zr^{93g} and Mo^{93g} are practically equal in mass.[26] The total decay energy of Zr^{93g} to Nb^{93g} has been reported[27] to be only 56 kev; hence the decay of Mo^{93g} must also occur with a small energy change.

Recently, samples of molybdenum irradiated in the MTR to 5.3×10^{20} *nvt* became available. This highly irradiated molybdenum was exhaustively purified, and the quantum radiations emitted were measured (in collaboration with E. Eichler) with a scintillation spectrometer. In addition to a well-defined niobium x ray, a gamma ray of about 55 kev present in low intensity was observed. Taking the neutron absorption cross section of Mo^{92} to be approximately the same as that for Mo^{98}, it may be estimated that about 10 ppm of Mo^{93g} was produced. If in the future an isotopic analysis can establish the concentration of Mo^{93g}, then a specific activity measurement will permit a half-life estimate.

THERMAL NEUTRON ABSORPTION CROSS SECTION OF Th^{233} AND RESONANCE INTEGRALS OF Th^{232}, Th^{233}, AND Co^{59}

F. J. Johnston[28] J. Halperin
R. W. Stoughton

Th^{233}

A number of Th^{232} samples along with cobalt and gold monitors were irradiated in the LITR both with and without cadmium covers. The amounts of Pa^{233} produced were determined ultimately by 4π beta-gamma coincidence counting. The amounts of Th^{234} produced were measured by counting the 1.18-min Pa^{234} daughter activity with 4π scintillation well counters which in turn were calibrated by counting the Th^{234}-Pa^{234} decay products in weighed samples of isotopically enriched U^{238}. A thermal cross section, σ_{th}, of 1450 ± 100 barns and a resonance integral,

$$I_0 = \int_{E_c} \sigma \frac{dE}{E} ,$$

of 400 ± 100 barns were found for Th^{233}.

The symbol conventions used here have been discussed by Stoughton and Halperin.[29] The thermal cross section for cadmium-absorbable neutrons corresponds approximately to that at 2200 m/s if the cross-section dependence of Th^{233} is $1/v$ in the thermal and near-thermal region. However, the ratio of I_0/σ_{th} is low even when compared with a pure $1/v$ absorber. Further, if the measured "effective" cross section of 1470 barns is compared with that computed from the data of Hyde and co-workers,[30] about 1900 barns, the difference would appear to lie outside the limits of errors of the two measurements. Since their experiment was performed in a flux with a significantly higher neutron temperature, it seems reasonable to suggest that there is a resonance in Th^{233} at an energy slightly above thermal and yet below the cadmium cutoff of ~0.5 ev.

A further argument that suggests a resonance for thermal neutrons in Th^{233} giving rise to the high thermal cross section may be made from systematics. In the absence of shell effects the addition of a pair of neutrons to a nucleus would be expected to increase the level spacing and on the average to lower the capture cross section of the augmented nuclide. The only other even-odd isotope of thorium for which a cross-section measurement has been reported[31] is Th^{229},

[24] H. S. Pomerance, *Phys. Rev.* 88, 412 (1952).

[25] J. P. Blaser *et al.*, *Helv. Phys. Acta* 24, 441 (1951).

[26] J. S. Geiger *et al.*, *Phys. Rev.* 89, 621 (1953).

[27] D. Strominger, J. M. Hollander, and G. T. Seaborg, *Revs. Modern Phys.* 30, 585 (1958).

[28] Summer Employee, University of Louisville.

[29] R. W. Stoughton and J. Halperin, "A Review of Cross Sections of Particular Interest to Thermal Reactor Operation: Conventions, Measurements and Preferred Values," *J. Nuclear Sci. Eng.* (in press).

[30] E. K. Hyde, R. J. Bruehlman, and W. M. Manning, *The Neutron Capture Cross Section of the 23 Minute Isotope, Th-233*, ANL-4165 (1948).

[31] D. J. Hughes and R. B. Schwartz, *Neutron Cross Sections*, BNL-325, 2d ed (July 1958).

$\sigma_f(Th^{229}) = 45 \pm 11$ barns. On the basis of the fission to capture cross-section correlations described by Huizenga and Duffield[32] and the neutron binding energies calculated by Glass and co-workers,[33] the capture cross section of Th^{239} may be estimated as about 5 barns. The additional two pairs of neutrons in Th^{233} suggest an even lower cross section for Th^{233} in the absence of resonances, making the measured value of 1450 barns inconsistent with this expectation by a factor of some 10^3. Of course since the level spacing for even-odd nuclides in this mass range is of the order of 1 ev, the likelihood of a resonance occurring at thermal energies is appreciable.

Th^{232}

The resonance absorption integral of Th^{232} at infinite dilution has been obtained by irradiating samples as thin as 0.2 mg/cm^2 with cadmium filters and gold monitors. The Pa^{233} produced was measured with a 4π high-pressure ionization chamber which was calibrated by 4π beta-gamma coincidence counting. A value of $I_0 = 85 \pm 8$ barns was measured. This value may be compared with a value of 99 barns which may be computed by summing the contributions from the individual resonances.[31] This consists of 74 barns from the first seven resonances of thorium up to 140 ev, 3 barns for the $1/v$ tail, and an estimated 22 barns for higher resonances computed by the method of Dresner with the correction of Kuhn and Dresner.[34] It may also be compared with a value measured by Macklin and Pomerance[35] of 70 barns and values ranging from 64 to 96 barns by Myasischeva and co-workers.[36]

Co^{59}

Cadmium ratio measurements have been carried out on thin samples of cobalt (about 1×10^{18} atoms/cm^2), with thin gold (I_0 = 1565 barns) used as a monitor. The Co^{60} produced was determined by measurements based upon 4π beta-gamma coincidence counting. An average value of 75 ± 5 barns was observed for the resonance absorption integral of Co^{59} at infinite dilution.

Harris and co-workers[37] report 41 barns for I_0 (Co) and Macklin and Pomerance[38] have corrected it to 49 barns in their compilation. Since Harris and co-workers used thick samples (6.1×10^{19} atoms/cm^2) in their experiment, some fiftyfold thicker than in the present work, they did not measure the resonance integral at infinite dilution. (The 132-ev resonance has a peak cross section of about 8600 barns.) Since the 132-ev resonance essentially accounts for the entire resonance integral of cobalt, the resonance absorption integral may be estimated from the thermal cross section. This leads to the expectation of about 90 barns for I_0 (Co). However, if negative-energy resonances contribute to the thermal cross section, then this value of 90 barns would have to be modified in the direction of lowering the resonance integral.

This work has been accepted for publication in the *Journal of Nuclear Energy.*

EFFECTIVE CADMIUM CUTOFF ENERGIES FOR REACTOR NEUTRONS

R. W. Stoughton J. Halperin
M. P. Lietzke[39]

Effective cadmium cutoff energies have been calculated for infinitely small $1/v$ samples at the centers of spherical and cylindrical cadmium shells. The effective cadmium cutoff energy was defined as the energy cutoff of a hypothetical perfect (i.e., infinitely sharp) filter which would allow the same reaction rate for a $1/v$ absorber as the actual cadmium filter. The flux outside the shells was assumed to be a superposition of a Maxwellian thermal component and a $1/E$ epithermal component which went to zero at five times[40]

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[32] J. R. Huizenga and R. B. Duffield, *Phys. Rev.* 88, 959–60 (1952).

[33] R. A. Glass, S. G. Thompson, and G. T. Seaborg, *J. Inorg. & Nuclear Chem.* 1, 3–44 (1955).

[34] L. Dresner, *J. Nuclear Energy* 2, 118–27 (1955); E. Kuhn and L. Dresner, *J. Nuclear Energy* 7, 69–70 (1958).

[35] R. L. Macklin and H. S. Pomerance, *J. Nuclear Energy* 2, 243–46 (1956).

[36] G. G. Myasischeva *et al.*, *Atomnaya Energ.* 2 (1), 22–26 (1957).

[37] S. P. Harris, C. O. Muehlhause, and G. E. Thomas, *Phys. Rev.* 79, 11–18 (1950).

[38] R. L. Macklin and H. S. Pomerance, chap 6 in *Progress in Nuclear Energy, Series I, Physics and Mathematics*, vol. 1, McGraw-Hill, New York, 1956.

[39] Reactor Experimental Engineering Division.

[40] C. H. Westcott, *J. Nuclear Energy* 2, 63 (1955).

the energy E_m corresponding to the Maxwellian modal (most probable) velocity. On the assumed model the effective thickness of the spherical shells for neutrons which passed through the centers was equal to the actual thickness. For the cylinders the thickness of cadmium traversed depended upon the angle between the neutron path and the axis of the cylinders. The product used for the macroscopic cross section for cadmium (per mil), Σ_{Cd}, times the thickness l (in mils) in terms of the neutron energy E in ev was[41]

$$\Sigma_{Cd} l = \frac{5.076 \times 10^{-3} l}{\sqrt{E}\ [4(E - 0.178)^2 + 0.013112]} .$$

The equation for calculating the effective cutoff E_c for the sphere becomes

$$\int_{E_c}^{\infty} R(E)\ dE = \int_0^{\infty} e^{-\Sigma_{Cd} l}\ R(E)\ dE ,$$

where $R(E)$ is the derivative of the total reaction rate with respect to energy.

The values of E_c were calculated by numerical integration. The method of Gaussian quadrature was used, with the further assumption that $e^{-\Sigma_{Cd} l} = 1$ for $E > 100E_m$. The error made in the worst case (100-mil Cd) is only about 0.1% by taking the upper limit at $100E_m$, if all integrals have the same upper limit.

In the case of the cylinders the Gaussian integration had to be carried out over both the spacial direction and the energy. Calculations for the sphere and cylindrical cases were carried out on the Oracle and on the IBM-704 computer at the ORGDP, respectively, in which E_c was evaluated for various values of l and E_m, as well as of r, the ratio of the Maxwellian flux to the $1/E$ flux per unit ln E. Some of the results are shown in Fig. 6 for spherical and cylindrical (height/diameter = 2) shells. For thicknesses of 20 mils or greater the E_c values are fairly close to the values of E for 50% transmission. By comparing the curves for the sphere for the two values of r, it can be seen that whenever E_m is too high or the cadmium thickness too low, the Maxwellian neutrons influence the cutoff. For this reason thicknesses of less than about 30 mils are not recommended; the authors suggest a 40-mil thickness.

Values of the "filter inefficiency," that is, ratios of total absorptions by neutrons below E_c to total neutrons absorbed by the $1/v$ samples, ranged from 7 to 15% for thicknesses of 20 mils or greater. As expected, corresponding inefficiencies were much greater for boron filters or for thinner cadmium filters.

Some calculations were carried out under the conditions assumed by Dayton and Pettus:[42] no Maxwellian neutrons and a lower limit of 0.025 ev for the $1/E$ flux. The calculations reported here showed higher values of E_c for the thicker filters (e.g., 0.58 ev vs 0.47 ev at 60 mils thickness in the sphere case).

CROSS SECTION FOR THE $Al^{27}(n,\alpha)Na^{24}$ REACTION AS A FUNCTION OF ENERGY

H. W. Schmitt[43] J. Halperin

This work was described in another progress report[44] and will be submitted to the *Physical Review*.

[41] D. J. Hughes and R. B. Schwartz, *Neutron Cross Sections*, BNL-325, 2d ed. (1958).

[42] I. E. Dayton and W. G. Pettus, *Nucleonics* 15 (12), 86 (1957).

[43] Physics Division.

[44] H. W. Schmitt and J. Halperin, *Phys. Semiann. Prog. Rep. Sept. 20, 1958*, ORNL-2610, p 15.

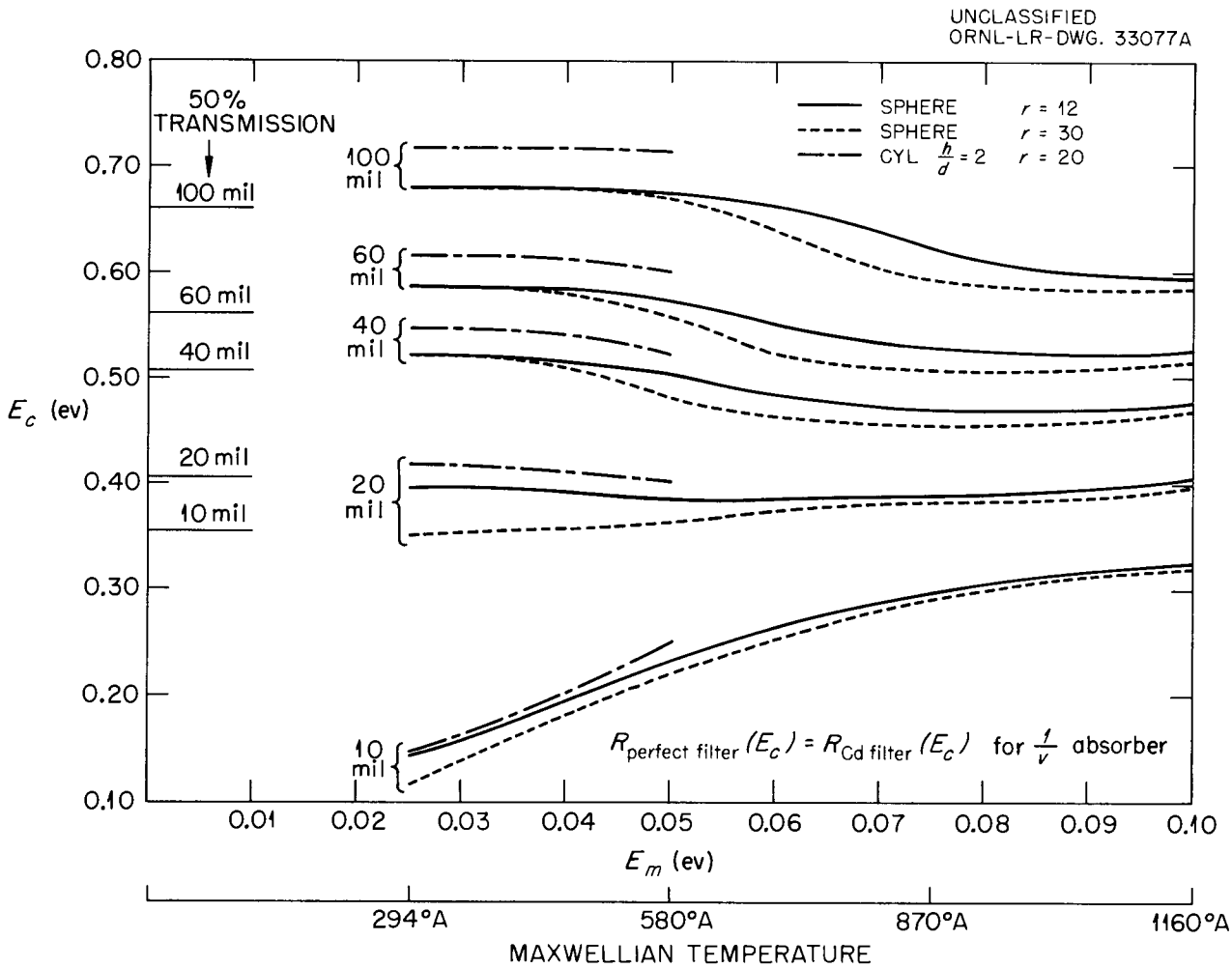


Fig. 6. Effective Cadmium Cutoff vs Characteristic Maxwellian Energy.

ISOLATION AND CHEMISTRY OF SYNTHETIC ELEMENTS

CHEMISTRY OF TECHNETIUM

Partial Separation of the Nuclear Isomers of Tc^{95}

G. E. Boyd Q. V. Larson

The incidence of nuclear isomerism among the isotopes of technetium is apparently fairly widespread, since five examples have been reported among the radionuclides of masses 92 through 102. Of these isomeric pairs, only those of masses 97 and 99 are well established; the evidence for the remaining three at masses 93, 95, and 96 has been circumstantial and is only partially satisfactory, if at all. An interesting and conveniently accessible pair from the point of view of experiment is the 60-day and 20-hour technetium periods assigned to mass 95. The former activity has been ascribed to the metastable Tc^{95m}, which decays either to stable Mo^{95} by orbital electron capture or to the 20-hour ground state, Tc^{95g}, by a highly internally converted 39-kev isomeric transition in an estimated 3% of the decays. The evidence for such an isomeric transition consists in the observation of low-energy internal conversion electrons measured by a magnetic beta-ray spectrometer,[1] and in the appearance of small quantities of 762-kev gamma rays known to be associated with the decay of Tc^{95g} in the gamma-ray spectrum of Tc^{95m} when measured with an NaI scintillation spectrometer.[2]

The possibility for effecting a chemical separation of Tc^{95m} and Tc^{95g}, if they are genetically related, depends on the oxidative nature of the isomeric transition in Tc^{95m}. Because of the small energy change in the transition the nuclear gamma ray is completely converted, leaving vacancies in the *K* and *L* shells of the technetium atom. Large positive charges are built up on the atom as a consequence of the Auger process, and this ionization is sufficient to break any chemical bonds which may hold it combined in a molecule. Thus, technetium would be oxidized in the isomeric transition from a lower to a higher valence state and ejected from its original state of chemical combination. Since the most stable valences of technetium are the tetravalent and the heptavalent states, a possible isomer separation procedure would be to combine the 60-day activity into a tetravalent compound, say, K_2TcCl_6; then the decay of Tc^{95m} to Tc^{95g} would produce heptavalent technetium, say, $KTcO_4$, containing the 20-hour activity only. The problem of the separation of the isomers, then, is that of fractionating $TcCl_6^{--}$ from TcO_4^-.

A variety of separation schemes were given a preliminary investigation, and it was found that an ion exchange process using an anion exchanger was the most efficient. Accordingly, several milligrams of K_2TcCl_6 were prepared from Tc^{99g} into which was mixed several hundred microcuries of Tc^{95m}. This compound was placed at the top of a Dowex 1 ion exchange column, and a mixture of 0.5 *N* $HClO_4$ + 2.5 *N* HCl was used to differentially elute TcO_4^- from $TcCl_6^{--}$. The gamma-ray spectrum measured on the eluant emerging from the column showed that Tc^{95g} had indeed been separated appreciably from Tc^{95m} (Fig. 7). In no case, however, was the separation complete; some contamination of the ground state by the metastable state activity always occurred. The cause for the lack of success in this attempt appeared to be the slow chemical decomposition of $TcCl_6^{--}$, possibly through hydrolysis and chemical oxidation, to give TcO_4^- during the time that it was held on the ion exchange column. A number of variants in the elution procedure were

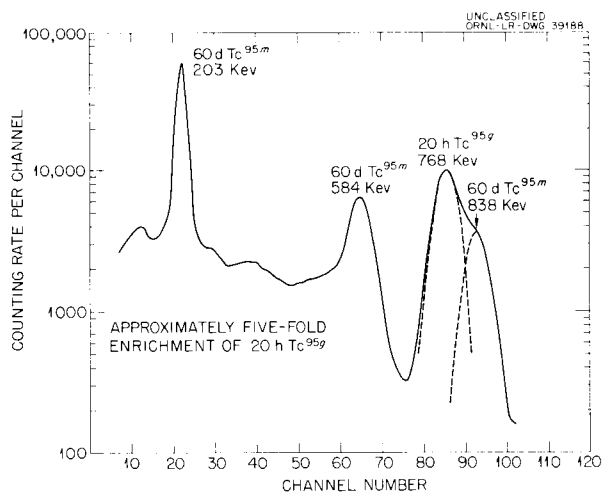


Fig. 7. Gamma-Ray Spectrum of TcO_4^- Fraction Taken from Ion Exchange Separation of Tc^{95} Isomers.

[1] H. A. Medicus and P. Preiswerk, *Phys. Rev.* 80, 1101 (1950).

[2] Unpublished observations at this Laboratory.

attempted but did not improve the separation. Thus far, therefore, it can be concluded only that a genetic relationship between the 60-day and the 20-hour periods in technetium does exist. It is hoped that a method for obtaining pure Tc^{95g} can be devised and that its yield in the decay of Tc^{95m} can be estimated.

Solvent Extraction of Technetium

G. E. Boyd Q. V. Larson

The extraction of pentavalent and tetravalent technetium contained in aqueous acid solutions was measured. Several insoluble organic liquids were used as solvents. It was found that Tc(V) formed in 12 *N* HCl does not extract into diethyl ether (extraction coefficient, E_a^o, less than 0.01) but that partial extraction ($E_a^o \sim 3$) is obtained with a 0.1 *M* trioctylphosphine oxide (TOPO) solution in cyclohexane and with a solution of trioctylamine (TOA) in 1,2-dichloroethane. The thiocyanate complex of Tc(V) contained in 3 *N* HCl was extracted efficiently by highly dilute solutions (i.e., 10^{-5} to 10^{-4} *M*) of TOA in cyclohexane and in 1,2-dichloroethane. Extraction from 4 *N* HCl by 0.1 *M* TOPO in cyclohexane was observed also.

Technetium(IV) as $TcCl_6^{--}$ in 3 *N* HCl was poorly extracted by 1-pentanol (E_a^o = 0.25) but $ReCl_6^{--}$ was extracted somewhat more efficiently (E_a^o = 1.4). Neither diethyl ether nor 2-ethyl-1-hexanol extracted $TcCl_6^{--}$. Efficient extraction of Tc(IV) from 6 *N* HCl was effected by TOPO dissolved in cyclohexane, and from 4.5 *N* HCl by 10^{-3} *M* solutions of TOA in 1,2-dichloroethane.

Chemistry of Technetium in Hydrochloric Acid Solutions

R. H. Busey

Technetium(V). – Potassium pertechnetate, $KTcO_4$, dissolved in 12 *M* HCl is reduced to Tc(V) by Cl^-. The oxidation state was established by a spectrophotometric titration with $SnCl_2$. The ultraviolet absorption spectrum of the Tc(V) species has two absorption bands, at 2925 and 2300 Å, with molar absorbancy indices of 4700 and 10,400, respectively. The same species was formed in 8 *M* HCl with H_3PO_2 as the reducing agent. No intermediate species between TcO_4^- and Tc(V) were detected. The Tc(V) species is slowly reduced in 12 *M* HCl by Cl^- to $TcCl_6^{--}$. Dilution experiments showed that Tc(V) is stable in 3 *M* HCl, but that in 1 *M* HCl it disproportionates into TcO_4^- and products of hydrolysis of $TcCl_6^{--}$.

The initial production of Tc(V) when $KTcO_4$ was dissolved in various concentrations of hydrochloric acid is given below:

Molarity of HCl	Mole % Tc(V)
11.86	100
10.62	98
9.86	93
9.35	80
8.90	61
8.41	23
7.92	5
6.82	0.4
5.92	0.0

On standing, the Tc(V) increased in all the solutions (except for the 11.86 *M* HCl solution) as a result of the loss of Cl_2 (evidenced by decreased absorption around 2250 Å) and a consequent shift in the equilibrium. Further loss of Cl_2 resulted in the formation of $TcCl_6^{--}$ by the reduction of Tc(V) by Cl^-.

The data tabulated above show that the equilibrium between TcO_4^- and the Tc(V) species is strongly dependent on the hydrochloric acid concentration. Preliminary calculations applicable to the case where a singly charged species is formed, such as $TcCl_6^-$, $TcOCl_4^-$, and $TcO_2Cl_2^-$, indicate that the singly oxygenated species is formed. The calculations do not exclude possible species such as $TcOCl_3$, $TcOCl_5^{--}$, or $TcO_2Cl_4^{---}$.

A different species of Tc(V) is formed when a 12 *M* HCl solution of $TcCl_6^{--}$ is irradiated in sunlight. The oxidation state was established by a spectrophotometric titration with $SnCl_2$. The ultraviolet absorption spectrum of this species consists of a strong absorption band at 3260 Å with a molar absorbancy index of 7800. As in the case of the above Tc(V) species, this species is slowly reduced by Cl^- in 12 *M* HCl back to $TcCl_6^{--}$. Presumably the Tc(V) is present as a completely chlorinated species such as $TcCl_6^-$.

Technetium(IV). – The $TcCl_6^{--}$ ion is not stable in 1 *M* HCl, as evidenced by a slow change

in its ultraviolet absorption spectrum. Presumably the ion slowly hydrolyzes. In order to determine the possible existence of oxygenated Tc(IV) species, reductions of TcO_4^- in several concentrations of hydrochloric acid were made; $SnCl_2$ was used as the reducing agent, and the course of the reduction was followed spectrophotometrically. Reduction of TcO_4^- in 5 *M* HCl produced only $TcCl_6^{--}$, but reductions in 1 and 2 *M* HCl produced a new Tc(IV) species with an absorption band at 3220 Å. Reductions in 0.75 and 0.5 *M* HCl gave a mixture of the same species and a second oxygenated species which appears to have an absorption maximum around 3500 Å. No intermediate oxidation states between Tc(VII) and Tc(IV) were detected. Excess $SnCl_2$ did not further reduce the technetium beyond Tc(IV).

The ultraviolet absorption spectrum of a month-old solution of K_2TcCl_6 in 1 *M* HCl shows weak absorption bands at 3225 and 3500 Å and evidence of the 2480-Å absorption band of TcO_4^-. The spectrum of the solution after a year shows that 98% of the technetium is present as TcO_4^- and 2% as a species with an absorption maximum at 3500 Å. Thus the fate of the $TcCl_6^{--}$ in 1 *M* HCl appears to be hydrolysis to at least two different oxygenated Tc(IV) species which in turn are slowly oxidized to TcO_4^-.

Lattice Constants for K_2TcCl_6 and K_2ReCl_6

G. E. Boyd

A recent publication[3] of the lattice spacing, a_0, for K_2TcCl_6 and K_2ReCl_6 has given values considerably different from those found by x-ray diffraction in this Laboratory in 1952 by R. D. Ellison.[4] New preparations of both compounds have been made with hypophosphorous acid used as the reducing agent in concentrated HCl rather than KI, which was used in all earlier work. The new measurements by R. L. Sherman (see Table 2) appear to confirm the earlier values from this Laboratory.

[3] J. Dalziel *et al.*, *J. Chem. Soc.* 1958, 4012.

[4] See: C. M. Nelson, G. E. Boyd, and W. T. Smith, Jr., *J. Am. Chem. Soc.* **76**, 348 (1954).

Table 2. Lattice Constants for K_2TcCl_6 and K_2ReCl_6

Year	Investigator	a_0 (Å)	
		K_2TcCl_6	K_2ReCl_6
1936	Aminoff[a]		9.861
1951	Zachariasen[b]	9.805 ± 0.002	9.821 ± 0.001
1952	Ellison[c]	9.89	9.842 ± 0.002
1958	Peacock[d]	9.82 ± 0.01	9.82 ± 0.01
1959	Sherman[e]	9.90 ± 0.01	9.839 ± 0.005

[a] B. Aminoff, *Z. Krist.* **A94**, 246 (1936).

[b] W. H. Zachariasen, Abstracts of the American Crystallographic Society, Washington, D.C., Meeting, February 1951.

[c] See: C. M. Nelson, G. E. Boyd, and W. T. Smith, Jr., *J. Am. Chem. Soc.* **76**, 348 (1954).

[d] J. Dalziel *et al.*, *J. Chem. Soc.* 1958, 4012.

[e] R. L. Sherman, private communication to G. E. Boyd, Jan. 22, 1959.

SOME TECHNETIUM ELECTRODEPOSITION STUDIES

M. H. Lietzke R. W. Stoughton

A brief survey of the electrodeposition of technetium from 0.5 *m* H_2SO_4 solutions at constant cathode potentials has produced semiquantitative data. At cathode potentials 200 to 300 mv more negative than the saturated calomel electrode, up to 97% of the technetium could be deposited on platinum and mercury cathodes from solutions containing 10^{-6} to 10^{-4} *m* $KTcO_4$. However, the rate of deposition was extremely slow and the plots of the logarithm of the percentage of the technetium left in solution vs time showed several linear portions. At 25°C, 10 to 30% of the technetium was deposited in about ½ hr, while 50% deposition was observed in 10 to 12 hr. The addition of 0.01 *m* HF to the solution did not increase the rate of deposition. At 80°C the rate of deposition was much more rapid; 60% of the technetium was deposited in about ½ hr and 97% in 5 hr from a solution containing 10^{-4} *m* $KTcO_4$. The complex nature of the rate plot may indicate that the solutions of $KTcO_4$ studied contained several species of ions.

FUEL ELEMENT CATASTROPHE STUDIES. HAZARDS OF FISSION-PRODUCT RELEASE FROM IRRADIATED HANFORD URANIUM

G. W. Parker W. J. Martin
G. E. Creek

The current status of the work on fuel element catastrophe studies has been described elsewhere.[5]

The initial measurements of the release of fission products by burning and melting Hanford-type production-irradiated metallic uranium have been completed. The design of the experiments permitted correlation with the extensive laboratory work on the nature of the oxidation of unirradiated uranium.[6] Attention was given to the detection and characterization of air-borne solid particles and the possible development of air decontamination procedures.

In order to gain experience with the analytical procedures necessary for the preparation of material balances, both unirradiated and slightly irradiated samples were prepared in the form of $\frac{1}{4} \times \frac{11}{16}$ in. cylindrical pellets which were turned from sections of a Hanford-type slug. Similar pellets were turned in a hot cell from fully irradiated slugs.

The burning experiments were carried out in a horizontal furnace tube using a ceramic boat to contain the oxides. Connected to the furnace tube was an absorption train having first a fine-porosity (Millipore) filter to retain particles, then a small activated-charcoal absorption trap kept at 300°C, which was found to be highly effective for absorbing volatile iodine; following this was the conventional refrigerated charcoal trap for adsorption of xenon and krypton.

The significant results of the burning experiments are shown in Figs. 8 and 9 and Tables 3 and 4. Fully irradiated Hanford uranium was found to oxidize at about twice the rate of slightly irradiated metal and to release fission products in proportion. In the same curves an atmosphere of 80% steam–20% air is shown to decrease the oxidation rate by a factor of 2. A 100% steam atmosphere is reported[7] to reduce the oxidation rate of unirradiated uranium by a factor of 5.

Figures 10 and 11 are photographs of a sample of air-borne particles collected on a filter paper in one experiment conducted at 1200°C. Only one experiment of a total of eight produced particles, and no correlation with temperature has been established. The smokelike character of the black solid particles (assumed to be UO_2) seems to indicate that the uranium has ignited in such a way as to produce a local hot spot with accompanying temperatures necessary to vaporize a small amount of metal. Figure 11*b* is an enlargement from which the particle size range 0.3 to 1.0 μ has been determined. Table 5 presents a comparison of the fission products collected on the above filter as a percentage of the total amount released.

Additional work including oxidation rates and release effects in other atmospheres is in progress.

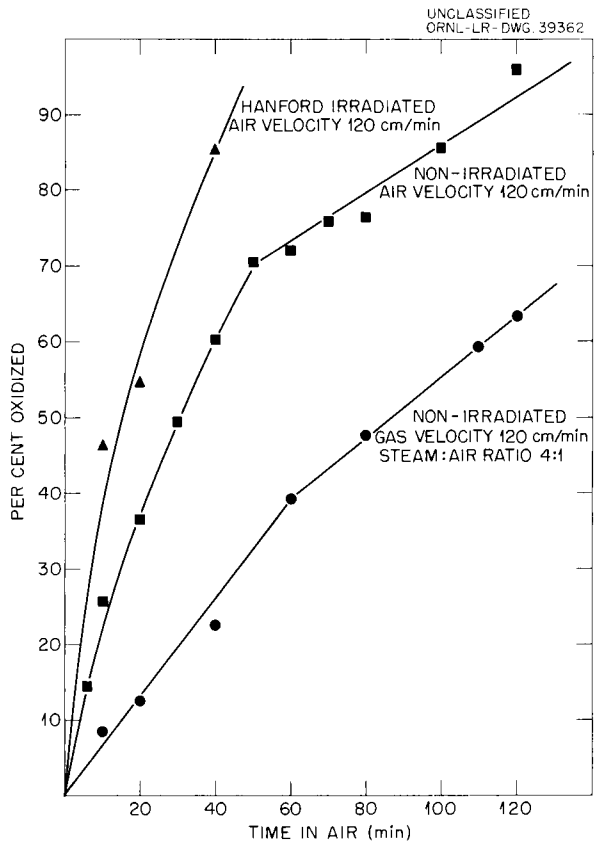


Fig. 8. Uranium Oxidation vs Time for $\frac{1}{4}$-in.-dia by $\frac{11}{16}$-in.-long Specimen at 1000°C.

[5] G. E. Creek, W. J. Martin, and G. W. Parker, *Experiments on the Release of Fission Products from Molten Reactor Fuels*, ORNL-2616 (July 7, 1959).

[6] R. K. Hilliard, *Oxidation of Uranium in Air at High Temperatures*, HW-58022 (December 1958).

[7] R. K. Hilliard and C. E. Linderoth, private communication.

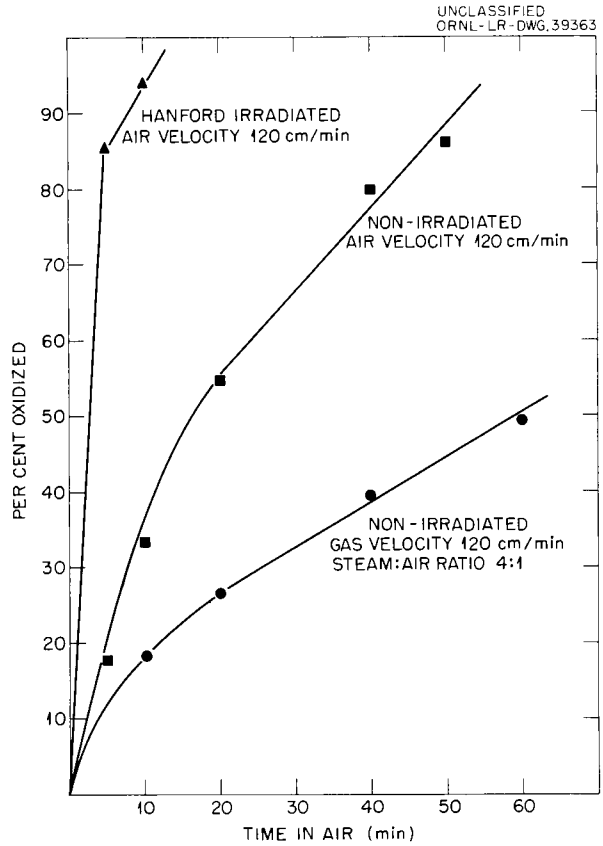


Fig. 9. Uranium Oxidation vs Time for $\frac{1}{4}$-in.-dia by $11\frac{1}{16}$-in.-long Specimen at 1200°C.

Table 3. Release of Fission Products from Hanford-Irradiated Uranium Heated in Air at 1000°C

Run No.	Time (min)	Per Cent of Uranium Oxidized	Per Cent of Total Activity Released							
			Rare Gases	Gross Gamma	I	Cs	Ru	Zr	Ce	Sr
4-20-1	10	46.9	100	0.064	1.09	2.4	0.104	0.0007	0.0001	0.05
4-15-1	20	53.2	100	0.1	67.3	2.8	0.13	0.005	0.008	0.055
4-16-1	40	86.9	100	0.8	79.5	18.4	5.2	0.018	0.0064	0.053

Table 4. Release of Fission Products from Hanford-Irradiated Uranium Heated in Air at 1200°C

Run No.	Time (min)	Per Cent of Uranium Oxidized	Per Cent of Total Activity Released									
			Rare Gases	Gross Gamma	I	Te	Cs	Ru	Zr	Ce	Sr	Pu
4-29-1	5	85.1		0.32	20.2	4.2	19.4	24.1	0.003	0.003	4.5	
4-20-2	10	94	100	0.145			11.2	0.5	0.05	0.06	2.7	
4-21-1*	20			0.82	82.3		60.3	1.8	0.04	32.7	15.8	3.5

*Smoke collected on Millipore filter with particles 0.3 to 1.0 μ.

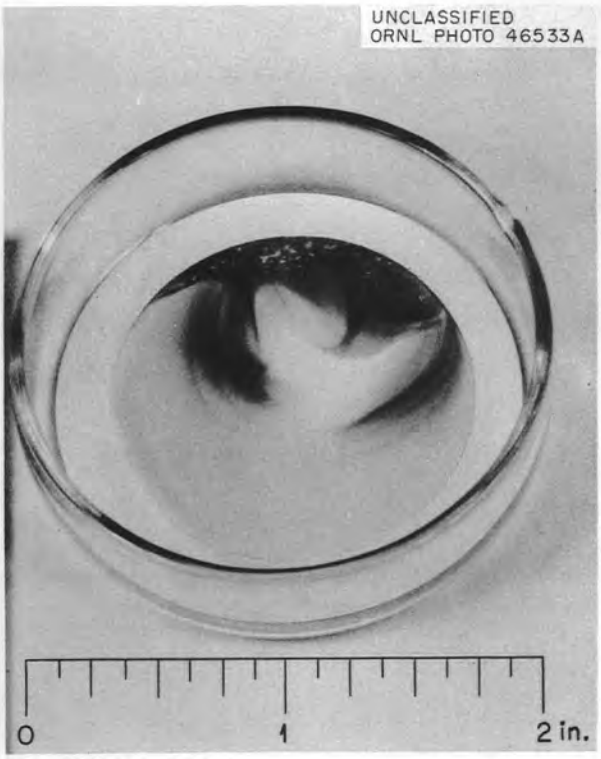


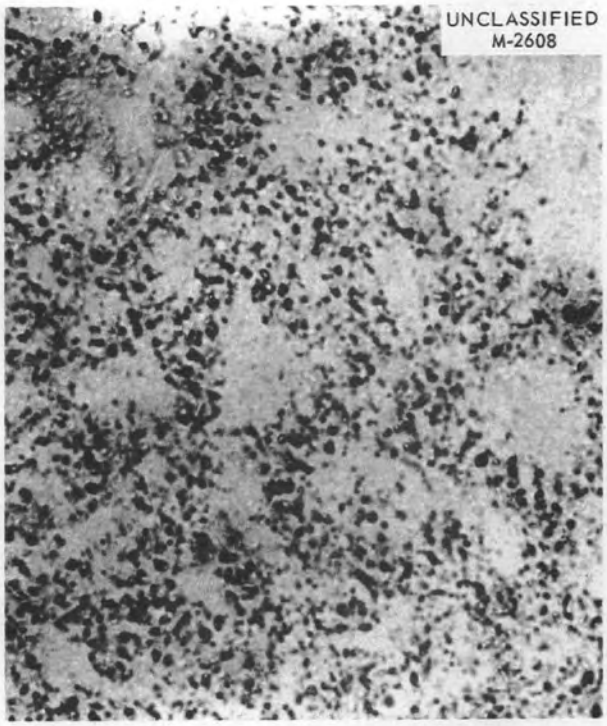
Fig. 10. Millipore Filter Showing Smokelike Particles from Burned Hanford Uranium.

Table 5. Analysis of Fission-Product Activities* Collected on AA Millipore Filter**

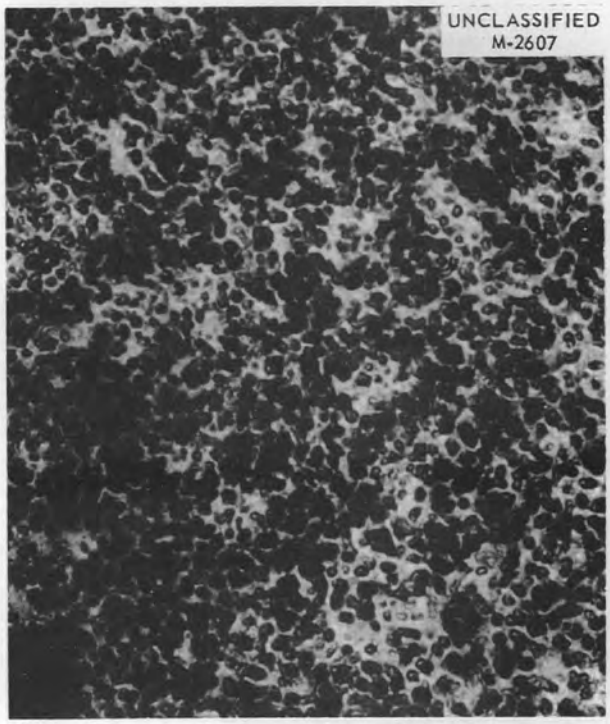
Run 4-21-1

Constituent	Per Cent of Total Activity Released	Per Cent of Total Collected on Millipore Filter
Gross gamma	0.82	0.19
I	82.3	0.17
Cs	60.3	14.0
Ru	1.8	0.07
Ce	32.7	9.8
Zr	0.04	0.02
Sr	15.8	0.65
Pu	3.5	0.1

*Hanford-irradiated uranium cooled 160 days.
**Pore size 0.8 μ.



(a)



(b)

Fig. 11. Photomicrographs of Smoke Particles Collected from Oxidation of Hanford-Irradiated Uranium. Millipore filter. 1000X.

CHEMICAL SEPARATION OF ISOTOPES

PRODUCTION OF LOW-TRITIUM D_2O AND D_2

W. M. Jackson

The Lotee facility was designed and constructed to produce low-tritium D_2O and D_2 gas to be used in bubble-chamber studies. The tritium content was reduced by the partial batch electrolysis of D_2O. The equipment included three electrolysis cells, together with a recombiner in which the resulting D_2 gas was burned in oxygen to D_2O. A fourth electrolysis cell was used to prepare D_2 gas, for bottling in standard gas cylinders, from the low-tritium D_2O product.

The operation of the Lotee facility was largely automatic. Total production of low-tritium D_2O, with a tritium/deuterium ratio ranging from 4.3 to 11.4×10^{-16}, was 458.40 kg. Of this amount, 53.88 kg was electrolyzed to D_2 gas having a tritium/deuterium ratio of from 4.4 to 8.8×10^{-16}.

LITHIUM ISOTOPE SEPARATION BY ION EXCHANGE

D. A. Lee

Studies were made to determine various parameters which may influence the single-stage separation factor α for lithium isotopes in an ion exchange system. The effects of various cations and anions in the eluting solution and the resin phase were investigated as well as the effect of methanol-water mixtures as solvents. The method which was used was described previously.[1]

In the experiments concerned with the cation and anion effects, Dowex 50-X16 resin columns were first washed thoroughly with the eluant to be used. Then a band of lithium ions was placed on top of the resin and the elution made. In the cation experiments all the anions were chloride, and in the anion experiments potassium and ammonium salts were used. All the eluants were 0.25 *N*. The cation and anion experiments are summarized in Tables 6 and 7, respectively. In the mixed solvent experiments (Table 8) the eluant was 0.5 *M* NH_4NO_3. When 95 and 100% methanol solutions were used as solvents, few theoretical plates were obtained, and meaningful analysis of the systems was not possible. Attempts to separate lithium

[1] D. A. Lee and G. M. Begun, *J. Am. Chem. Soc.* **81**, 2332 (1959).

Table 6. Variation of α with the Nature of the Eluting Cation

Eluting Cation	α
NH_4^+	1.0023
K^+	1.0029
NH_3OH^+	1.0033
H^+	1.0037
Ca^{++}	1.0037
Cu^{++}	1.0045
Cr^{+++}	1.005
Al^{+++}	1.005

Table 7. Variation of α with the Nature of the Eluting Anion

Eluting Anion	α	Plates*	Sample Break-Through No.
	Potassium Salts		
OH^-	1.0037	350	141
Cl^-	1.0029	500	144
F^-			199
SO_4^{--}	1.0027	700	223
$Fe(CN)_6^{4-}$	1.0027	1100	257
	Ammonium Salts		
$Citrate^{--}$	1.0030		
Cl^-	1.0023		

*All experiments with K^+ were performed in the same column.

Table 8. Variation of α in Methanol-Water Mixtures

Mole % Methanol	Plates	α
0	816	1.0023
50	460	1.0028
75	133	1.0035

isotopes by ion exchange in methanol, glacial acetic acid, and anhydrous ethylenediamine failed. No workable elution curves could be obtained, presumably because the dielectric constants of these solvents were too low for such a highly cross-linked resin.

The results shown in Table 6 indicate that α for lithium isotopes increases as the degree of hydration of the eluting cation increases. In Fig. 12 the logarithm of the heat of hydration[2] of the various ions is plotted against α. An attempt to measure α in the presence of thorium ions failed because the equilibrium so greatly favored thorium over lithium on the resin that insufficient plates were obtained. The increase in α in the presence of highly hydrated cations is probably due to partial lithium ion dehydration in the resin phase. Certainly in the concentrated solutions of the resin phase there is strong competition for water between the cations.

In the anion study the higher values for α for hydroxyl and citrate ions may be attributed to localized hydrolysis of the hydrated lithium ion in the resin phase.[3] Both hydroxyl and citrate ions are strong proton acceptors which could disrupt the water dipoles around the lithium ion, effectively causing dehydration. From the data in Table 7 it may be seen that both the number of plates and the sample break-through number increase as higher-valent anion solutions are used. This effect is probably associated with the lower activities of these solutions. The fluoride ion experiment failed because of the insolubility of LiF. The elution curve was unsuitable for plate calculations.

The increase in α as the methanol content of the solvent increased may also be due to dehydration of the lithium ion. Further studies are planned to determine the effect of the dielectric constant of the solvent upon α.

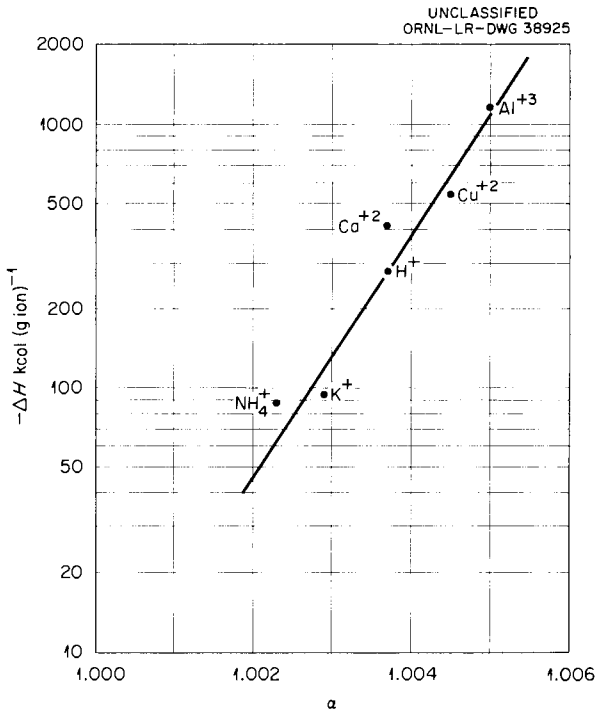


Fig. 12. Single-Stage Separation Factor as a Function of Heat of Hydration of Eluting Cations.

BORON ISOTOPE SEPARATION

A. A. Palko

The study of the BF_3-thioether complexes has continued in an effort to correlate single-stage isotopic separation factors for boron with the heats of formation, bond strengths, types of bonding, etc., for various BF_3 organic complexes. The methods employed in these studies were described in earlier reports.[4,5]

The vapor pressures of various mixtures of ethyl sulfide and BF_3 and of methyl sulfide and BF_3 were measured as a function of temperature so that heats of complex formation could be calculated. The vapor pressures of the 1:1 BF_3-sulfide complexes are shown in Fig. 13. The methyl sulfide–BF_3 complex freezes at −21°C, and the ethyl sulfide–BF_3 complex freezes below −60°C. The heats of complex formation of both sulfides are approximately −10 kcal/mole. More accurate determinations of ΔH are in progress.

Variation of the single-stage isotopic separation factor with temperature for the reaction

$$B^{10}F_3(g) + B^{11}F_3\cdot\text{sulfide}(l) \rightleftharpoons B^{11}F_3(g) + B^{10}F_3\cdot\text{sulfide}(l)$$

[2] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* 1, 515 (1933).

[3] R. A. Robinson and H. S. Harned, *Chem. Revs.* **28**, 419 (1941).

[4] A. A. Palko, R. M. Healy, and L. Landau, *J. Chem. Phys.* **28**, 214 (1958).

[5] A. A. Palko, *J. Chem. Phys.* **30**, 1187 (1959).

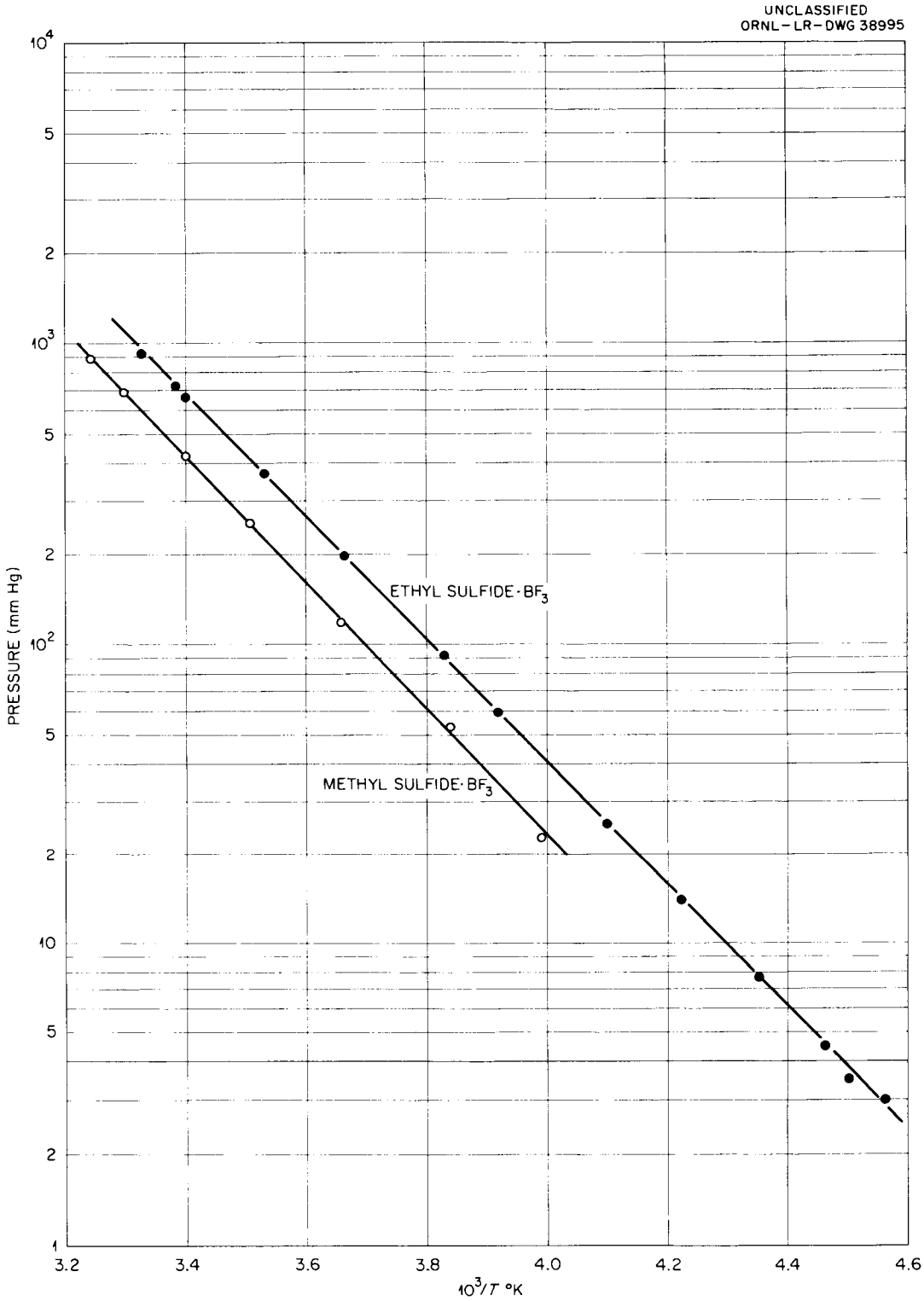


Fig. 13. Vapor Pressure of BF_3-Sulfide Complexes as a Function of Temperature.

was measured from −33 to +20°C for the ethyl sulfide–BF_3 system and from −20 to +26°C for the methyl sulfide–BF_3 system. These measurements are shown in Fig. 14.

A similar study of the phenol- and thiophenol-BF_3 complexes is planned for the near future. A study of the Raman spectra of the various complexes is under way.

ENRICHMENT OF C^{13}

D. Zucker

A suitable separation factor for the CO–cuprous ammonium lactate system having been previously established,[6] the feasibility of this system for enriching C^{13} was further examined. The solubility of CO in this solvent at 25°C was found to be roughly proportional to Cu^+ concentration and CO pressure and independent of lactate concentration, provided that it is greater than the Cu^+ concentration. The solubility increases with NH_3 excess, although not quite in proportion to the excess. The exchange rate is fast, equilibration being essentially complete in 3 sec or less.

Substitution of less volatile organic bases for NH_3 is being studied with a view to eliminating the difficulties involved in thermal reflux of a solution in which part of the solvent (NH_3) is boiled out along with the CO. The solubility of CO in monoethanolamine is about the same as in NH_3 solution, but use of this solution leads to excessive deposition of metallic Cu, presumably with oxidation of CO to CO_2. Other organic bases are being evaluated as substitutes for NH_3.

Exchange half times of the order of a few hours were observed for carbon between $Fe(CO)_5$ and C*O, with a slight indication that two or more rates are involved. This is quite different from

[6] D. Zucker, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 13.

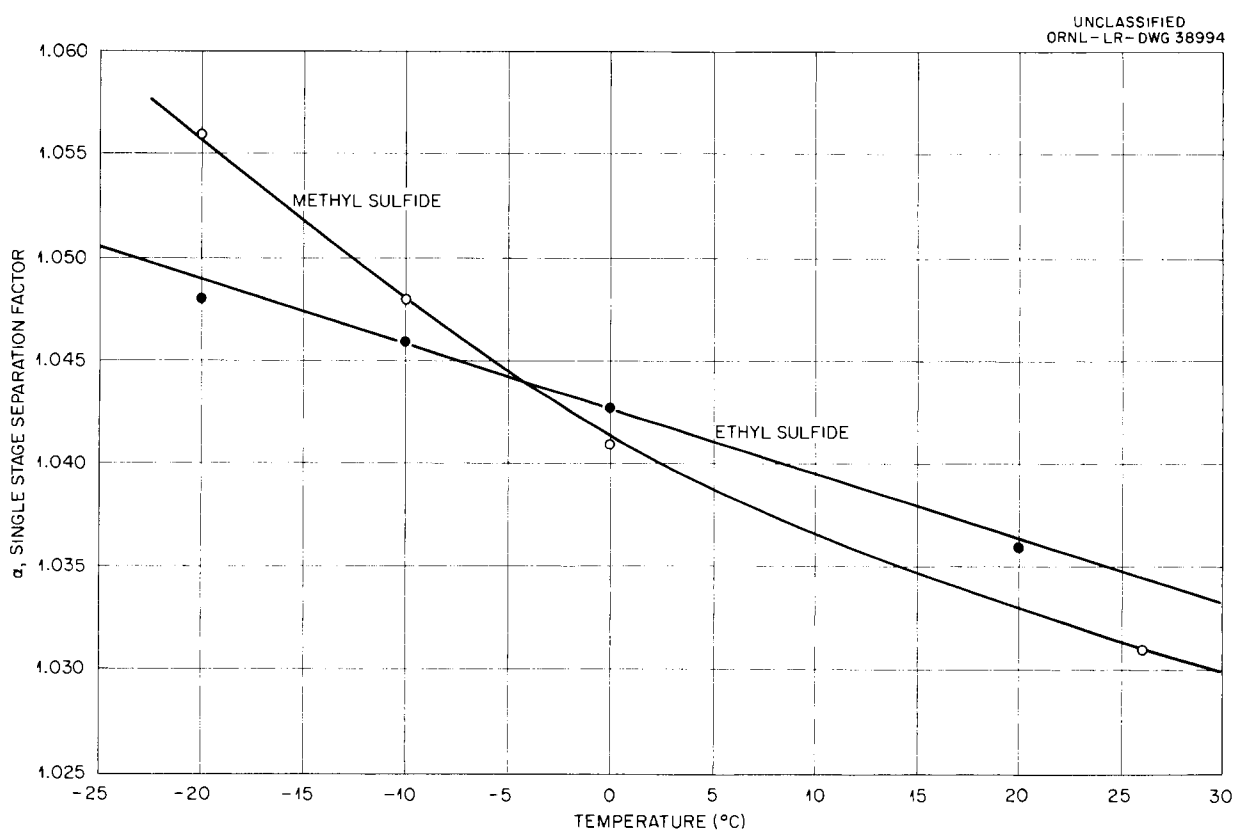


Fig. 14. Single-Stage Separation Factor vs Temperature for Systems $BF_3(g)$–BF_3·Sulfide(l).

Sheline's[7] results with benzene solutions of $Fe(CO)_5$.

The potentialities of fractionating carbon isotopes by equilibrating CO with solutions of the hexacarbonyls of molybdenum, tungsten, and chromium are also being investigated. A search was made for a suitable solvent for these solids, and $CHCl_3$ was selected because of its greater solvent power and the stability of the resulting solutions. Chromium hexacarbonyl is soluble in $CHCl_3$ to the extent of 0.098 *M* at 25°C; $Mo(CO)_6$ and $W(CO)_6$ are more soluble.

NITROGEN ISOTOPE SEPARATION

Distillation of Nitric Oxide for the Enrichment of N^{15} and O^{18}

L. L. Brown L. B. Yeatts, Jr.

Following the publication by Clusius and Schleich[8] of the vapor pressures of the pure isotopic species $N^{14}O^{16}$, $N^{14}O^{18}$, and $N^{15}O^{16}$, work was started to evaluate the economic and technical feasibility of enriching the isotopes of nitrogen and oxygen by the distillation of NO.

A sample of isotopically normal NO was equilibrated with its vapor in a sealed glass tube at −152 ± 1°C for 4 hr. The isotopic analyses were performed directly on NO. A nitrogen α (N^{15} concentrated in liquid phase) of 1.024 ± 0.002 (95% confidence interval) was measured. The oxygen factor could not be obtained because the NO reacted inside the mass spectrometer to give an erroneous contribution to the mass-32 peak.

Further data were obtained by distilling NO in a 200-cm-long packed column. The NO withdrawn from four sampling ports along the length of this column showed progressive fractionation of the isotopes of both elements.

Additional experiments are being performed to obtain further data on both nitrogen and oxygen fractionation in this system.

[7] R. K. Sheline, R. W. Wolfgang, and R. E. Johnson, *The Structure and Bond Type in Molecular Complexes*, AD-137398 (final technical report for the period Feb. 1, 1955, to June 30, 1957, Florida State University, Tallahassee).

[8] K. Clusius and K. Schleich, *Helv. Chim. Acta* 41, 1342 (1958), and *Second United Nations International Conference on the Peaceful Uses of Atomic Energy*, paper No. A/Conf 15/P 255.

Production of N^{15}

W. M. Jackson

Operation of the Nitrox facility[9] was continued during the year with only minor modification of the equipment and procedures. The amount of N^{15} produced, with an isotopic purity of 90% or higher, was 71 g.

OXYGEN ISOTOPE FRACTIONATION STUDIES

Fractionation of Oxygen Isotopes Between Water and Sulfur Dioxide

L. L. Brown

Sulfur dioxide gas and liquid water were equilibrated at 21°C in two different single-stage experiments. One run utilized water enriched to 1.5% in O^{18}; normal water was used in the other run. Isotopic samples were taken from both gas and liquid phases in each experiment. The SO_2 samples were converted to H_2O, and the latter was contacted with CO_2 to provide mass spectrometer samples for O^{18} analysis. The water-phase samples were equilibrated directly with CO_2, which was then analyzed for O^{18}. The average value of the single-stage separation factor

$$\alpha = \frac{(O^{18}/O^{16})_{SO_2}}{(O^{18}/O^{16})_{H_2O}}$$

is 1.016 ± 0.003.

Enrichment of O^{18} and C^{13} by Several Aliphatic Amine Carbamates

L. B. Yeatts, Jr.

The fractionation of the stable isotopes of oxygen and carbon between the vapor and liquid phases of several lower-molecular-weight aliphatic amine carbamates was investigated. These salt-like compounds were prepared by reacting the purified amine with carbon dioxide and were found by analysis to be composed of 2 moles of amine for each mole of carbon dioxide. This composition is in agreement

[9] G. M. Begun *et al.*, *Chemical and Isotopic Studies of the Nitrox System for N^{15} Enrichment*, ORNL-2291 (June 6, 1957).

with that found by Fichter and Becker[10] for earlier syntheses of this nature. Presumably, the reactions involving primary and secondary amines with CO_2 are

$$2RNH_2 + CO_2 = RNHCOOH_3NR$$

$$2R_2NH + CO_2 = R_2NCOOH_2NR_2$$

For most of the isotopic fractionation studies a small distilling column packed with glass helices was operated at total reflux for at least 17 hr before a two-drop sample of condensed vapor was withdrawn for subsequent mass analysis. Since the carbamate in the liquid form was always present in large molar excess during equilibration of the two phases, a sample of the carbamate taken before distillation was used to establish the isotopic abundances in the liquid at equilibrium. In two instances, a single-stage equilibration of the vapor and liquid carbamate was conducted at the boiling point of the particular compound.

All carbamate samples were reacted with excess concentrated H_3PO_4 to liberate CO_2, which was analyzed in the mass spectrometer for carbon and oxygen isotopic ratios. In every case studied C^{13} was found to concentrate in the liquid phase and O^{18} in the gas phase. The results of this study are given in Table 9.

Upon distilling diethylamine carbamate at 62°C Holmberg[11] found approximate α values for O^{18} and C^{13} of 1.007 and 1.002, respectively.

Di-*n*-propylamine carbamate is a liquid at room temperature and decomposes considerably below the boiling point of the amine. These properties suggest its possible use in a gas-liquid system, CO_2 vs carbamate, with thermal reflux.

Table 9. O^{18} and C^{13} Distillation Fractionation Factors for Several Aliphatic Amine Carbamates

Amine Carbamate	Boiling Point (°C)	α O^{18}/O^{16}	α C^{12}/C^{13}
Primary Amine Carbamates			
Ethyl	Decomposes[a]		
n-Propyl	82	1.0014	1.0002
Isopropyl	Decomposes at ~67°C		
n-Butyl	91	1.0044	1.0005
sec-Butyl	76	1.0060[b]	1.0024[b]
Isobutyl	86	1.0063[b]	1.0028[b]
tert-Butyl	Decomposes[c]		
Secondary Amine Carbamates			
Dimethyl	62	1.0039	1.0016
Methylethyl	60	1.0032	
Di-*n*-propyl	Decomposes at ~79°C		
Diisopropyl	Decomposes at ~34°C		

[a]Sealed-tube melting point, 113–114°C.
[b]Single-stage equilibration.
[c]Sealed-tube melting point, 107–108°C.

SULFUR ISOTOPE FRACTIONATION STUDIES

A. C. Rutenberg

Distillation of SO_3

Sulfur trioxide gas has been shown to be monomeric, while Raman spectra and other physical chemical data indicate that the liquid contains polymeric species. Due to the possibility of breaking sulfur-oxygen bonds on going from the liquid to the vapor state, it was of interest to measure the isotopic fractionation achieved by distilling SO_3.

The distillation column was ½ in. in diameter and packed to a height of 29 in. with 1/16-in. glass helices. The system was vented through a P_2O_5 drying tube. The gas phase was sampled above and below the packed section of column. The SO_3 reacted in sealed tubes at 400°C with powdered, out-gassed spectrographic-grade graphite to yield SO_2 and CO_2, which were analyzed for sulfur and oxygen isotopic abundances.

An initial experiment, which had to be terminated due to leakage at greased joints and stopcocks, indicated both sulfur and oxygen isotopic fractionation. A second 7-hr distillation was carried out in a revised, grease-free system. A total separation of 1.022 ± 0.012 (95% confidence interval) for sulfur and 1.041 ± 0.075 (95% confidence interval) for oxygen was measured. Both S^{34} and O^{18} enriched at the bottom of the column.

[10]F. Fichter and B. Becker, *Ber. deut. chem. Ges.* **44**, 3481 (1911).

[11]K. E. Holmberg, p 202 in *Proceedings of the International Symposium on Isotope Separation*, North Holland Publ. Co., Amsterdam, 1958.

HSO_3^-(Resin) vs H_2SO_3

The equilibrium constant of the reaction

$$H_2S^{34}O_3 + HS^{32}O_3^-(R) \rightleftharpoons H_2S^{32}O_3 + HS^{34}O_3^-(R)$$

where R = Dowex 2 resin, has been reported[12] to be 1.0100 ± 0.0005 based on column experiments at 20°C. This value is significantly different from that of 1.019 at 25°C measured by Thode[13] and co-workers between SO_2 gas and aqueous HSO_3^-. A separation factor of 1.0094 at 23°C was measured in a single-stage equilibration experiment, which appears to confirm the reported column data. A more detailed study of this system has been deferred pending mass spectrometer modifications to permit more accurate sulfur isotopic analysis.

CS_2, S^{--}, CS_3^{--} Isotopic Equilibrium

An aqueous solution containing 0.47 *M* Na_2S and 1.89 *M* Na_2CS_3 was equilibrated with a pure CS_2 phase for 35 hr at 18.5°C. Isotopic analyses were performed on SO_2 prepared from H_2S and CS_2 liberated on acidifying the aqueous phase, and from the pure CS_2 phase. The S^{32}/S^{34} ratios measured are given below:

$$\frac{H_2S \text{ from aq. phase}}{CS_2 \text{ phase}} = 1.014 \pm 0.010$$

$$\frac{CS_2 \text{ from aq. phase}}{CS_2 \text{ phase}} = 1.001 \pm 0.011$$

A possible explanation for the observed results is the nonequivalence of sulfur atoms in CS_3^{--}. Additional experiments are in progress with more dilute aqueous solutions to give a higher S^{--}/CS_3^{--} ratio.

INFRARED AND RAMAN SPECTRA OF ISOTOPIC MOLECULES

Spectral studies of the fundamental vibrational frequencies of isotopic molecules yield information concerning the bonding and configuration of the molecules, as well as data for the calculation of isotopic separation factors for isotopic exchange equilibria. The production of multigram quantities of highly enriched N^{15} by the isotope separation group has presented a unique opportunity for studying the spectra of nitrogen-containing compounds.

Infrared and Raman Spectra of N_2O_4 and NO_3^-

G. M. Begun W. H. Fletcher[14]

The infrared and Raman spectra of $N_2{}^{15}O_4$ as well as $N_2{}^{14}O_4$ were studied in the gas and liquid states. As a result the 11 active fundamental frequencies of N_2O_4 were assigned and the isotopic shifts of each frequency measured. Table 10 gives the measured frequencies and their assignments. The infrared frequencies (*u*) are for gaseous N_2O_4 and the Raman frequencies (*g*) for supercooled liquid N_2O_4 at −35°C. Measurements of many combination bands were also made. The data strongly support the planar N–N bonded structure for N_2O_4. A complete account of this work will be published soon.

Observations of the infrared and Raman spectra of $N^{14}O_3^-$ and $N^{15}O_3^-$ resulted in the frequencies shown in Table 11 for the isotopic molecules. These frequencies were used to calculate theoretical separation factors for the isotopic exchange

Table 10. Fundamental Vibrational Frequencies of N_2O_4

Assignment			Frequency (cm^{-1})	
			$N_2{}^{14}O_4$	$N_2{}^{15}O_4$
A_g	ν_1	(NO stretching)	1379.6	1360.2
	ν_2	(NO_2 bending)	808	797
	ν_3	(NN stretching)	266	264
A_u	ν_4	(torsion)	Inactive	
B_{1g}	ν_5	(NO stretching)	1711.6	1672.2
	ν_6	(NO_2 rocking)	482	476
B_{1u}	ν_7	(NO_2 wagging)	429	420
B_{2g}	ν_8	(NO_2 wagging)	672	654
B_{2u}	ν_9	(NO stretching)	1748	1707
	ν_{10}	(NO_2 rocking)	381	377
B_{3u}	ν_{11}	(NO stretching)	1262	1251
	ν_{12}	(deformation)	750	739

[12] S. Forberg *et al.*, p 243 in *Proceedings of the International Symposium on Isotope Separation*, North Holland Publ. Co., Amsterdam, 1958.

[13] H. G. Thode, R. L. Graham, and J. A. Zeigler, *Can. J. Research* 23B, 40 (1945).

[14] Consultant, University of Tennessee, Chemistry Department.

Table 11. $N^{14}O_3^-$ and $N^{15}O_3^-$ Vibrational Frequencies

Assignment	Frequency (cm^{-1})		Isotopic Shift (cm^{-1})
	$N^{14}O_3^-$	$N^{15}O_3^-$	
ν_1	1049.2	1049.2	0.0
ν_2	830.9	809.0	21.9
ν_3 (2)	1375.6	1343.7	31.9
ν_4 (2)	716.8	714.8	2.0

of nitrogen between NO and NO_3^-. The values have been compared with experimental separation factors and the results reported in the literature.[15]

Infrared Spectrum and Potential Function of Nitrosyl Chloride

L. Landau W. H. Fletcher[14]

The infrared spectra of $ClN^{14}O$ and $ClN^{15}O$ have been examined with a Perkin-Elmer model 112 prism spectrometer. All the fundamental bands and many of the overtone bands were observed.[16] The data obtained were sufficient to calculate the anharmonic constants, the zero-order frequencies, and the Fermi shift due to the interaction of ν_2 (N-Cl stretching) with $2\nu_3$, where ν_3 is the Cl-N-O bending frequency (Table 12).

The data were fitted by Oracle calculations to F matrices, first on the assumption that a van der Waals repulsion between the oxygen and chlorine atoms is predominantly responsible for the off-diagonal elements, and secondly on the assumption that the interaction is primarily due to orbital hybridization, coupling the bending vibration with the N-Cl stretching vibration. The two sets of force constants are quite similar, the first giving

$K_{N\text{-}O}$ = 14.12 millidynes/Å,
$K_{N\text{-}Cl}$ = 1.70 millidynes/Å,
$K_\gamma = 0.827 \times 10^{-11}$ ergs/radian^2,
A (van der Waals constant) = 0.014 millidynes/Å,

and the second giving

F_{11} = 14.11 millidynes/Å,

Table 12. Frequencies and Anharmonic Constants

Values in cm^{-1}, corrected to vacuum

	$ClN^{14}O$	$ClN^{15}O$
Observed frequencies		
ν_1	1800*	1769*
ν_2	595.5*	581.5*
ν_3	332.4	330.6
Fermi shift for ν_2	+9.2	+8.2
Anharmonic constants		
x_{11}^0	−18.3	−17.7
x_{22}^0	−8.0	−7.6
x_{33}^0	−2.0	−2.0
x_{12}^0	−8.0	−7.6
x_{13}^0	−3.9	−3.9
x_{23}^0	−4.9	−4.8
Zero-order frequencies		
ω_1	1842.6	1810.1
ω_2	626.8	610.8
ω_3	340.8	339.0

*Band origins were measured at the mid-point of the leading edge of the Q branches.

F_{22} = 1.72 millidynes/Å,
$F_{33} = 0.846 \times 10^{-11}$ ergs/radian^2,
$F_{23} = 3.1 \times 10^{-5}$ ergs/cm·radian.

A more detailed account of this work will be published in the near future.

Raman Studies of Metal Ammonia Complexes

A. C. Rutenberg

A solution of ~1.7 M $Zn(ND_3)_4Br_2$ in D_2O was prepared and its Raman spectrum observed. The spectrum gave no indication of H_2O contamination. A shift of 33 cm^{-1} for ν_1 (symmetric breathing frequency) was observed upon comparing the above solution with the hydrogen-containing complex. The values of ν_1 for the NH_3 and ND_3 complexes were inversely proportional to the square root of their masses, as would be the case for a simple harmonic oscillator.

[15] L. L. Brown and G. M. Begun, *J. Chem. Phys.* 30, 1206 (1959).

[16] L. Landau, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 15.

A value for ν_1 of 370 cm^{-1} was measured for a 3 *M* $Ag(NH_3)_2NO_3$ solution.

The Raman spectrum of a solution of composition $LiCl \cdot 2.1NH_3 \cdot 1.5H_2O$ failed to reveal any peaks which could be definitely attributed to an Li-N bond.

Mass Spectroscopy for Isotopic Assay

L. Landau

A 60°, dual-collector mass spectrometer has been acquired from Nuclide Analysis Associates. It was designed for the rapid comparison of the ratios of two adjacent (or near-adjacent) masses in the range of 10 to 100 in a pair of samples. A similar instrument has been described by Nier, Ney, and Inghram.[17]

Routine high-precision isotopic analyses have been performed on CO, CO_2, N_2, O_2, and NO. Modifications in the design of the mass spectrometer are in progress which may reduce memory effects sufficiently to allow high-precision analysis of SO_2 and BF_3.

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[17] A. O. Nier, E. P. Ney, and M. G. Inghram, *Rev. Sci. Instr.* 18, 294 (1947).

RADIATION CHEMISTRY

EFFECT OF IONIZING RADIATION ON CATALYSTS

H. W. Kohn G. E. Moore
E. H. Taylor

Previous work[1] has shown that ionizing radiation can cause substantial changes in the catalytic activity of several nonmetals and has encouraged the hope that particular kinds of point-defects could thereby be related to catalysis. Much of the work of the past year, with silica, is summarized in the following abstract:[2]

"Catalytic activity for H_2-D_2 exchange has been found in all of the types of silica examined, gel, quartz, α-cristobalite, vitreous and amorphous. The activity per unit surface differs widely, being highest for quartz and vitreous silica. Since these were prepared by grinding, the high activity may have been introduced by that process. The activity observed immediately after activation declines by a factor of ten or more over ten days, and more slowly for several weeks. Irradiation with gamma rays or neutrons produces a dramatic increase in the activity of these silicas. The activation energy with the gel is reduced by irradiation from about 9 to about 2 kcal./mole. Quartz and vitreous silica show low activation energies even before irradiation. The enhanced activity declines with time, but at a rate indistinguishable from that of the unirradiated materials. The activity obtained by irradiation has not been equalled in an unirradiated catalyst by any activation procedure. With the low activation energies observed, only a small number of sites is needed to explain the increases in activity. Since the yields of sites are likewise small, a primary process of low probability, such as atom displacement, is suggested. The activity per displaced atom is even lower for the neutron bombardments. Within rather large uncertainties, the activity increase per unit dose is nearly equal for the different types of silica. Three silica-alumina hydrocarbon cracking catalysts behaved much like the silicas. The similarities shown by the different silicas (and silica-alumina) may mean that the local arrangement of silicon and oxygen atoms is responsible for the catalytic activity, for the only common feature of the structures is the silicon-oxygen tetrahedron."

The two general mechanisms which may most likely account for the effects of radiation on catalysts are the displacement of atoms and the displacement of electrons. Irradiation with soft electrons or x rays can distinguish between these with metals or valence crystals, since there is a fairly sharp threshold energy for displacement of atoms when this occurs only by electron recoil. With ionic crystals there is not a sharp threshold, since mechanisms other than electron recoil can produce displacements. Silica gel has been irradiated with 250- and with 50-kev x rays, and a marked enhancement of activity for H_2-D_2 exchange was observed. Since the threshold for displacement by electron recoil would be not less than 150 kev, this suggests that ionization rather than atom displacement is responsible for the catalytic changes. The uncertainty lies in the possibility that silica is sufficiently an ionic crystal to permit displacements at a reasonable yield by 50-kev x rays.

Irradiation of silica gel, α-cristobalite, and quartz with gamma rays (10^{20} to 10^{21} ev/g) induces a measurable activity for ethylene hydrogenation, as well as the hydrogen-deuterium exchange activity already studied in detail.

Visible coloration, attributed to electrons or holes trapped at lattice imperfections, frequently results from irradiation of valence or ionic crystals. Because such physical properties may assist in characterizing the radiation damage which also results in catalytic changes, the colors of irradiated catalysts have been noted, but without any interesting correlations appearing. Recently, however, it was observed that the amethyst color of irradiated silica gel was destroyed instantly on exposure to the H_2-D_2 mixture used for assessing catalytic activity. Further experiments showed that C_2H_4, H_2O, NH_3, and Hg behaved similarly, except that the rate of bleaching was lower than with H_2. The color was unaffected by O_2 or by daylight and was thermally stable to around 250°C. The depth of color produced by radiation was the greater, the higher the temperature at which the

[1] H. W. Kohn and E. H. Taylor, *J. Phys. Chem.* **63**, 500 (1959).

[2] H. W. Kohn and E. H. Taylor, *J. Phys. Chem.* **63**, 966 (1959).

gel had been degassed, and varied somewhat between particles in coarse samples.

A weak, sharp paramagnetic resonance absorption line near the free-electron position ($g = 2$) was observed in irradiated silica gel and varied in strength from sample to sample approximately with the depth of color. It was, however, not identical with the color center, since it persisted after the latter was bleached with H_2.

Freshly degassed, unirradiated silica gel adsorbs almost no H_2 at room temperature and 100 μ. An irradiated, colored sample adsorbs H_2 under these conditions, becoming saturated with the disappearance of the color. Further irradiation produces more color, which can again be bleached in the same way. A few hours of irradiation have rendered a sample capable of adsorbing about 2×10^{18} molecules of H_2 per gram, and possessing, presumably, that number of color centers before bleaching (or twice as many if one molecule bleaches two centers).

A natural extension of the previous work is the study of heavy-particle irradiation of metals, where ionization cannot be stored. As a preliminary to this, some experiments in which metals (principally) have been irradiated with gamma rays in the presence of H_2-D_2 have shown that a measurable excess exchange occurs over that in the absence of the solid. This is apparently the result of energy transfer from solid to adsorbed gas, as suggested by Caffrey and Allen in the case of pentane adsorbed on various solids.[3] The principal conclusion to date is that at −196°C the various materials studied fall into two classes. One class shows a rate of exchange (for a given dose rate and ratio of gas to solid) of from 0.03 to 0.7 and consists of freshly reduced Pt, Ni, Cu, and Ge (both *n*- and *p*-type). The other shows a rate between 10^{-3} and 10^{-2} and consists of Au, Ag, activated charcoal, and air-poisoned Ni and Cu. Since these two groups are, respectively, catalysts and noncatalysts for the thermal exchange reaction, it appears that there is a connection between catalytic properties and efficiency for energy exchange.

[3] J. M. Caffrey and A. O. Allen, *J. Phys. Chem.* **62**, 33 (1958).

KINETICS OF THE RADIATION-INDUCED REDUCTION OF Ce(IV) IN SOLUTION CONTAINING Ce(IV), Ce(III), H_2, AND H_2SO_4 [4]

J. W. Boyle C. J. Hochanadel

Hydrogen enhances the yield for reduction of Ce(IV) by cobalt gamma rays. The yield depends not only on the ratio $[H_2]/[Ce(III)]$ but also on $[H_2]/[H_2SO_4]$, indicating a competition of these three solutes for OH radicals. Representing the yields of intermediates (H, OH, H_2, and H_2O_2) produced in the decomposition of water by G_H, G_{OH}, G_{H_2}, and $G_{H_2O_2}$, the maximum initial yields for Ce(IV) reduction in the absence and presence of H_2 are related to these quantities by

$$G[Ce(III)] = 2G_{H_2O_2} + G_H - G_{OH} ,$$

$$G[Ce(III)]_{H_2} = 2G_{H_2O_2} + G_H + G_{OH} .$$

The maximum value in the presence of H_2 is approached only at low acidities. Assuming that the species produced by reaction of OH with H_2SO_4 (presumably HSO_4) reacts with Ce(III) but not with H_2 and that Ce(IV) is reduced by H, HO_2, and H_2O_2, the derived rate equation expresses the results if the relative reactivities of Ce(III), H_2, and H_2SO_4 with OH radicals are as 650:100:1. Helium purging during radiolysis lowered the Ce(III) yield, presumably by removing O_2 as it was formed. The difference between helium-saturated and helium-purged solutions increased with increasing acidity and amounted to a factor of 2 in 4.0 *M* solutions. This effect may suggest that Ce(IV) reduction by H atoms occurs mainly through the HO_2 radical. Particular attention was addressed to purification, not only of the water, but also of the acid, cerium salts, and hydrogen. Results in all cases were reproducible. In air-saturated 0.4 *M* acid solution containing 4×10^{-4} *M* Ce(IV), the production of Ce(III) was linear with dose, $G[Ce(III)] = 2.38$, and the line passed through the origin, indicating no effect of impurities. By observing reasonably simple purification procedures, the latter reaction is reproducible and provides an excellent dosimeter.

[4] Abstract of paper presented at the International Congress of Radiation Research, Burlington, Vt., Aug. 11, 1958.

KINETICS OF THE RADIATION-INDUCED REACTION OF Fe(III) WITH Sn(II)[5]

J. W. Boyle S. Weiner[6]
C. J. Hochanadel

Cobalt gamma rays induce reaction of Fe(III) with Sn(II). For dilute solutions in deaerated 0.4 *M* H_2SO_4 the initial product yields per 100 ev of energy absorbed are

$$G[\mathrm{Fe(II)}] = 6.62 \ ,$$

$$G[\mathrm{Sn(IV)}] = 3.75 \ ,$$

$$G(\mathrm{H_2}) = 0.45 \ .$$

Assuming the primary chemical species in the decomposition of water to be H, OH, H_2, and H_2O_2 produced with yields G_H, G_{OH}, G_{H_2}, and $G_{H_2O_2}$, the initial product yields are related to these quantities as follows:

$$G[\mathrm{Fe(II)}] = G_H + G_{OH} \ ,$$

$$G[\mathrm{Sn(IV)}] = G_{H_2O_2} + G_{OH} \ ,$$

$$G(\mathrm{H_2}) = G_{H_2} \ .$$

The initial yields indicate a mechanism in which Sn(II) is reduced by H to Sn(I) and oxidized by OH to Sn(III), Fe(III) is reduced by Sn(I) and Sn(III), and Fe(II) is oxidized by H_2O_2. The presence of Sn(II) in deaerated Fe(II) solutions lowers the yield for oxidation of Fe(II), and, at concentration ratios [Sn(II)]/[Fe(II)] > 0.02, oxidation of Fe(II) is completely suppressed. Irradiation of deaerated Sn(II) solution produces Sn(IV) and H_2 with a yield of 0.49, which is equivalent to G_{H_2}. On the basis of proposed mechanisms and the dependence of yields on relative concentrations, the following ratios of rate constants were evaluated:

$$k_{[\mathrm{Fe(II)+OH}]} : k_{[\mathrm{Sn(II)+OH}]} = 1:7.0 \ ;$$

$$k_{[\mathrm{Fe(II)+H}]} : k_{[\mathrm{Sn(II)+H}]} : k_{[\mathrm{Sn(IV)+H}]} : k_{[\mathrm{Fe(III)+H}]} = 1:\sim 5000:0.16:0.081 \ ;$$

$$k_{[\mathrm{Fe(II)+H_2O_2}]} : k_{[\mathrm{Sn(II)+H_2O_2}]} = 100:1 \ .$$

The rapid rate of reduction of Sn(II) by H atoms is especially noteworthy.

VAN de GRAAFF IRRADIATION OF FUSED $NaNO_3$

J. W. Boyle

Irradiation of molten $NaNO_3$ (300–320°C) with Van de Graaff electrons gave an oxygen yield of $\sim 0.35 \pm 0.1$ molecule per 100 ev, similar to that observed in the gamma irradiation of solid $NaNO_3$ at room temperature.[7] The only products detected were O_2 and NO_2^-, produced in equivalent yields. As the nitrite concentration built up, N_2 and oxides of nitrogen were produced with increasing yields and the melt changed from colorless to pale yellow. In a 10% $NaNO_2$ mixture the total gas yield was approximately one-tenth the gas yield in pure $NaNO_3$. In a mixture of 20% $NaNO_3$ and 80% $NaNO_2$, O_2 was not observed and N_2 and N_2O were present in about equal amounts. Molten $NaNO_2$ gave mainly N_2 with some N_2O and no O_2.

CERIC REDUCTION AND THE RADIOLYTIC HYDROGEN YIELD[8]

H. A. Mahlman

The hydrogen yields[9] observed in the Co^{60} gamma-ray irradiation of 0.4 *M* H_2SO_4 solutions

[5] J. W. Boyle, S. Weiner, and C. J. Hochanadel, *J. Phys. Chem.* **63**, 892 (1959).

[6] Summer research participant, 1958, University of Wisconsin, Wausau Extension Center, Wausau.

[7] C. J. Hochanadel and T. W. Davis, *J. Chem. Phys.* **27**, 333 (1957).

[8] H. A. Mahlman, *J. Am. Chem. Soc.* **81**, 3203 (1959).

[9] C. J. Hochanadel and S. C. Lind, p 83 in *Annual Reviews of Physical Chemistry* (ed. by H. Eyring), vol. 7, Annual Reviews, Palo Alto, Calif., 1956.

and dilute H_2SO_4 solution with pH = 2 have been generally accepted to be 0.40 and 0.45, respectively. In disagreement, the hydrogen yields in 0.4 *M* H_2SO_4 and 0.5×10^{-3} to 0.5×10^{-6} *M* H_2SO_4 solutions containing 10^{-3} *M* KBr were observed[10] to be the same and were equal to 0.45. The extrapolated hydrogen yield observed in the irradiation of sulfuric acid solutions of ceric ion is 0.44 and indicates an acid independence up to 0.8 *M* H_2SO_4. The suppressive action of the solute may be expressed by the equation

$$G(H_2) = -0.21[\mathrm{Ce(IV)}]^{1/3} + 0.44 \quad .$$

Furthermore, the scavenging effect of ceric ion indicates that the theoretical cerous yield may be obtained only in infinitely dilute ceric solutions.

THE ACTIVITY COEFFICIENT IN RADIATION CHEMISTRY[11]

H. A. Mahlman

The hydrogen yields observed in the Co^{60} gamma-ray irradiation of sodium nitrate solutions have been shown to be a linear function of the cube root of the sodium nitrate activity[12] for solutions less than 1.0 *M*. A rigorous test of this hypothesis was obtained by alteration of the scavenging solute activity by the addition of electrolytes. The electrolytes NaCl (1.0–5.0 *M*), $CaCl_2$ (0.30–2.02 *M*), and $AlCl_3$ (0.066–1.02 *M*) were added to sodium nitrate solutions that were 0.01 to 1.07 *m*. The hydrogen yields as calculated by means of the equation

$$G(H_2) = 0.46 - 0.46(\gamma[\mathrm{NaNO_3}])^{1/3}$$

and as observed are in agreement.

RADIATION-INDUCED GAS-PHASE REACTIONS

A. R. Jones

Methane and oxygen mixtures of various mole ratios were irradiated with fast electrons in a static system near room temperature. Periodic infrared analysis of the reaction mixtures identified the products of the oxidation and the number of molecules of each formed as a function of the energy absorbed by the gas mixture. For mixtures containing more than 95 mole % oxygen, the only products are carbon dioxide, water, and ozone. For mixtures containing less than 62 mole % oxygen, the carbon-containing products (in order of decreasing abundance) are methanol, formic acid, carbon monoxide, carbon dioxide, ethylene, and acetylene. The last two compounds have not been previously reported as products of this reaction. Only traces of peroxidic compounds were apparent. The absence of formaldehyde was confirmed.

Earlier workers, lacking sensitive and specific analytical methods, had to carry this reaction much farther than in the present experiments, and the presence of liquid water during much of the reaction, as well as the restriction to conventional gas analysis, led to the differences between their results and the present results. Thus Lind and Bardwell[13] reported that the oxidation proceeded directly to carbon dioxide and water. These products and, in addition, small amounts of carbon monoxide, hydrogen, and formic acid were found by McLennan and Glass.[14] The final products appear to result from rearrangement, decomposition, and reaction of the primary product, the peroxy radical CH_3O_2.

Infrared analysis of cuprene, the product of the radiation-induced polymerization of acetylene, suggests that it is a network of aromatic rings. This result is in keeping with its physical properties and the fact that the only other chemical species produced is benzene. The low-molecular-weight polymer from the radiation-induced, gas-phase polymerization of benzene was similarly shown to consist of short aliphatic chains with pendant aromatic rings, some of which interconnect chains. The spectrum strongly resembles that of irradiated polystyrene.

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[10] H. A. Mahlman and J. W. Boyle, Jr., *J. Am. Chem. Soc.* **80**, 773 (1958).

[11] Abstract of paper presented at the 134th Meeting of the American Chemical Society, Chicago, September 1958.

[12] H. A. Mahlman, "The Activity Coefficient in Radiation Chemistry," *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 21.

[13] S. C. Lind and D. C. Bardwell, *J. Am. Chem. Soc.* **48**, 2335–51 (1926).

[14] J. C. McLennan and J. V. S. Glass, *Can. J. Research* **3**, 241 (1930).

ORGANIC CHEMISTRY

CALCULATION OF ISOTOPE EFFECT FUNCTIONS FOR HOMOCOMPETITIVE FIRST-ORDER REACTIONS

C. J. Collins M. H. Lietzke

The Oracle has been employed to determine, for first-order irreversible reactions, the relation between the fraction of reaction

$$f = 1 - e^{-kt}$$

and the accumulated product ratio

$$R = \frac{1 - e^{-k^*t}}{1 - e^{-kt}}$$

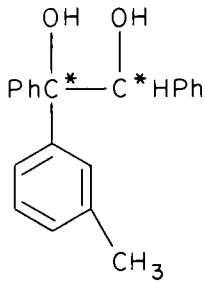
over a range of values for the isotope effect (k^*/k) of 0.05 to 0.999, where k^* and k are the appropriate first-order specific reaction rate constants. Similar calculations have been made for f as a function of the ratio x of the differentials of the fractions of labeled to unlabeled molecules formed. The results have been presented in tabular[1] and graphical[2] form and have been discussed[2] with respect to their relation to the validity of isotopic tracer experiments.

MOLECULAR REARRANGEMENTS

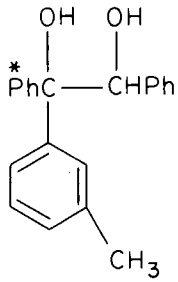
Pinacol Rearrangement of the Diphenyl-*m*-tolylethylene Glycols

C. J. Collins N. S. Bowman[3]

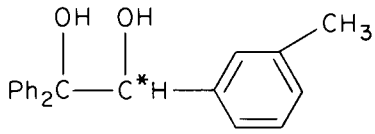
Erythro-I*ab* (70.9% C^{14} in C-1, 29.1% in C-2), threo-I*c*, and II*a*, as well as the two ketones IV and V, were prepared by standard methods:[4]



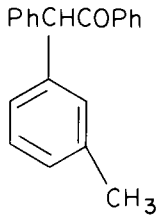
Erythro-I*ab*



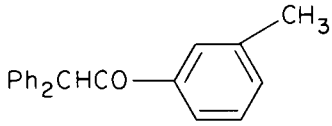
Threo-I*c*



II*a*



IV



V

The radiochemical structures of I*ab* and I*c* were proved by oxidative degradation of the glycols to

[1] M. H. Lietzke and C. J. Collins, *Tables of Isotope Effect Functions for Homocompetitive First-Order Reactions*, ORNL-2678 (April 24, 1959) and supplement thereto.

[2] C. J. Collins and M. H. Lietzke, "The Isotope Effect and Its Relation to the Validity of Isotopic Tracer Experiments," *J. Am. Chem. Soc.* 81 (1959) (in press).

[3] Research participant, University of Tennessee, summer, 1958.

[4] See, for example: C. J. Collins, *J. Am. Chem. Soc.* 77, 5517 (1955); B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.* 78, 4329 (1956); V. F. Raaen and C. J. Collins, *J. Am. Chem. Soc.* 80, 1409 (1958); L. W. Kendrick, Jr., B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.* 80, 4057 (1958).

phenyl *m*-tolyl ketone and benzoic acid, followed by radioactivity assay of these fragments. Similarly the radiochemical structure of II*a* was shown by oxidation to *m*-toluic-C^{14} acid and nonradioactive benzophenone. The yields of the ketones IV and V, upon rearrangement of erythro-I*ab*, threo-I*c*, and II*a* in the presence of concentrated sulfuric acid at 0°C, were determined as before[4] by the isotope dilution method. The results of these yield determinations are given in Table 13.

The determination of the percentage C^{14} scrambling exhibited by ketones IV and V after rearrangement of the appropriate glycol was carried out in standard[4] fashion. Results of degradative experiments performed on glycols I*ab*, I*c*, and II*a* are given in Table 14.

The significance of the foregoing data is discussed in the paper by Collins and Bowman.[5] These data support in every respect the mechanism previously[4] proposed for the pinacol rearrangement.

[5]C. J. Collins and N. S. Bowman, "Molecular Rearrangements. XVI. The Pinacol Rearrangement of the Diphenyl-*m*-Tolylethylene Glycols," *J. Am. Chem. Soc.* 81 (1959) (in press).

[6]ORINS predoctoral Fellow, University of Florida.

[7]C. J. Collins, W. A. Bonner, and C. T. Lester, *J. Am. Chem. Soc.* 81, 466 (1959).

Table 13. Yields of Ketones IV and V upon Rearrangement of I or II in Concentrated H_2SO_4 at 0°C

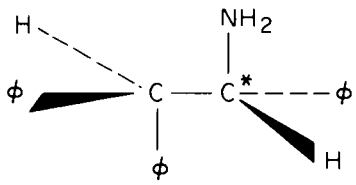
Reactant	Combined Yields of IV and V (%)	Yield (%) of Ketone*	
		IV	V
Erythro-I*ab*	94.9**	69.7	30.3
Threo-I*c*	97.0	70.9	29.1
II*a*	99.5	63.2	36.8

*Adjusted to 100%.
**In a gravimetric determination the yield was 94.6%.

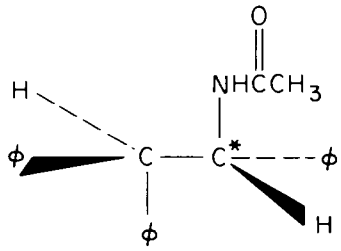
Configurational Relationship of (+)-1,2,2-Triphenylethylamine with (+)-1,2,2-Triphenylethanol

C. J. Collins J. B. Christie[6]

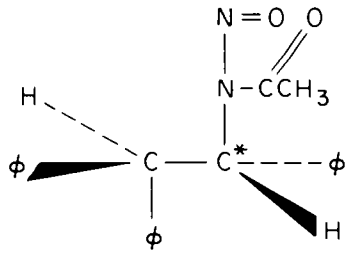
The stereochemistry of the deamination of 1,2,2-triphenylethylamine in aqueous solution containing a small concentration of acetic acid has been reported.[7] Thus, for example, D-(+)-1,2,2-triphenylethylamine (I) yielded, in addition to olefin, acetate, and racemic carbinol, approximately 25% of D-1,2,2-triphenylethanol (V), representing a net retention of configuration:



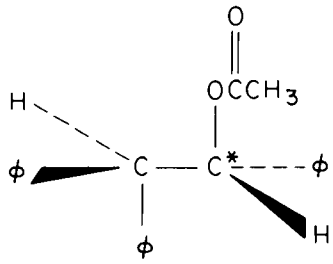
D-I*a*



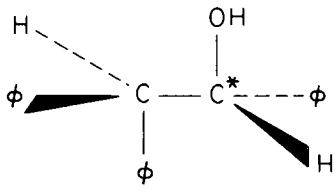
D-II*a*



D-III*a*



D-IV*a*



D-V*a*

Table 14. Molar Radioactivities of Degradation Products of Ketones IV and V Obtained by the Action of Concentrated H_2SO_4 at 0°C upon I*ab*, I*c*, and II*a*

Molar radioactivities of reactants taken as 1.000

Reactant	*m*-Benzoylbenzoic Acid from IV	Benzophenone from V
I*ab*[a]	0.709 ± 0.003	0.704 ± 0.002
I*c*	0.596 ± 0.003	1.000[b]
II*a*[c]	0.042 ± 0.000	0.012 ± 0.000

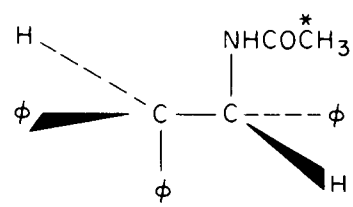
[a] I*ab* contains 0.709 C^{14} in the tertiary carbon and 0.291 C^{14} in the secondary carbon.

[b] Single determination.

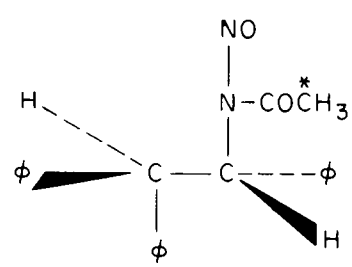
[c] II*a* upon oxidative degradation exhibited 0.009 C^{14} in the tertiary carbon.

Resolution of the carbinol produced from labeled reactant, followed by determinations of the C^{14} distributions in these resolved products, served as evidence that rearranging, open, unbridged carbonium ions were responsible for the retention. Presumptive evidence for like configurations of amine I and carbinol II of like signs of rotation was based upon optical rotary dispersion data,[7,8] upon comparison with the results of solvolyses of labeled, optically active 1,2,2-triphenylethyl tosylate, and upon melting-point-composition diagrams.[9,10] The thermal decomposition of (–)-*N*-nitroso-*N*-acetyl-1,2,2-triphenylethylamine (III) to produce acetate containing 70% (+)-1,2,2-triphenylethyl acetate (IV) and 30% of the (–)-isomer, however, was the chemical evidence upon which the configurational assignment was made. The work of Huisgen[11] and of White[12] has established that the thermal decompositions of *N*-nitrosoamides ordinarily proceed with partial retention of configuration. Although solvent competition[11,12] can in some cases produce inversion, that portion of the decomposition which proceeds intramolecularly yields esters of predominantly retained configuration. The *N*-nitroso derivative III is sufficiently different[13] from the compounds studied by Huisgen[11] and by White,[12] however, that we sought additional confirmation of the mechanism of its decomposition prior to a rigorous assignment of configuration. The present data not only leave no doubt concerning the configuration of the D-(+)-carbinol (V) produced upon deamination of the D-(+)-amine (I), but also offer some interesting evidence concerning the mechanism of the thermal decomposition of IV. These data, which were referred[7] to in a preliminary manner, are now recorded.

1,2,2-Triphenylethylamine (I) and 1,2,2-triphenylethyl-1-C^{14}-amine (I*a*) were prepared and resolved as previously reported,[7,12] then converted to the isotope position isomers II*a* and II*c*. The *N*-nitroso derivatives III*a* and III*c* were prepared by a modification of the method of France, Heilbron, and Hey:[14]



D – II*c*



D – III*c*

[8] Although the optical rotary dispersion curves of (+)-II and (+)-IV were very similar, no Cotton effect was exhibited, so these data alone could not be used as configurational evidence.

[9] A. Fredga in *The Svedberg*, p 261 ff, Almqvist and Wiksells, Uppsala, Sweden, 1955; *Arkiv Kemi* 11, 23 (1957).

[10] K. Mislow and M. Heffler, *J. Am. Chem. Soc.* **74**, 3668 (1952); K. Mislow and W. C. Meluch, *J. Am. Chem. Soc.* 78, 5920 (1956). We are indebted to K. Mislow for pointing out the utility of the Fredga method and for interpretation of our data in this connection reported in ref 7.

[11] R. Huisgen and C. Rüchardt, *Ann. Chem., Liebigs*, 601, 21 (1956).

[12] E. H. White, *J. Am. Chem. Soc.* 77, 6011, 6014 (1955); E. H. White and C. A. Aufdermarsh, *J. Am. Chem. Soc.* 80, 2597 (1958).

[13] C. J. Collins and W. A. Bonner, *J. Am. Chem. Soc.* 75, 5372, 5379 (1953); *J. Am. Chem. Soc.* 77, 92, 99, 6725 (1955); *J. Am. Chem. Soc.* 78, 5587 (1956).

[14] H. France, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.* 1940, 369.

The kinetics of the decomposition of III*a* in *p*-cymene at 34.7°C were followed polarimetrically, as were the decompositions at 34.7, 40.5, and 47.7°C in acetic acid. The first-order rate constants (k_1) with respect to III*a* were calculated by means of the equation

$$k_1 = \frac{1}{t} \ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty},$$

where t is the time in hours, α_0, α_t, and α_∞ being the respective polarimeter readings at $t = 0$, $t = t$, and $t = \infty$. The rate constants, k_1, and α_0 and α_∞ were all determined with the assistance of the Oracle,[15] those values being chosen for which the standard errors in k_1 were minima. The results are listed in Table 15, together with the results of determinations of the per cent inversion (and retention) under all of the same conditions. Also given in Table 15 are the percentages of C^{14} rearrangement exhibited by the retained and inverted products derived from III*a* and the percentages of radioactive acetate kept by the retained and inverted products derived from III*c*. The chemical purity of each carefully crystallized fraction was ordinarily demonstrated by its infrared spectrum. The infrared determinations proved very useful in proving the absence of small percentages of amide (II) from these acetate (IV) fractions.

Finally, D-(+)- and L-(–)-1,2,2-triphenylethyl-1-C^{14}-amine (I*a*) were subjected to deamination in acetic acid solution to which sodium nitrite was gradually added, the D-(+)- or L-(–)- and DL-acetates were separated, and the per cent rearrangement in each was determined by methods previously[7,12] employed. The results of these experiments are recorded in Table 16.

The data of Table 15 clearly indicate that in the solvents employed nitrosoamide (III) undergoes thermal decomposition to 1,2,2-triphenylethyl acetate (IV) with predominant retention of configuration. Two mechanisms have been proposed for the nitrosoamide decomposition, the concerted, cyclic mechanism of White[12] and the ion-pair mechanism of Huisgen.[11] In both mechanisms the diazo ester is assumed to be an intermediate. Streitwieser and Schaeffer,[16] on the basis of their

[15] M. H. Lietzke assisted with the calculations.

[16] A. Streitwieser and W. D. Schaeffer, *J. Am. Chem. Soc.* 79, 2893 (1957).

Table 15. Summary of Kinetic, Stereochemical, and C^{14} Data for the Thermal Decompositions of III*a* and III*c* to IV*a* and IV*c*

Reactant	Solvent	Temperature (°C)	k_1 (hr^{-1})	Standard Error	Per Cent Inversion	Per Cent Retention	Per Cent C^{14} Rearrangement	
							Retained	Inverted*
III*a*	None	94–95			24.4	75.6	15.7	29.1
III*a*	Benzene	23			23	77	15.4	22.4
III*a*	*p*-Cymene	34.7	0.067	$\pm 1.5 \times 10^{-4}$	25, 24	75, 76		
III*a*	Acetic acid	34.7	0.323	$\pm 0.9 \times 10^{-4}$	29, 30	71, 70		
III*a*	Acetic acid	40.5	0.830	$\pm 1.0 \times 10^{-2}$	30, 29.5, 29	70, 70.5, 71	28.1	38.8
III*a*	Acetic acid	47.7	1.76	$\pm 1.3 \times 10^{-2}$	29, 28.5	71, 71.5	28.7	40.1
III*a*	Acetic acid	59.0			30.5	70.5	28.9	39.4
III*c*	Acetic acid	40.5					41.7	11.0
III*c*	Acetic acid	40.5					42.2	12.3

*Calculated from the observed rearrangements in the retained and racemic products.

Table 16. Summary of Radiochemical Data for the Products of Deamination of D- and L-1,2,2-Triphenylethyl-1-C^{14}-amine (I*a*) in Acetic Acid at 23°C

Reactant	Per Cent Retention	Per Cent Inversion	Per Cent Rearrangement		
			Retained	Racemic	Inverted*
D-(+)-I*a*	69.9	30.1	20.2	24.5	28.8
L-(−)-I*a*	70.0	30.0	24.9	27.1	29.3

*Calculated from the rearrangements in the retained and racemic products.

observations upon the decomposition of *N*-(1-butyl-1-*d*)-*N*-nitrosoacetamide, seem to favor the ion-pair[11] mechanism. Whatever mechanism is assumed, however, it appears axiomatic that the enantiomeric product identified with the radioactive acetoxyl moiety (Table 15) should have the same configuration as the reactant. The configurations of I and V are thus established.

Radiochemical Studies on the Rearrangement of 1,1-Diphenyl-2-aminopropane

B. M. Benjamin

Data obtained from a study[17] of the rearrangement with nitrous acid of 1,1-diphenyl-2-aminopropanol stereospecifically labeled with C^{14} in one of the phenyl groups were interpreted as demonstrating the first clear-cut case of open carbonium-ion intermediates in this type of reaction. This experiment suggested that it should be possible to synthesize stereospecifically labeled compounds which were not previously obtainable and that the deamination of 1,1-diphenyl-2-aminopropane (I) should be studied and the results compared with the data involving the similar compound containing the hydroxyl group. Accordingly, phenyl-C^{14}-labeled 1,2-diphenyl-1-amino-2-propanol (II) was prepared, and resolved by fractional crystallization of its *d*-tartaric acid salt. Optically pure (−)-aminoalcohol hydrochloride (II*a*) was deaminated in aqueous solution, and the ketonic product was converted to phenyl-C^{14}-labeled 1,1-diphenyl-2-aminopropane (I). The amine (I) was then resolved by fractional crystallization of the *d*-10-camphorsulfonic acid and the *d*-camphoric acid salts. The optically pure (−)-amine hydrochloride I*a* was subjected to the conditions of deamination. The rearrangement product was separated into three components, an olefinic material, L-(+)-threo-1,2-diphenyl-1-propanol, and L-(+)-erythro-1,2-diphenyl-1-propanol. No racemic carbinol fraction was found. The carbinol fractions were subjected to degradative procedures to yield benzoic acid and acetophenone oxime. These degradation products were assayed for their C^{14} content.

In a similar manner the (+)-aminoalcohol hydrochloride II*b* was deaminated and the ketonic product was converted to 1,1-diphenyl-2-aminopropane. The latter compound was then resolved. Pure (−)-aminohydrochloride I*b* upon deamination gave, as before, a product consisting of (1) an olefinic fraction, (2) L-(+)-threo-1,2-diphenyl-1-propanol, and (3) L-(+)-erythro-1,2-diphenyl-1-propanol. The results of C^{14} assay of the degradation products of the carbinols were then obtained. From the data involving amine I*a* [prepared from (−)-aminoalcohol hydrochloride II*a*] it appears that migration of the radioactive phenyl group took place preferentially, 73% of the time, in the formation of both the threo and erythro diastereoisomeric products. A consistent result was obtained from amine I*b* prepared from (+)-aminoalcohol hydrochloride II*b*. In this case the radioactive phenyl group underwent migration 27% of the time.

In addition to the above experiments, chain-labeled 1,1-diphenyl-2-aminopropane (I*c*) was prepared and deaminated in the same way as was the phenyl-labeled compound. The product was separated into three equal aliquots. Two aliquots were used to determine the yields of threo- and erythro-1,2-diphenyl-1-propanol by the isotopic dilution technique. The product was found to contain 54.7% of the threo carbinol and 10.6% of

[17] B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J. Am. Chem. Soc.* 79, 6160 (1957).

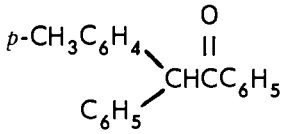
the erythro carbinol. Thus the threo to erythro ratio was 5.2. A sample of pure threo-carbinol was isolated from the third aliquot above. Oxidative degradation of this material and assay of the degradation fragments showed that C^{14} in the chain underwent less than 1% scrambling during the deamination rearrangement reaction.

It is possible to draw several conclusions from the above data concerning the deamination of 1,1-diphenyl-2-aminopropane: no methyl migration takes place; the mechanism must involve classical, open carbonium-ion intermediates; and rotation about the central carbon-carbon bond in the ionic intermediate is not infinitely fast compared with phenyl migration.

STEREOCHEMICAL STUDIES OF AN OXIDATION AND A BROMINATION REACTION

V. F. Raaen

Optically active *p*-tolyldesoxybenzoin



was treated with a mixture of boiling nitric and acetic acids. The *p*-tolylbenzoin that was produced in this reaction was reduced with lithium aluminum hydride; the glycol formed was optically inactive.

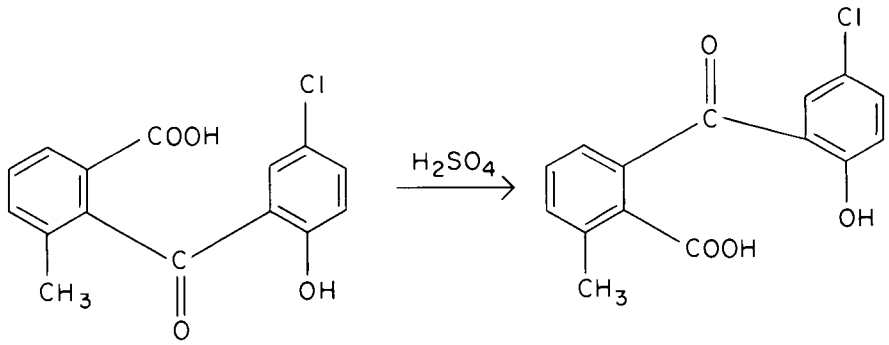
The optically active *p*-tolyldesoxybenzoin was also racemized rapidly by passage through a short column of chromatographic-grade alumina and also by boiling in acetic acid solution containing 10% concentrated hydrochloric acid. Optical activity was retained when the compound was dissolved at 0° C in concentrated sulfuric acid and permitted to stand for a period of 16 hr.

There is little evidence for the retention of optical activity by compounds that undergo a free-radical reaction at the optically active carbon atom. Because bromination by *N*-bromosuccinimide is thought to occur by a free-radical mechanism, it was of interest to allow this brominating agent to interact with *p*-tolyldesoxybenzoin. The reaction appeared to involve the methyl group, with little or no reaction taking place at the hydrogen alpha to the carbonyl group. The sign of rotation was reversed, but the experiment must be regarded as inconclusive.

A TRACER STUDY OF THE CYCLIZATION OF *o*-BENZOYLBENZOIC ACID

G. A. Ropp

Certain substituted *o*-benzoylbenzoic acids are known to undergo the Hayashi rearrangement[18] under conditions which are favorable for cyclization:

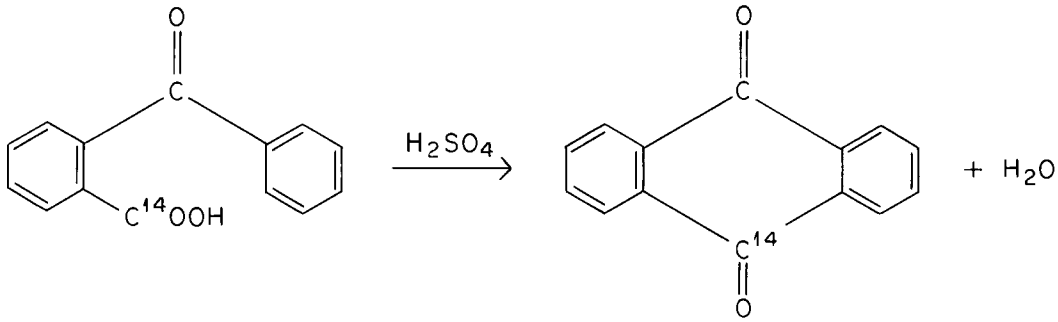


In this case rearrangement can be observed because the ring bearing the carboxyl group also bears a methyl group. That is to say, the product

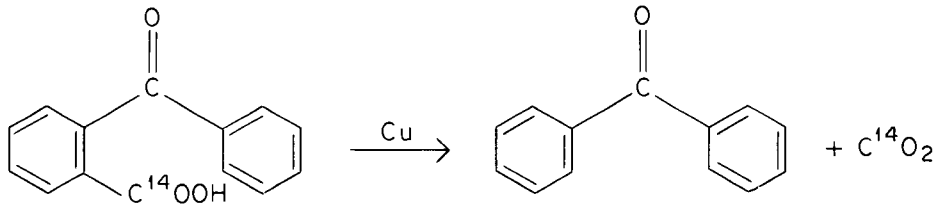
[18] R. B. Sandin *et al.*, *J. Am. Chem. Soc.* 78, 3817 (1956).

and the starting material are distinguishable because the methyl and carboxyl groups are meta in the starting material and ortho in the product. With unsubstituted *o*-benzoylbenzoic acid, such a rearrangement could not be detected since the starting material and the product would be identical. However, a Hayashi rearrangement of *o*-benzoylbenzoic acid-carboxyl-C^{14} could be detected by an isotopic tracer technique.

To test for Hayashi rearrangement, a sample of *o*-benzoylbenzoic acid-carboxyl-C^{14} was heated to 80°C in concentrated sulfuric acid. Under the conditions used about 16.5% of the acid was cyclized to anthraquinone:



The remaining uncyclized acid was recovered[19] and degraded to benzophenone by decarboxylation in the presence of copper at 280°C:



The benzophenone was converted to the pure 2,4-dinitrophenylhydrazone derivative. Radioassay indicated only negligible C^{14} activity in the derivative. Hence no appreciable amount of rearrangement had occurred, since a Hayashi rearrangement would have led to C^{14} activity in the keto group.

[19] G. A. Ropp, *J. Chem. Phys.* 23, 2196 (1955).

ISOTOPIC EVIDENCE FOR THE MECHANISMS OF DECARBONYLATION OF CARBOXYLIC ACIDS IN SULFURIC ACID

G. A. Ropp

The general equation for decarbonylation of carboxylic acids in sulfuric acid is:

$$RCOOH \xrightarrow{H_2SO_4} ROH + CO\uparrow$$

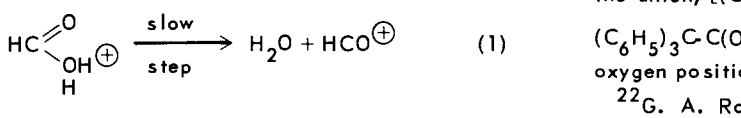
The dependence of reaction rate on acidity has frequently been used as a criterion of the reaction mechanism. It is significant that the mechanism proposed[20] on this basis for the decarbonylation of triphenylacetic acid in concentrated sulfuric acid is *not* supported by isotopic studies.

A small C^{14} isotope effect, $k_{12}/k_{14} \leqq 1.01$, found for decarbonylation of triphenylacetic-2-C^{14} acid is not nearly as large as that to be expected if carbon-carbon bond cleavage were rate-determining, as was suggested.[20] Furthermore, this decarbonylation, in O^{18}-enriched sulfuric acid,

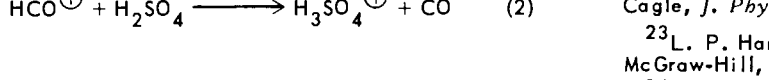
[20] N. C. Deno and R. W. Taft, Jr., *J. Am. Chem. Soc.* 76, 248 (1954).

was shown to produce carbon monoxide having an enrichment of only about 20% of that of the sulfuric acid. Hence equilibrium between the oxocarbonium ion and the free acid is not attained[21] as Deno and Taft proposed.[20] It appears rather that the mechanism of triphenylacetic acid decarbonylation is similar to the formic acid decarbonylation mechanism discussed below and differs from it only in that there is time for a small amount of back reaction of the oxocarbonium ion with water.

Isotope effects, $k_H/k_D = 1.5$ with formic-*d* acid and the previously reported[22] value of $k_{12}/k_{14} = \sim 1.09$ with formic-C^{14} acid, are in accord with the usually quoted Hammett[23] mechanism of decarbonylation of formic acid in sulfuric acid. The large C^{14} effect indicates that carbon-oxygen cleavage of the protonated species is rate-determining:



(1)



(2)

The deuterium isotope effect, which has the magnitude of a secondary effect, indicates that some alteration of the carbon-hydrogen bond occurs as the carbon-oxygen bond is stretched.

For the decarbonylation of benzoylformic acid in sulfuric acid, two measured C^{14} isotope effects are consistent with the previously proposed mechanism,[24] in which the slow step is loss of a hydronium ion from the di-protonated species:

Thus the recently measured isotope effect,[25] $k_{12}/k_{14} = \sim 1.1$ for decarbonylation of benzoylformic-1-C^{14} acid, is to be expected if cleavage of the carbon-oxygen bond of the carboxyl group controls the rate.[26] A smaller C^{14} isotope effect with benzoylformic-2-C^{14} acid, $k_{12}/k_{14} = 1.036$, is probably due to the effect of isotopic substitution at the number 2 carbon atom on the equilibrium constant of reaction (3).

When formic acid and benzoylformic acid were decarbonylated in O^{18}-enriched sulfuric acid, the isotopic composition of the carbon monoxide was normal in both cases. This is further evidence in favor of the mechanisms written for these reactions.

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[21] Rapid equilibrium involving O^{18}-enriched water should lead to complete enrichment of the carbon monoxide. Although the two oxygen atoms in the free acid are not quite equivalent, transient formation of either the anion, $[(C_6H_5)_3C\text{-}COO]^-$, or the protonated species, $(C_6H_5)_3C\text{-}C(OH)_2^+$, should rapidly equilibrate the two oxygen positions in the acid molecule.

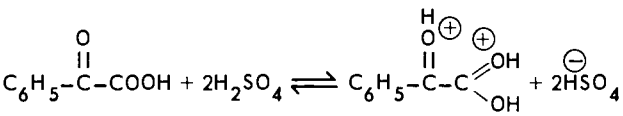
[22] G. A. Ropp, A. J. Weinberger, and O. K. Neville, *J. Am. Chem. Soc.* **73**, 5573 (1951); H. Eyring and F. W. Cagle, *J. Phys. Chem.* **56**, 889 (1952).

[23] L. P. Hammett, *Physical Organic Chemistry*, p 283, McGraw-Hill, New York, 1940.

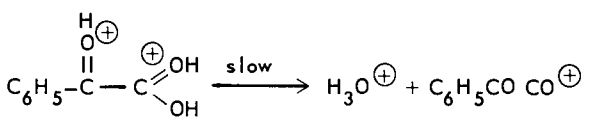
[24] W. W. Elliott and D. L. Hammick, *J. Chem. Soc.* 1951, 3402.

[25] B. Fingerman and R. M. Lemmon, "Isotope Effect in the Decarbonylation of Benzoylformic Acid," *Bio-Organic Chemistry Quarterly Report of the Radiation Lab., Univ. of California, Berkeley, Calif., December, January, and February, 1958*, UCRL-8204.

[26] As reported earlier by K. Banholzer and H. Schmid, *Helv. Chim. Acta* **39**, 548 (1956), the carbon monoxide comes from the carboxyl group. The carbon monoxide from decarbonylation of benzoylformic-2-C^{14} acid was not radioactive.



(3)



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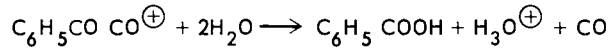

(5)

SOLUBILITY OF TRIBUTYLPHOSPHINE OXIDE IN WATER

C. E. Higgins W. H. Baldwin
R. W. Higgins[27]

Interactions between tributyl phosphate and aqueous electrolytes have been reported.[28,29] Tributylphosphine oxide has a lower molecular weight (218 compared with 266 for tributyl phosphate) and has stronger specific interactions with aqueous electrolytes.

The solubility of tributylphosphine oxide in water at 25°C is much greater than that of tributyl phosphate (55 compared with 0.4 g/liter). Hydrochloric acid in the aqueous phase had little effect on the solubility until the concentration of HCl exceeded 3 *M*, when the solubility of tributylphosphine oxide increased. Tributylphosphine oxide was less soluble in aqueous nitric acid than in water.

The investigation of the effect of a temperature rise[29] that inevitably occurs on centrifuging upon the observed solubility of both tributyl phosphate and tributylphosphine oxide in water has been extended. The temperature has an inverse effect upon the solubility. The system reaches equilibrium quite rapidly, and it has been found possible to measure the solubility at higher temperatures by centrifuging the solution that was equilibrated at 25°C and then measuring the resulting temperature and the concentration of the phosphorus compound.

The mutual miscibility of water and tributylphosphine oxide has been studied over a wide range of temperatures (13 to 99°C) with the aid of the refractometer standard solutions. At 13°C the two were completely miscible, with the solubility decreasing as the temperature was increased. The refractive index was measured at 25°C. The dilute solutions from the higher temperature equilibrations were merely cooled to 25°C before measurement. Solutions that had been saturated at temperatures below 25°C were diluted with sufficient water so that on warming to 25°C a homogeneous solution was obtained.

These results are being submitted for publication in *Analytical Chemistry.*

"POLYMER" FORMATION DURING RADIOLYSIS OF NEUTRAL PHOSPHATE ESTERS

W. H. Baldwin

The radiolysis of tributyl phosphate by cobalt gamma rays has been shown to produce gases, acid, and "polymer."[30] The gases have been identified and shown to include large yields of hydrogen and some hydrocarbons (saturated and olefinic) from one to seven carbons.[31] The strong-acid component was assumed to be dibutyl hydrogen phosphate. The assumption has been confirmed here by the identification of its anilinium salt, mp 67–68°C.

The acid-free polymer from tributyl phosphate contained 11.2% phosphorus and had a molecular weight of 1400 (cryoscopic in benzene). The calculated values for tributyl phosphate are 11.65% phosphorus and a molecular weight of 266. The combined acid and "polymer" from triethyl phosphate contained 16.8% phosphorus and had a molecular weight of 770. Calculated values for triethyl phosphate are 17% phosphorus and a molecular weight of 182.

The polymer is assumed to be a mixture of compounds, but the phosphorus content being so close to that of the starting material would imply polymerization through the hydrocarbon chain rather than through generation of anhydride linkages of the type P-O-P.

The assumption that polymerization occurs through the hydrocarbon chain was tested by dealkylation of the mixture of acid and "polymer" from triethyl phosphate with 8 *N* HBr (3.4 g to 50 ml). Gas chromatography was used to examine the halide products. Ethyl bromide has been identified, and preliminary examination indicates the presence of *n*-propyl and *n*-butyl bromides and a high-boiling product that has been tentatively identified as 1,3-dibromobutane. The fact that the acidic dealkylation of the mixture caused charring indicates an unidentified reaction.

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[27] Temporary employee, summer 1958.

[28] C. E. Higgins, W. H. Baldwin, and B. A. Soldano, *J. Phys. Chem.* 63, 113 (1959).

[29] W. H. Baldwin, C. E. Higgins, and B. A. Soldano, *J. Phys. Chem.* 63, 118 (1959).

[30] J. G. Burr, Jr., *Chem. Semiann. Prog. Rep. Dec. 20, 1955*, ORNL-2046, p 71.

[31] R. M. Wagner and L. H. Towle, Stanford Research Institute Project No. SD-2080-1, June 30, 1958 (unpublished).

FATE OF ALKYL GROUPS DURING THE DEALKYLATION OF PHOSPHATE ESTERS

W. H. Baldwin

Certain dealkylation reactions have been used previously to prepare partly esterified phosphorus acids. Previously, very little attention was given to the fate of the alkyl groups that were removed. The techniques of gas chromatography have been used, here, to analyze the products of several different dealkylation reactions on tributyl phosphate.

When sulfuric acid (0.2 volume of 12 *M* acid) was used at reflux temperature, a mixture of butyl alcohol with some butene and dibutyl ether was produced.

When constant-boiling halogen acids (6 *N* HCl or 8 *N* HBr) were used in large excess, high yields (greater than 90%) of pure *n*-butyl halides were obtained. Metallic halide catalysts ($ZnCl_2$, $FeCl_3$) when employed in aqueous HCl induced isomerization so that *tert*-butyl chloride and isobutyl or *sec*-butyl chloride (not separated by gas chromatography) contaminated the *n*-butyl chloride.

The reaction of tributyl phosphate with 2.5 moles of $POCl_3$ was 15% complete in 2 hr. The product contained *n*-butyl chloride and *sec*-butyl or isobutyl chloride in the molar ratio of 5.5 to 1.

A 12% yield of pure *n*-butyl chloride was obtained with $SOCl_2$ (5 moles to 1 of tributyl phosphate) under reflux for 2 hr.

The yield of butyl chlorides from the reaction of PCl_5 with tributyl phosphate exceeded 90%. The product was a mixture that contained mostly *n*-butyl chloride but also significant amounts of *sec*-butyl or isobutyl chloride and *tert*-butyl chloride.

Dealkylation of tributyl phosphate with alkali halides or hydroxides generally becomes immeasurably slow after the removal of one alkyl group.

It is assumed that those reagents that produce isomerization involve ionic mechanisms.

CHEMISTRY OF AQUEOUS SYSTEMS

THERMODYNAMIC PROPERTIES OF HYDROCHLORIC ACID FROM EMF MEASUREMENTS

R. S. Greeley Wm. T. Smith, Jr.[1]
M. H. Lietzke R. W. Stoughton

Electromotive force measurements have been made of the cell

$$Pt;\ H_2(g),\ HCl(m)\ ||\ HCl(m),\ AgCl(sat.);\ Ag$$

from 25 to 200°C and in some cases to 275°C under hydrogen pressures of about 1 atm and with hydrochloric acid concentrations from 0.005 to 1.0 m. The potentials observed were corrected to exactly 1 atm by means of the Nernst equation, assuming that the fugacity of hydrogen was equal to the pressure of hydrogen, and to exactly even temperatures by adding the temperature difference times the slope of the quadratic equation representing the change in emf vs temperature. It was necessary to correct the concentration of hydrochloric acid for changes occurring during the test that were due to the reduction of silver ion by hydrogen. This correction was made from the slope of the emf vs time at constant temperature. The mean molality and ionic strength of the solution were calculated on the assumption that the solution was saturated with silver chloride and that all the chloride in solution existed as free chloride ion. Liquid-junction potentials were assumed to be insignificant.

The mean ionic activity coefficient of hydrochloric acid was written in the form of the extended Debye-Hückel equation, and the resulting expression was substituted into the Nernst equation. Rearrangement of the latter gave a term $E^{0''}$ as a linear function of the ionic strength of the solution, where $E^{0''}$ was the collection of all terms measurable or calculable. The ion size parameter in the Debye-Hückel part of $E^{0''}$ was chosen so as to make the standard error of fit of the $E^{0''}$ values to a straight line a minimum for solutions of concentration up to 0.1 m. Extrapolation of the line to infinite dilution gave values of E^0, the standard potential of the silver–silver chloride electrode (assuming the standard potential of the hydrogen electrode to be zero at each temperature), which fitted the following equation to within 0.19 mv to 200°C:

$$E^0 = 0.23735 - 5.3783 \times 10^{-4} t - 2.3728 \times 10^{-6} t^2 \text{ (in volts)} .$$

The Nernst equation was then solved for the mean ionic activity coefficient of hydrochloric acid at the temperatures and concentrations of interest. The pH values for the same solutions and temperatures were calculated on the assumption that the activity coefficient of chloride ion was equal to the mean ionic activity coefficient. Finally, the mean ionic activity coefficients were fitted to quadratic functions of the centigrade temperature over the range 25 to 200°C at each concentration and these equations differentiated to give the relative partial molal heat contents. A second differentiation gave the relative partial molal heat capacities.

The over-all error in the reproducibility of the emf's was about ±0.5 mv up to 225°C, probably ±2 mv at 250°C, and ±5 mv at 275°C. Agreement with previous investigators at temperatures below 100°C was satisfactory, both for the emf's and the derived quantities. Agreement with the single investigation at high temperatures was within the probable error of the other investigation.

On the other hand, systematic errors in the results could have been caused by assuming that the hydrogen fugacity was equal to the hydrogen pressure, neglecting liquid-junction potentials, and neglecting the possibility that the hydrogen–hydrogen ion exchange current on the silver–silver chloride electrode could have been significant in relation to the chloride–silver chloride exchange current. The maximum error attributable to the first effect was estimated as less than 1 mv at 200°C, with the errors for the other two effects unknown.

The extended Debye-Hückel equation expresses the data satisfactorily, although the ion size parameter appears to be simply an adjustable parameter.

[1]Consultant, University of Tennessee Chemistry Department.

SOLUBILITY OF SILVER SULFATE IN MAGNESIUM SULFATE SOLUTIONS

M. H. Lietzke R. W. Stoughton

The solubility of Ag_2SO_4 in KNO_3 (ref 2), K_2SO_4 (ref 3), H_2SO_4 (ref 4), and HNO_3 (ref 5) solutions was discussed in previous papers, and it was shown that expressions of the Debye-Hückel type could be used to describe the solubility data in each system over a wide range of temperature and ionic strength. Since it seemed to be a logical extension of this solubility program to determine whether similar expressions could be used to describe the solubility of Ag_2SO_4 in polyvalent electrolyte solutions, a study has been made of the solubility of Ag_2SO_4 in 0.1, 0.5, and 1.0 m $MgSO_4$ solutions to above 150°C. Again a high-speed digital computer was used in making the calculations.

Experimental

The solubility measurements were carried out by means of the technique described previously.[6] As in the case of the KNO_3 and K_2SO_4 systems, it was fairly difficult to get a good reproducible set of data, since the attainment of equilibrium was rather sluggish. The measurements were extended at each concentration of $MgSO_4$ to an upper temperature limit imposed by interference from hydrolysis of both the Ag_2SO_4 and the $MgSO_4$. It is believed, however, that the solubility data reported represent, at least at the higher temperatures, metastable solubility values for Ag_2SO_4 in $MgSO_4$ solutions, since the establishment of solubility equilibrium was more rapid than the onset of hydrolysis in the case of the points given. The measurements were reproducible to about ±2°C in 0.1 m $MgSO_4$ and to about ±5°C in 0.5 and 1.0 m $MgSO_4$ solutions.

[2]M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.* 63, 1183 (1959).

[3]M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.* 63, 1186 (1959).

[4]M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.* 63, 1188 (1959).

[5]M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.* 63, 1190 (1959).

[6]M. H. Lietzke and R. W. Stoughton, *J. Am. Chem. Soc.* 78, 3023 (1956).

Results and Discussion

In Fig. 15 the circled points represent the experimentally observed solubilities of Ag_2SO_4 in H_2O and in 0.1, 0.5, and 1.0 m $MgSO_4$ solutions. The results in H_2O up to 100°C were obtained from the work of Barre.[7]

On the assumption of complete dissociation of both electrolytes, the stoichiometric ionic strength I of the Ag_2SO_4-$MgSO_4$ solutions is given at any molality m of $MgSO_4$ by

$$I = 4m + 3s \quad , \tag{1}$$

where s represents the molal solubility of Ag_2SO_4 in the $MgSO_4$ solution. The stoichiometric solubility product of Ag_2SO_4 on a molality basis S at any molality m of $MgSO_4$ was assumed to be given in terms of the solubility product in pure H_2O by a Debye-Hückel expression of the type

$$\ln S = \ln S_0 + \mathcal{S}_T \left(\frac{\sqrt{I}}{1 + A_S \sqrt{I}} - \frac{\sqrt{I_0}}{1 + A_S \sqrt{I_0}} \right) . \tag{2}$$

In this equation S_0, the molal solubility product of Ag_2SO_4 in pure H_2O, equals $4s_0^3$ at ionic strength $I_0 = 3s_0$; $\mathcal{S}_T$ is the appropriate Debye-Hückel limiting slope at the given temperature; and A_S is a concentration-dependent but temperature-independent parameter. In computing the change

[7]M. Barre, *Ann. et chim. phys.* [8], 24, 211 (1911).

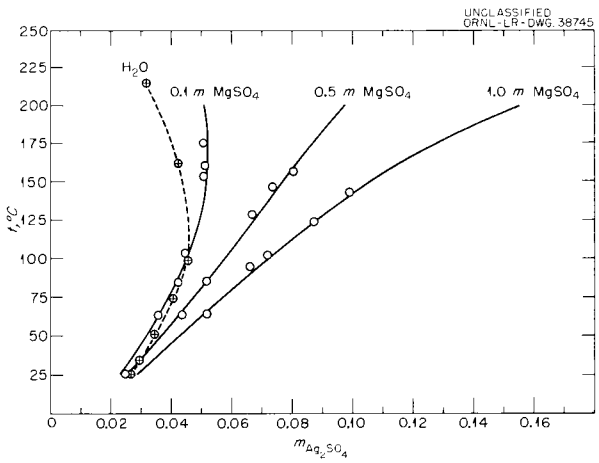

Fig. 15. Solubility of Ag_2SO_4 in $MgSO_4$ Solutions.

of $\mathcal{S}_T$ with temperature, the equation for the variation of the dielectric constant D of water with temperature given by Åkerlöf and Oshry[8] was used. At any temperature and concentration of $MgSO_4$ the solubility product S of the Ag_2SO_4 is given by

$$S = 4s^2(s + m) \quad . \tag{3}$$

In starting the calculations at each concentration of $MgSO_4$, the observed solubility of Ag_2SO_4 at each temperature was used to compute a value of I. Then, from Eqs. (2) and (3), a value of s_{calcd} (the calculated solubility of Ag_2SO_4) was obtained. This value was used to correct I [Eq. (1)] and the process repeated until successive values of s_{calcd} agreed to within 0.1%. The calculations were carried out at 25°C intervals from 25 to 200°C at each concentration of $MgSO_4$ and with a range of values of A_S. Then from a plot of s_{calcd} vs A_S at each temperature and concentration of $MgSO_4$ it was possible to find the value of A_S which gave closest agreement with the observed solubility. It was found that the value of A_S varied little with temperature at each concentration but did show a decrease with increasing concentration. In Fig. 15 the solid lines indicate the calculated solubilities corresponding to the values of A_S averaged at each concentration of $MgSO_4$. The values are as follows: for $m = 0.1$, $A_S = 0.82$; for $m = 0.5$, $A_S = 0.77$; for $m = 1.0$, $A_S = 0.72$. The decrease in the values of A_S with concentration (and hence of the ion size parameter $\mathring{a}$ which is contained in the A_S) is consistent with a hypothesis involving smaller hydration spheres for the ions as the concentration of $MgSO_4$ increases.

Calculations were also performed with the assumption of an average temperature- and concentration-independent value of A_S (= 0.77). In this case, however, the solubility values calculated at $m = 0.1$ were too high, while those calculated at $m = 1.0$ were too low. Hence it appears that the value of A_S must be considered to be concentration-dependent.

It is evident that a Debye-Hückel type of expression for the variation in the molality solubility product of Ag_2SO_4 with ionic strength in $MgSO_4$ solutions can be used to fit the solubility data over a wide range of concentration and temperature.

Acknowledgment

The authors wish to express their appreciation to L. C. Meers for performing the experimental solubility measurements.

LIQUID PHASE SPECTROPHOTOMETRY AT ELEVATED TEMPERATURES AND PRESSURES

W. C. Waggener R. W. Stoughton

Experiments demonstrating the practicability of making precise spectral measurements and analyses of liquids involving radioactive nuclides at elevated temperatures and pressures have been briefly described previously.[9] For example, the fate of the neptunyl ion in a nitric acid solution was followed spectrophotometrically from 0.6 to 1.3 μ for a period of 45 hr and over a temperature range from 4.5 to 252°C.

The work during the present period consisted principally in (1) assessing the results obtained with the first equipment and (2) designing and constructing a second cell assembly which will permit the use and study of solutions containing dissolved gas. This cell will have a path length of 3.81 cm, one-half that of the presently used cell (7.62 cm), and the cavity will be modified to incorporate a reservoir space above the liquid sample. The new cell will also provide data for a test of Lambert's law. This test is necessary in order to establish any artifacts in data which may be due to cell geometry.

HIGH-TEMPERATURE AQUEOUS ISOPIESTIC MEASUREMENTS

C. S. Patterson[10] B. A. Soldano
R. W. Stoughton

The high-temperature isopiestic unit was used for investigating the following salts as a function of concentration at 100°C: LiCl, NaCl, KCl, CsCl, $BaCl_2$, $MgSO_4$, Na_2SO_4, and UO_2SO_4. The concentration range studied was about 0.5 to over 4 m. Duplicate samples agreed, in the poorest

[8] G. C. Åkerlöf and H. J. Oshry, *J. Am. Chem. Soc.* 72, 2844 (1950).

[9] W. C. Waggener and R. W. Stoughton, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 43–45.

[10] ORINS summer participant, Furman University, Greenville, S.C.

cases, to within 0.4% in the final calculated molality. This figure includes the total integrated error from all known factors affecting the osmotic data at elevated temperatures. In many cases duplicate samples agreed to within 0.1%.

With NaCl used as the standard, the osmotic coefficients were calculated as a function of concentration. As expected, NaCl, KCl, and CsCl showed very little change with temperature. The other electrolytes, except for Na_2SO_4, showed lower osmotic coefficients at 100°C than at 25°C at all concentrations. The 100°C coefficients for Na_2SO_4 appeared to be somewhat higher at low concentrations and somewhat lower at the higher concentrations than those at 25°C.

PHYSICAL CHEMISTRY OF ION EXCHANGERS

Equilibrium Measurements with Cation and Anion Exchangers of Variable Capacity[11]

S. Lindenbaum G. E. Boyd

Measurements of the equilibrium ion exchange selectivity coefficients for several pairs of exchanging ions on cation and anion exchangers of varying capacity have been reported.[12] The results obtained have indicated that as the exchange capacity (milliequivalents per dry gram of exchanger) increased, the selectivity for the preferred ion decreased. This result was in apparent conflict with predictions from the statistical thermodynamic theory of Rice and Harris.[13]

Several new systems were studied with different series of cation and anion exchangers of varying capacities, and the earlier findings were confirmed. Equivalent volumes and equivalent water contents under the conditions of the selectivity coefficient experiments were measured also, so that it was possible to calculate the exchange site density in the exchanger (i.e., equivalents per liter of exchanger). It was generally found that even with the capacity expressed in this form the selectivity increased as the capacity decreased. The opposite result was found only in one case, with a series of extremely weakly cross-linked variable-capacity cation exchangers.

It has been concluded that the Rice and Harris model for ion exchangers is not adequate for appreciably cross-linked resinous exchangers. The failure of the theory may result from the fact that in cross-linked exchangers the ratio of organic to aqueous content of the gel increases as the exchange site density decreases. This change in composition would lead to a decrease in the dielectric constant in the exchanger phase and consequently to stronger ion binding.

Model Studies of Ion Exchange Mechanisms with Liquid Ion Exchangers

G. E. Boyd S. Lindenbaum

The bromide-chloride exchange reaction with the liquid anion exchanger tri-*n*-octylamine hydrochloride (TOA) dissolved in toluene was studied with varying concentrations of HCl in the aqueous phase. It was found that the uptake of microamounts of bromide ion as a function of HCl concentration could be accounted for quantitatively when corrections were made only for the thermodynamic ionic activity coefficients in the aqueous phase. Thus (see Fig. 16) a straight line of slope −1 was obtained when the extraction coefficient was corrected by the appropriate aqueous activity coefficient ratio. The possible nonideal behavior of ions in the organic phase evidently does not contribute significantly to the equilibrium partition of bromide ion.

The extraction of cationic species from aqueous solution was measured with a liquid ion exchanger prepared by dissolving dinonylnaphthalenesulfonic acid (DNNS) in benzene. The dependence of the extraction coefficient on the concentration of DNNS is displayed on log-log plots for the extraction of Zn(II) (Fig. 17), Fe(III) (Fig. 18), and Cs(I) and Ce(III) (Fig. 19). The slope was unity in each case. A slope corresponding to the charge of the extracted species was to be expected if the DNNS were present in the organic phase in monomeric form. The observed lack of dependence on the charge of the extracted ion is best explained by the occurrence of DNNS micelles, in agreement with the findings of Kaufmann and Singleterry.[14]

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[11] S. Lindenbaum, C. F. Jumper, and G. E. Boyd, *J. Phys. Chem.* (in press).

[12] S. Lindenbaum, C. F. Jumper, and G. E. Boyd, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 38.

[13] S. A. Rice and F. E. Harris, *Z. physik. Chem. (Frankfurt)* 8, 207 (1956).

[14] S. Kaufman and C. R. Singleterry, *J. Colloid Sci.* 10, 139 (1955); *J. Colloid Sci.* 12, 465 (1957).

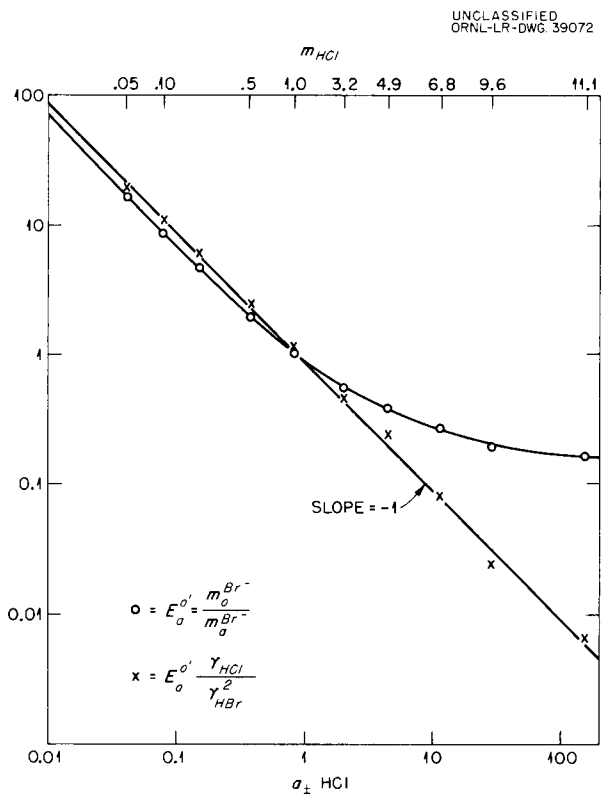

Fig. 16. Extraction of Tracer Quantities of Bromide Ion by 0.1 *N* TOA·HCl in Toluene from Aqueous HCl Solutions.

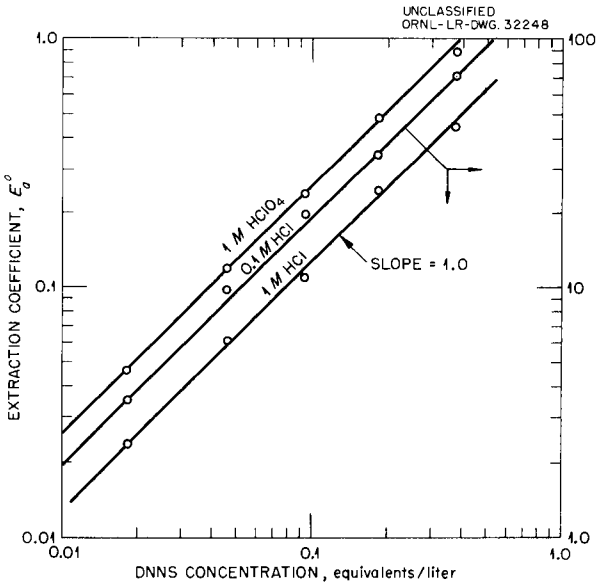

Fig. 17. Concentration Dependence of the Extraction of Trace Quantities of Zn(II) by DNNS from HCl and $HClO_4$ Solutions.

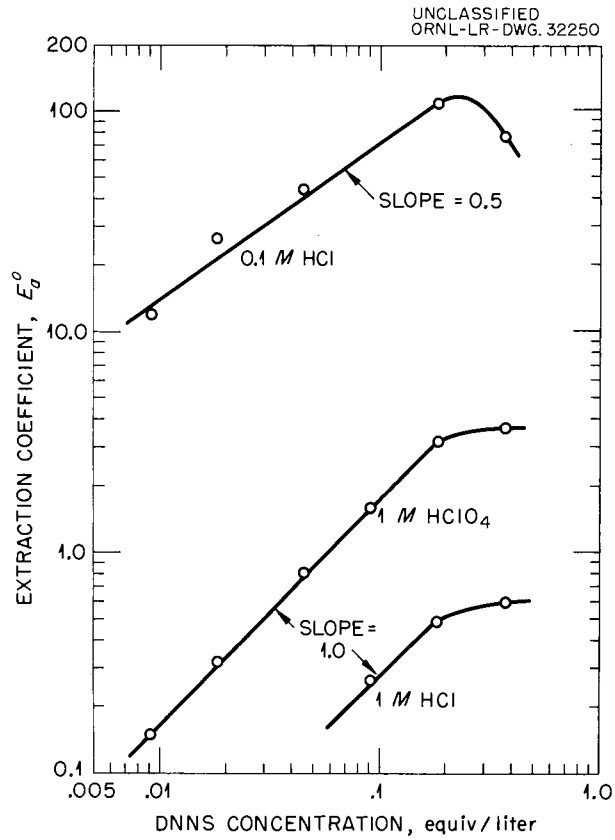

Fig. 18. Extraction of Trace Quantities of Fe(III) from HCl and $HClO_4$ vs Concentration of DNNS in Benzene.

Analogous experiments with the liquid anion exchanger dimethyldidodecenylammonium chloride (DDA) indicated that this exchanger was also aggregated in its organic solutions.

Thermodynamic Calculations of Anion Exchange Selectivities. The Bromide-Fluoride Ion Exchange Equilibrium

G. E. Boyd S. Lindenbaum

It has been observed previously that the fluoride form of Dowex 2 was unstable and slowly decomposed even at room temperature. The thermodynamic calculation of the bromide-fluoride selectivity has therefore not been successful for fluoride loadings of the exchanger greater than 50%. The calculation of the selectivity coefficients for the distribution of tracer quantities of fluoride between the bromide form of Dowex 2 and 0.10 *m* sodium bromide solutions was re-examined. Selectivities were determined for several preparations of Dowex 2, the

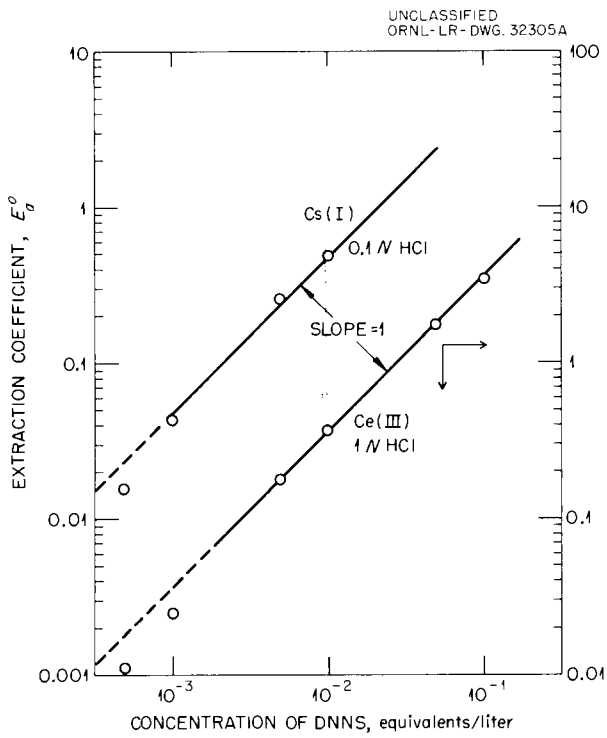

Fig. 19. Extraction of Cs^{137} and Ce^{144} from HCl as a Function of Concentration of DNNS in Benzene.

1.9-hr F^{18} tracer (the F^{18} activity was prepared by irradiating $Li_2^6CO_3$ in the LITR) used to measure the extent of exchange. A fair agreement with the calculated values was obtained except with the more highly cross-linked exchangers.

Calorimetric Measurements of the Silver-Sodium Ion Exchange

F. Vaslow G. E. Boyd

Measurements of the standard free energies, heats, and entropies were completed for the ion exchange reaction

$$\text{NaR } (a = 1 \text{ in equilibrium with } 0.1\ N\ NaNO_3) + \\ + AgNO_3\ (aq,\ a = 1) \rightleftharpoons \\ \text{AgR } (a = 1 \text{ in equilibrium with } 0.1\ N\ AgNO_3) + \\ + NaNO_3\ (aq,\ a = 1) + xH_2O\ (a_w = 1)\ ,$$

using Dowex 50 of 1, 4, 8, and 24% nominal divinylbenzene content. Interestingly, the differential heats observed were positive (i.e., heat absorbed) and almost independent of the equivalent fraction of silver ion in the exchanger, x_{Ag^+}, above values of 0.1 to 0.2. At lower x_{Ag^+} values the differential heats rapidly became negative and tended to values less than −5.0 kcal/mole for the highest cross-linked exchangers.

The positive values for the standard heats and entropies contrast with those obtained in earlier studies[15] of the exchange of H^+, Li^+, K^+, and Cs^+ ions with the sodium form of the exchanger where heat was evolved and the entropy change was always negative. The observed behavior with silver ion is reminiscent of the well-known association observed with silver salts in aqueous solutions. Here, the association process is generally accompanied by positive heat and entropy values.

The observation of the evolution of heat for the uptake of small amounts of Ag^+ ion possibly may be explained by the formation of benzene–silver ion charge transfer compounds in the exchanger. The charge transfer energy for each of the two benzene-silver bonds formed in the silver perchlorate–benzene compound has been computed as about 16 kcal per mole of silver ion. While this compound ordinarily does not form in the presence of water, under circumstances where benzene rings and silver ions are constrained to favorable configurations, as might occur in a highly cross-linked exchanger, the formation of such charge transfer bonds is conceivable.

In the measurements on the silver-sodium ion exchange the temperature-sensing element of the calorimeter was a pair of 2000-ohm thermistors placed at opposite sides of a bridge circuit. A highly stable sensitivity of about (1.5×10^{-5})°C, i.e., 0.002 ohm, was obtained. This sensitivity compares favorably with thot observed in earlier measurements with a 36-junction thermocouple.

Theoretical Calculations on Ion Exchange Selectivity

F. Vaslow

In attempting to obtain a better understanding of the influence of electrostatic interactions on ion exchanger selectivity, some calculations were made on the basis of a highly idealized model

[15] F. Vaslow and G. E. Boyd, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 39.

of an exchanger. For Dowex 50 resins above 8% divinylbenzene content the volume of water within each resin particle is about the same as or less than the volume of organic material. Under such circumstances a reasonable model might be one in which the water content is divided up into small cells within the continuous matrix of the organic material. To keep the model tractable it was assumed that the cells were spherical and of the same size and that each contained one fixed and one exchangeable ion. Only the electrostatic interaction within each cell was considered, since the organic matrix would tend to isolate the fields within each cell. The influence of one cell upon another could be considered as a higher-order effect. The fixed ion is held with its center in the cavity wall, and the mobile ion is allowed to move in regions determined by the different hydrated radii of the fixed and mobile ions in aqueous solutions of the ions. The water and resin were taken as homogeneous media with their normal dielectric constants, that is, 80 and 2, respectively. The Laplace equation with appropriate boundary conditions for the system was set up and solved (in Legendre polynomial series) for the electrostatic potentials relative to the two ions at infinite separation in water.

In spite of the simplicity of the model, several results of interest were derived. It was found that although the negative interaction potential of the fixed and mobile ions is much greater than it would be in water at the same distance, this is proportionately balanced by the positive self-potential energy of the two ions. As a result, it appeared that the net electrostatic potential is not greatly different from that in an all-aqueous system at the same concentration. The sign and actual magnitude of the net potential energy could only be determined by a much finer calculation.

The second result was that the interaction between the two ions in the cell depends primarily on the radius of the cell and not on the distance of closest approach of the ions. The excess potentials are nearly constant over the cell volume and thus there would appear to be no additional incentive for the formation of ion pairs at the normal closest approach distance. However, if the charge centers actually penetrate or neutralize one another, then a very considerable decrease in the potential of the system occurs, and a high selectivity should be obtained.

ANION EXCHANGE STUDIES

F. Nelson D. C. Michelson
K. A. Kraus M. L. Hyder[16]

Studies on the utilization of anion exchange resins for separations were continued. Increasing emphasis was placed on the elucidation of the properties of ion exchange resins, both from a kinetic and equilibrium point of view. Particular effort was devoted to the investigation of properties of quaternary amine salt solutions and their correlation with properties of cross-linked anion exchange resins. The principal conclusions of this work are summarized below.

Selection of Amine. – Benzyltrimethylammonium chloride (abbreviated RCl) was chosen for extensive studies since it duplicates in part the active group on the anion exchanger, Dowex 1, with which most of our earlier anion exchange studies had been carried out. The active group of this resin is a trimethylammonium ion attached via a methylene link to the polystyrene network. In addition, the amine selected is readily available and extremely soluble, thus permitting studies up to concentrations of $m \cong 20$ at room temperature. Although it does not have the organic side chain typical of the polystyrene network, its solutions appear to reproduce satisfactorily many of the characteristic properties of ion exchangers.

Density and Apparent Molal Volumes. – The densities of RCl solutions were measured in the range $0.2 \leqq m_{RCl} \leqq 23$, and the apparent molal volume of RCl (ϕ_{RCl}) was calculated from these data; ϕ_{RCl} is approximately 170 cc at low RCl concentrations and decreases slightly with increasing concentration.

From density measurements with RCl-LiCl solutions at a constant total molality of 16.0, the mean apparent molal volume of the mixed solute was obtained. It decreases linearly with the fraction of RCl from 167 at $F_{RCl} = 1$ to 21 at $F_{RCl} = 0$. Thus the apparent molal volumes of the two solutes are essentially additive at constant total molality, which implies that apparent molal volumes in resins invaded by electrolytes could, with considerable confidence, be estimated from the composition of the invaded resin and the apparent molal volumes of the solutes in pure two-component systems.

[16] Summer employee, 1958.

Viscosity. – Viscosities (η) of RCl solutions were measured in the range $0 \leqq m_{RCl} \leqq 23$. In this range the viscosity varies by more than a factor of 100. A plot of log η vs m_{RCl} is linear, as a first approximation, though it shows a definite quadratic overtone.

Viscosities of concentrated RCl-LiCl and RCl-HCl mixtures at constant m_{Cl} were also determined. Plots of log η vs the fraction of RCl in the solutions (F_{RCl}) showed shallow maxima.

Diffusion Coefficients. – Diffusion coefficients, D, of Br^- and $AuCl_4^-$ (tracers) were determined in RCl solutions as a function of m_{RCl} and in RCl-HCl and in RCl-LiCl mixtures of constant total molality. In general the diffusion coefficients varied as anticipated from the viscosities of the solution; that is, $D\eta$ is constant as a good first approximation in spite of the fact that D varied in some solutions as much as two orders of magnitude.

Diffusion coefficients of tracer Br^- were also determined for an 8% cross-linked quaternary amine exchanger (Dowex 1). The resin was immersed in HCl and LiCl solutions, where it imbibes substantial amounts of the electrolytes. The diffusion coefficients decrease substantially as the amount of imbibed electrolyte increases; the decrease is much greater for LiCl solutions than for HCl solutions and is essentially as expected from the diffusion properties of the RCl-LiCl and RCl-HCl mixtures. Indeed, the diffusion coefficients in the resin parallel closely those observed for corresponding quaternary amine solutions, implying that cross-linking of the exchangers has only a minor effect on the diffusion coefficients of ions in the resin.

Osmotic Coefficients and Activity Coefficients of RCl. – The osmotic coefficients of RCl in the range $0.1 \leqq m_{RCl} \leqq 20$ were determined isopiestically with NaCl and H_2SO_4 solutions used as standards.

The osmotic coefficients of RCl (ϕ_{RCl}) decrease extremely rapidly with increasing m_{RCl}, reaching a minimum, ϕ_{RCl} = *ca.* 0.68 near m_{RCl} = *ca.* 2.5. They then rise gradually to ϕ_{RCl} = *ca.* 1.23 near m_{RCl} = 19. The minimum in the osmotic coefficients is substantially lower than expected for a 1:1 electrolyte.

Activity coefficients of RCl ($\gamma_{\pm RCl}$) were computed from the osmotic coefficients by using a special extrapolation function. The values of $\gamma_{\pm RCl}$ decrease rapidly with m_{RCl}, reaching a minimum near $m_{RCl} = 6$, where $\gamma_{\pm RCl}$ = *ca.* 0.25; $\gamma_{\pm RCl}$ then rises slowly with increasing molality to a value of almost 0.4 near $m_{RCl} = 19$. As was apparent from the osmotic coefficient measurements, the activity coefficients of RCl are very much lower than normally expected for a 1:1 electrolyte. It appears that RCl may be partially associated in aqueous solutions.

Activity Coefficients of Benzyltrimethylammonium Chloroaurate ($RAuCl_4$). – The extremely high selectivity of anion exchange resins for $AuCl_4^-$ suggested that activity coefficients of $RAuCl_4$ would be extremely low in RCl solutions. To test this, activity coefficients of $RAuCl_4$ were evaluated from measurements of the solubility of $RAuCl_4$ in RCl solutions.

The activity coefficients of $RAuCl_4$ decrease extremely rapidly with increasing m_{RCl}, reaching values as low as 10^{-3} for $m_{RCl} = 20$. There appears to be little doubt that $RAuCl_4$ is only partially dissociated even at moderate RCl concentrations, a fact which might be considered surprising since we are dealing with a 1:1 electrolyte.

While the decrease in the activity coefficients of $RAuCl_4$ with RCl concentration is, qualitatively, as expected from the selectivity of the anion exchangers, there remains a substantial discrepancy for a quantitative correlation. A more quantitative correlation might be anticipated with other model electrolytes more closely resembling the hypothetical monomer of the anion exchanger.

ADSORPTION ON INORGANIC MATERIALS

H. O. Phillips K. A. Kraus

Investigations of properties of inorganic materials and their applications to chromatographic separations were continued during the past year. Zirconium phosphate precipitates having varying ratios of phosphate to zirconium were prepared and their properties systematically investigated. The behavior of a number of oxides in contact with acidic and basic solutions was investigated with a pressurized chromatographic column at 200°C. Some results of these studies are summarized below.

Properties of Zirconium Phosphate. – Physical properties and composition of the precipitates were markedly dependent on the phosphorus-to-zirconium

ratio in the precipitation media. In addition, the capacity of the precipitates for adsorption of simple cations (NH_4^+ or Na^+) increased with increasing phosphorus-to-zirconium ratio in the materials, the increase roughly paralleling the phosphorus contents. Capacities decreased significantly on firing the materials near 100°C. X-ray analysis of samples heated near 300°C indicated that some zirconium pyrophosphate is formed, particularly in preparations having high phosphorus-to-zirconium ratios. The stability of some of these preparations in Na_2CO_3, $NaHCO_3$, NH_3, and NaOH solutions was also studied. Considerable amounts of phosphate were displaced from the materials only in NaOH solutions.

Adsorption Studies at High Temperature (200°C). – Oxides of Zr(IV), Ti(IV), Sn(IV), Nb(V), and Ta(V), prepared as described earlier[17] and fired at 200°C, were found to have reasonably good physical stability in aqueous 0.05 *M* HNO_3 and 0.05 *M* NaOH solutions at 200°C. Alternate treatment of columns of the oxides with the acid and base solutions at 200°C showed that some loss of adsorptive capacity for acid or base occurs with Zr(IV) and Ti(IV) oxides. Uptake of acid or base by oxides of Sn(IV), Nb(V), or Ta(V), however, was relatively little affected even after several alternating acid-base treatments. Thorium oxide, prepared by hydroxide precipitation[17] and fired at 200°C, was dissolved by dilute nitric acid at 200°C. However, if the oxide was first conditioned by treatment with dilute NaOH solution at 200°C, its stability in acid markedly improved.

ULTRACENTRIFUGATION STUDIES OF INORGANIC POLYMERIZATION

J. S. Johnson, Jr. R. M. Rush
K. A. Kraus

Oracle Program. – A program has been written for the Oracle which computes the concentration c_2' of a polymeric charged solute as a function of radial distance x for any given assumed charge per monomer unit, z', in a three-component system (solute, supporting electrolyte, and water) from equilibrium ultracentrifuge data obtained with interference optics. The theory has been presented elsewhere.[18] The centrifugation results are recorded as photographs of the interference fringes resulting from recombination of light passing through the solution and solvent compartments. The observational data consist of comparator readings of the horizontal (radial) position of the fringes, corrected for cell distortion. Additional input information required are the initial concentration of the supporting electrolyte in the solution and solvent compartments, the partial specific volumes and refractive index increments of the polymeric solute and supporting electrolyte, molecular weight of the monomer unit of the polymeric solute, density of the solution, speed of rotation, temperature, the radial magnification of the optical system, the radius at one point on the interference photograph, and the change in refractive index difference corresponding to one fringe interval.

The output is presented as a table of x^2 and log c_2' at each fringe position for each desired value of the charge, z'. The degree of polymerization, N, could be obtained from these data by using the equations presented in ref 18. Since several differentiations are involved in the computation of N from the log c_2' vs x^2 table, additional Oracle programs were written by which this differentiation may be carried out automatically.

Polymerization of U(VI). – The degree of polymerization N of U(VI) was determined as a function of hydroxyl number n by equilibrium ultracentrifugation of UO_2Cl_2 partially neutralized with NaOH. The supporting electrolyte was 1 *M* NaCl except at $n = 0$ (unhydrolyzed UO_2^{++}), where the supporting electrolyte was 1 *M* HCl. The maximum hydroxyl number was $n = ca.$ 0.9, since at higher values of n precipitation of U(VI) occurs.

The data were analyzed assuming

$$[UO_2(OH)_nCl_{2-n}]N$$

to be the sedimenting component. The results (Fig. 20) indicate that the degree of polymerization N increases approximately linearly with n

[17] K. A. Kraus, H. O. Phillips, T. A. Carlson, and J. S. Johnson, Jr., *Proc. U.N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd Geneva, 1958* **28**, 3–16 (1959).

[18] J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.* **63**, 787 (1959).

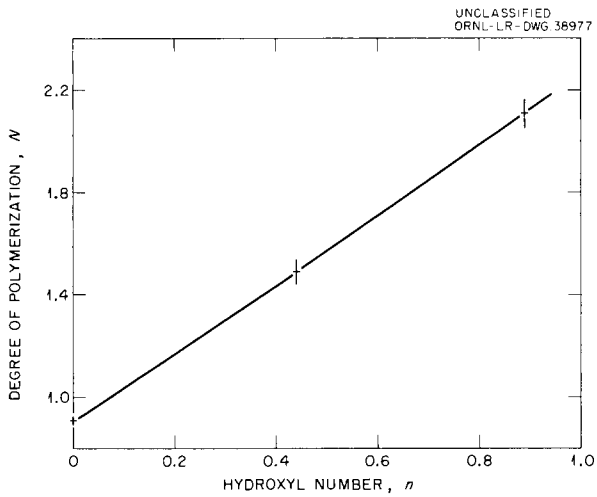

Fig. 20. Polymerization of U(VI).

in the region studied. In agreement with earlier work[19] we find N to be quite small.

The computed degree of polymerization at $n = 0$ is slightly less than unity (0.9). The difference between observed and theoretical ($N = 1$) is almost certainly an activity coefficient effect. Interestingly, under these conditions the charge z' computed for the cation from the ultracentrifugations is 2.0, which appears slightly high considering that UO_2^{++} is usually considered somewhat complexed by chloride ions under these conditions. At $n = 0.44$ and 0.89 the computed values of z' are 1.6 and 0.9, respectively, indicating that these low-molecular-weight polymers are not extensively complexed by chloride ions.

[19] J. J. Katz and G. T. Seaborg, *The Chemistry of the Actinide Elements*, Wiley, New York, 1957.

CHEMISTRY OF CORROSION

The work of this group includes several aspects of electrochemical kinetics related to corrosion. Since it has been demonstrated that adsorbed species have an important role in determining the kinetics of processes involved in corrosion,[1-3] one phase of current studies is devoted to polarization of active iron in various media containing inhibitors, the action of which is believed to depend upon competitive adsorption. In other studies, the kinetics of the formation of films by anodic polarization of zirconium has been investigated. Since the production and maintenance of passivity require a suitable cathodic process, another phase of the program deals with the kinetic analysis of several reduction processes at electrodes of stainless steel, zirconium, or iron passivated in the presence of an inhibitor. These measurements include a determination of the effect of complexing and hydrolysis upon the reduction of UO_2^{++} and Cu^{++} ions.

STUDIES ON PASSIVATING INHIBITORS

G. H. Cartledge

In a study of the action of nonoxidizing inhibitors, it was shown that benzoate, phthalate, and phosphate solutions of suitable concentration and pH value permit air or oxygen to raise iron or mild steel to passive potentials. The passivity showed the same sensitivity to the presence of foreign ions, such as the sulfate ion, as was previously found[1,2] for various inhibitors of the XO_4^{n-} type. During activation by added sulfate ions, the potential of iron passivated in benzoate solutions halted in the vicinity of the Flade potential, as shown in Fig. 21. An example of the results obtained by cathodic polarization of such passivated specimens is shown in Fig. 22. It is noteworthy that, in the presence of oxygen in a benzoate solution, the potential may be polarized very considerably below the Flade potential without immediate activation of the specimen, so that the cathodic process consists in the reduction of oxygen almost exclusively. By measuring the polarization in atmospheres both of oxygen and of helium, it was shown that the chief cathodic process in aerated solutions is the reduction of oxygen, even when a potentially reducible inhibitor such as the pertechentate ion is present. Similar behavior was exhibited in the presence of chromate ions in the pH range of 4.2 and above, with the exception that the reduction of the chromate ion alone (in an atmosphere of helium) was so sluggish that steady states were not attained. The results obtained on similar systems are being prepared for publication. The general result is the accumulation of additional evidence[4] that the action of oxidizing inhibitors does not necessitate their own reduction, but involves specific competitive adsorption, whereby alteration in the kinetics of one or more steps in the corrosion process is induced.

INHIBITORY ACTION OF BENZOATE IONS

E. J. Kelly G. H. Cartledge

Benzoate ions in aerated solution are known to be effective as an inhibitor of the corrosion of iron,[5] and it was shown (see above) that a passive potential may be attained within a certain range of concentration and pH values. In order to discover the mechanism of this action, cathodic polarization measurements have been made both in the active region, in the absence of oxygen, and in the passive region. In the absence of oxygen (hydrogen atmosphere), measurements have been made in buffered benzoate solutions and in a perchlorate solution to which benzoate was added, all solutions being at pH 5.0.

It was observed that the corrosion (open-circuit) potential in the pure benzoate solution is some 125 mv more noble than has been observed in a sulfate solution of the same pH value.[6] The corrosion rate indicated by extrapolation of the cathodic Tafel line appears to be 2×10^{-6} amp/cm^2 in the benzoate solution, which demonstrates considerable inhibition in the active region. Within a range of benzoate concentrations of 3×10^{-3} to 1.5×10^{-2} *f*, the overvoltage of hydrogen evolution is unchanged. The results, although they are only

[1] G. H. Cartledge, *J. Phys. Chem.* 60, 28, 32 (1956).

[2] R. F. Sympson and G. H. Cartledge, *J. Phys. Chem.* 60, 1037 (1956).

[3] K. E. Heusler, *Z. Elektrochem.* 62, 582 (1958).

[4] Cf. also R. F. Sympson and G. H. Cartledge, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 64–65.

[5] F. Wormwell and A. D. Mercer, *J. Appl. Chem. (London)* 2, 150 (1952).

[6] K. F. Bonhoeffer, *Z. Elektrochem.* 55, 151 (1951).

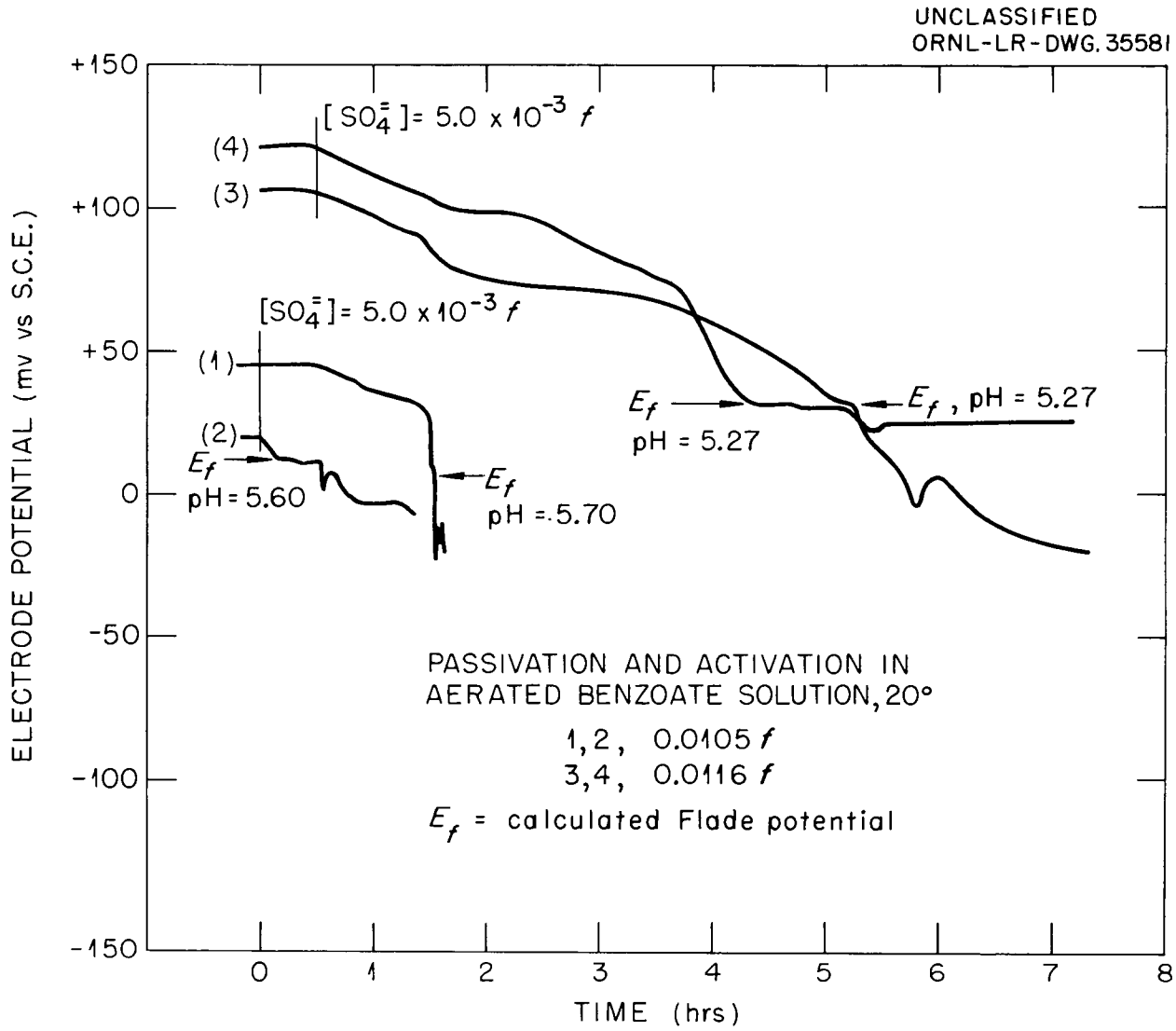

Fig. 21. Halts Approximating the Flade Potential in Potential-Time Curves During Activation of Passive Iron Electrodes by Addition of Sulfate Ions.

preliminary, indicate that the inhibitor causes a substantial diminution of the exchange current for hydrogen below that observed in the absence of inhibitor. It is also indicated, provisionally, that the passivation which occurs in the presence of oxygen is greatly accelerated by ferric ions (or complexes) formed in the solution. This was demonstrated by conducting passivation experiments (and polarizations) in the presence of a cationic exchanger to hold the iron ions at a very low concentration.

INHIBITION OF THE DISSOLUTION OF IRON BY IODIDE IONS AND CARBON MONOXIDE

K. E. Heusler

The influence of certain inhibitors on the anodic dissolution of active iron has been studied in oxygen-free mixtures of sulfuric acid and sodium sulfate with a constant total sulfate concentration of 0.5 *f*. As shown previously,[3] the dissolution of iron is catalyzed by hydroxyl ions, without influence by sulfate ions. The corrosion rate is

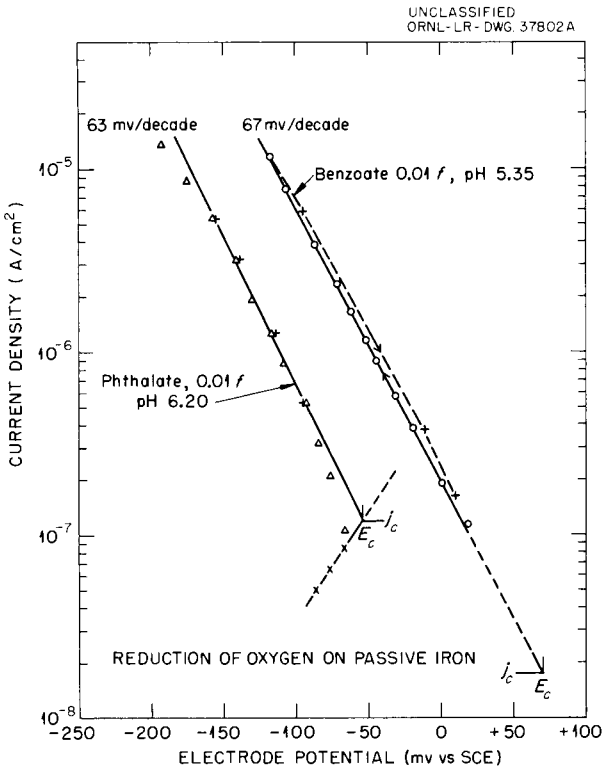

Fig. 22. Cathodic Polarization Curves for Passive Iron in Solutions of Inhibitors. E_c = open-circuit potential; j_c = corrosion current density.

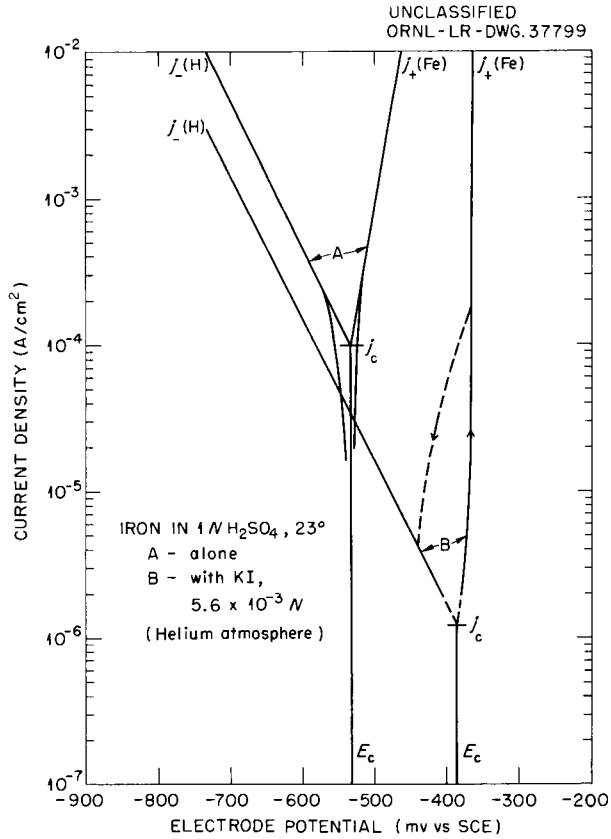

Fig. 23. Polarization Curves for Iron Electrodes With and Without Inhibiting Iodide Ions. Note the ennobling of the corrosion potential, E_c, and the decrease of the corrosion current density, j_c. The system becomes essentially unpolarizable only slightly above the corrosion potential. The dashed curve is a hysteresis loop.

decreased and the rest potential ennobled by addition of Cl^-, Br^-, I^-, or CO, Cl^- having the least effect and I^- and CO the greatest. Inorganic and organic cations were shown to have no inhibiting effect in pure sulfate solutions, although certain organic cations, such as tetrabutylammonium or isoquinolinium ions, may increase the inhibiting action of the halogenide ions. Formic acid and acetic acid also act as inhibitors of the iron dissolution.

The kinetics of the action of I^- and CO was investigated by polarization measurements, which included oscilloscopic determination of transient phenomena as well as steady states. Iodide ions and CO reduced the rates of both the cathodic evolution of hydrogen and the anodic dissolution of iron. The Tafel line corresponding to the deposition of hydrogen was shifted to smaller current densities. On the anodic side, Tafel lines were not obtained in the steady state, the results being as shown in Fig. 23. The potential E_u corresponding to unpolarizability varied with both concentration of the inhibitor and pH. For iodide solutions, the relations are given by

$$E_u = +80 + 59(\log a_{I^-} - \mathrm{pH}) \ , \qquad (1)$$

where E_u is in millivolts referred to the normal hydrogen electrode. (The activity coefficient of I^- was taken as 0.2 for all iodide concentrations in 0.5 *f* sulfate solution.) Figures 24 and 25 show the results of the measurements for constant pH and constant $[I^-]$, respectively. A similar variation of E_u with pH was observed in solutions saturated with pure CO at a total pressure of 1 atm.

As shown previously,[3] the steady-state anodic Tafel line has a slope of approximately 30 mv/decade, whereas a different Tafel line of 60 mv slope may be observed oscilloscopically by increasing

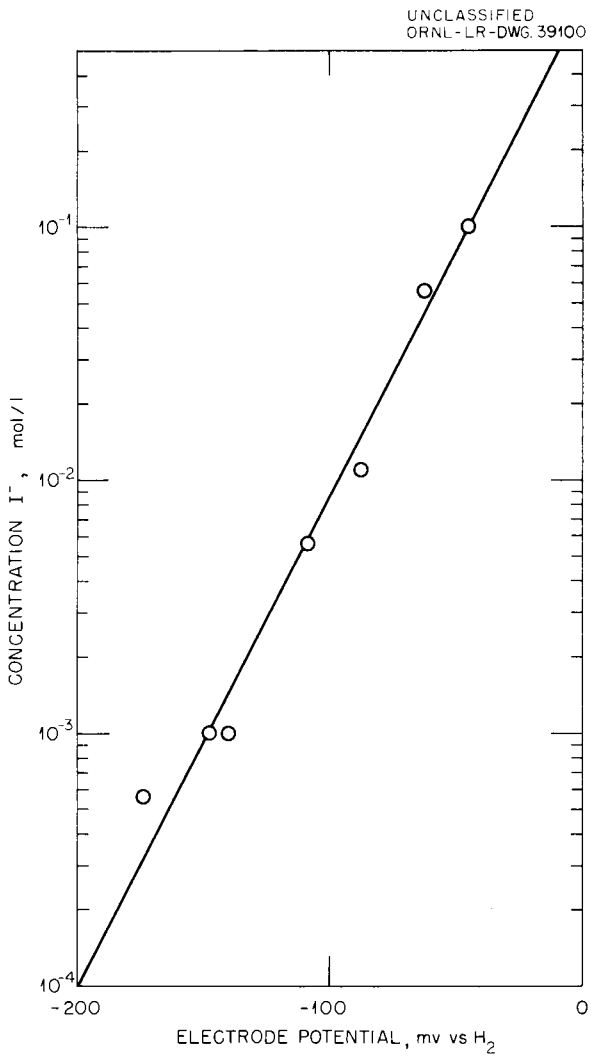

Fig. 24. Variation of the Potential of Unpolarizability, E_u, with Iodide Ion Concentration in 0.5 *f* H_2SO_4.

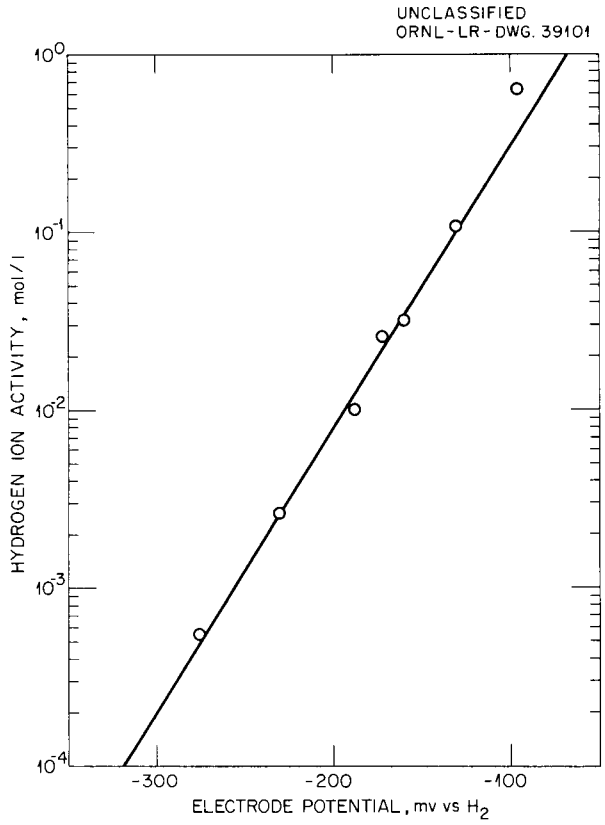

Fig. 25. Variation of the Potential of Unpolarizability, E_u, with pH at an Iodide Ion Concentration of 1×10^{-2} *f* in 0.5 *f* Sulfate Solution.

the current density abruptly. Similar transient measurements were made with both iodide ions and CO as inhibitors. Certain results are shown in Fig. 26. A Tafel line of 60 mv slope was observed also in the presence of the inhibitor, but at a given potential the current density was several decades lower than in solutions without inhibitor. In solutions containing CO or high concentrations of I^- (>0.1 *f*), the data may be interpreted by considering that a process having an ohmic resistance is operating in parallel with the process by which the Tafel line is produced. The ohmic resistance of that process ($\Delta E/\Delta j = R$) changed in inverse proportionality to the anodic steady-state current density. Prepolarization with anodic current also shifted the Tafel line of 60 mv slope to higher current densities.

Experiments to determine the surface concentration of iodide on iron as a function of iodide concentration, pH, and anodic polarization have been started. The decrease of the concentration of I^{131} in a small volume of solution after bringing it in contact with a large iron electrode was measured. The first experiments showed qualitatively that anodic polarization decreases the surface concentration of iodide ions. A theoretical discussion will be presented in a subsequent paper.

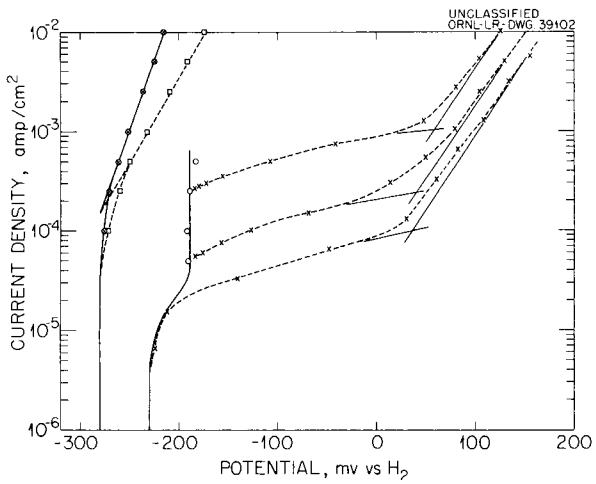

Fig. 26. Anodic Steady-State and Maximum-Overvoltage Curves in 0.5 *f* H_2SO_4 With or Without Saturation of the Solution with Carbon Monoxide. Steady states: ⊗ pure acid; O acid saturated with CO. Maximum overvoltages: □ pure acid; X acid saturated with CO, lowest curve without prepolarization, the two upper curves starting from the steady state corresponding to a prepolarization of 50 and 250 $\mu a/cm^2$ and measured by switching on additional currents.

FILM GROWTH AND REDUCTION PROCESSES ON ZIRCONIUM

R. E. Meyer

In a previous report,[7] the kinetics of the growth of thin films on zirconium immersed in oxygen-saturated Na_2SO_4 solutions was described. In order to study the mechanism of the oxidation and reduction partial processes occurring during film growth, attention was directed to experiments which isolated the individual partial processes.

The oxidation of zirconium (represented by $Zr + 2H_2O \longrightarrow ZrO_2 + 4H^+ + 4e^-$) was studied by maintaining a zirconium electrode at constant potential in an oxygen-free solution and measuring the current passed through the cell as a function of time. This current measured the oxidation rate directly, because the potential and environment were so adjusted that all possible competing reactions were negligible compared with the oxidation of zirconium. The potentiostat was set at values only a few tenths of a volt above the S.C.E. so that the potential would correspond to the values likely to be encountered in normal oxidation and corrosion processes.

By making use of the model suggested previously[7] for the growth of thin films under open-circuit conditions in oxygenated solutions, the following rate-time expression for film growth at constant potential was derived:

$$\frac{dI}{dt} = -AI^2 \left(\ln \frac{I}{K} \right)^2 . \qquad (1)$$

Here I is the current, t is the time, A is the product of the potential across the film and several constants, and K has the significance of a rate constant. This rate-time expression is the same as that derived for the open-circuit case except that the constant term A is different. Equation (1) integrates to a hyperbola if the term $(\ln I/K)^2$ is held constant. If I/K is greater than about 10^6 to 10^7, then the variation in $(\ln I/K)^2$ is small compared with the variation in I^2, and the deviations from a hyperbola are quite small. The experimental and derived curves may be made to fit quite closely by proper choice of K and A. In most cases there was very little deviation from a hyperbola, but in a few experiments the deviations were significant. Possibly metallurgical variables influence the value of K and explain the observed differences.

The film-covered electrodes formed in the oxygen-free solutions at constant potential have about the same electrochemical properties as those formed in oxygenated solution under open-circuit conditions and are therefore presumably similar structurally.

A new electrode potentiostat made possible the precise determination of reaction orders and rates of reduction of various oxidizing agents on zirconium. The order for O_2 with respect to its reduction at 75°C was unity. An earlier determination at 25°C on an aged electrode gave zero order. A small but complicated dependence of the reduction rate on pH was observed.

Measurements were also made of the orders and rates of reduction of cupric ion and hydrogen peroxide in oxygenated and acidified Na_2SO_4 solution. Both exhibited the peculiar but reproducible order of two-thirds with respect to their reduction. As shown previously[7] these orders are best explained by a dual-barrier model.

[7] R. E. Meyer, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 69–71.

The rates of reduction of both hydrogen peroxide and cupric ion were unusually small compared with reduction on most other electrode materials.

KINETICS OF GALVANIC COUPLES

F. A. Posey

The electrochemical kinetics of polyelectrode systems[8] has been extended to include the case of galvanic couples under activation control. A rigorous analysis of the electrochemical variables of circuitry used in measuring electrode potentials of galvanic couples reveals the particular importance of distinguishing between *measurable* electrode potentials of the elements of a couple and (unmeasurable) *interfacial* potential differences. Recognition of the relation between the two types of potential materially aids in understanding the behavior of galvanic couples.

Exact and explicit equations, derived for one of the simplest cases, relate properties of the couple (i.e., measurable potential, total anodic or corrosion current, and net current flowing between elements of a couple) to properties of the isolated elements (i.e., measurable potentials and rates of anodic and cathodic charge-transfer steps of processes occurring at interphases of elements). The treatment permits an unambiguous comparison between the concepts and quantities of electrochemical kinetics and those of older corrosion theory. Although explicit formulas for all quantities of interest are derivable only for the particular case examined, the method of treatment is appropriate for all galvanic couples under activation control and may serve as a starting point for the analysis of systems of still greater complexity. Details of the derivations have been published elsewhere.[9]

KINETICS AND EQUILIBRIA IN THE REDUCTION OF URANYL ION ON PASSIVE STAINLESS STEEL

F. A. Posey

Studies have continued on the mechanism of reduction of uranyl ion at the surface of passive stainless steel in acidic sulfate solutions. An earlier report[10] summarized results on the over-all rate of reduction of uranium species as a function of electrode potential and uranium concentration in oxygenated 0.010 *f* H_2SO_4 + 0.090 *f* Na_2SO_4 at 44, 67, and 85°C. Subsequent work has been concerned with the nature of the species existing in these solutions. Specifically, attention has been directed toward characterization of the important equilibria involving hexavalent uranium and determination of the individual electrochemical specific rate constants for reduction of all important species. Such information is essential to an understanding of the effect of hydrogen-ion concentration on the rate of reduction of uranyl ion on passive stainless steel in sulfate systems, and of deviations from over-all first-order kinetics for the reduction reaction at higher concentrations of hexavalent uranium.

Analysis of the aqueous acidic uranyl sulfate system, using electrochemical methods, is complicated by the situation that not only the equilibrium concentrations but also the specific rate constants of solution species may depend on the concentration of hydrogen ions in solution. Nevertheless, appropriately conceived potentiostatic experiments may provide all information necessary to characterize the system. However, interpretation of potentiostatic data on the uranyl sulfate system requires one additional set of data, namely, the dissociation quotient of the bisulfate ion for the ionic strength of the solutions used and covering the necessary temperature range. Several complementary methods, potentiostatic and galvanostatic, have been developed for determining the bisulfate-ion dissociation quotient in solutions of interest. Though all methods yielded usable data, only the following one was precise enough for the present purposes.

The potential of the glass electrode is a function of hydrogen-ion concentration at constant ionic strength. In fact, it was found that, for the experimental conditions of the present work,

$$\frac{dV}{d \log [H^+]} = \frac{RT}{F}$$

at all temperatures. Therefore, measurements of the potential of the glass electrode in perchloric acid solutions of ionic strength 0.3 (with sodium perchlorate as added neutral salt), as a function of added sodium sulfate, provided data from which the dissociation quotient of the bisulfate ion could be calculated. A least-squares analysis of all

[8] F. A. Posey, *Chem. Ann. Prog. Rep. June 20, 1957*, ORNL-2386, p 110.

[9] F. A. Posey, *J. Electrochem. Soc.* **106**, 571 (1959).

[10] F. A. Posey, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 65.

data, covering a temperature range from 22 to 85°C, led to Eq. (1):

$$\log_{10} K_{HSO_4^-} = -5.93 + 1.39 \times 10^3 \frac{1}{T} . \quad (1)$$

Here $K_{HSO_4^-}$ is the (concentration) dissociation quotient of the bisulfate ion at an ionic strength of 0.3, and T is the absolute temperature. Values of $K_{HSO_4^-}$ at lower temperatures calculated from Eq. (1) agree well with the best data reported in the literature.

Both hydrolysis and sulfate complex formation are important in the uranyl sulfate system, and potentiostatic studies are in progress on the equilibrium and kinetic aspects of these problems. Preliminary results in acidic perchlorate medium at 85°C indicate that, in agreement with observations of other investigators,[11,12] the first stage of hydrolysis of uranyl ion is adequately represented by the stoichiometry:

$$2UO_2^{++} + H_2O = UO_2UO_3^{++} + 2H^+ \quad (2)$$

The electrochemical specific rate constant of the uranyl ion is nearly an order of magnitude larger than that of its first hydrolysis product at 85°C. A comparison of these results with earlier data[10] shows that the electrochemical specific rate constant for reduction of the sulfate complex of uranyl ion on passive stainless steel is considerably larger than that of uncomplexed uranyl ion. Therefore, on the basis of the known magnitudes of the rate and equilibrium constants of the system, it seems possible to advance a qualitative explanation of the observation that the addition of acid markedly decreases the rate of reduction of hexavalent uranium on passive stainless steel in the presence of moderate amounts of sulfate ion. The determining factor in this effect is apparently the dissociation of the bisulfate ion; the addition of acid consumes free sulfate in the system, thereby also reducing the concentration of the sulfate complex of uranyl ion, which has the largest specific rate constant of any important uranyl species in solution. Deviations from over-all first-order reduction kinetics occur because the equilibrium expressed by Eq. (2) becomes important at higher uranium concentrations, reducing the relative concentrations of uranyl species having large rate constants for reduction.

[11] J. Sutton, *J. Chem. Soc. (Suppl. Issue No. 2)* 1949, S275.

[12] S. Ahrland, S. Hietanen, and L. G. Sillén, *Acta. Chem. Scand.* 8, 1907 (1954).

ANION EFFECTS IN CORROSION SYSTEMS

R. F. Sympson[13] F. A. Posey

In earlier reports[14-16] it was shown that chloride and thiocyanate ions in low concentrations produced an ennobling of the potential of iron electrodes passivated in an aerated inhibitor solution, or of stainless steel in aerated sulfate solutions without added inhibitor. It was thus indicated that the added ions accelerate some cathodic process when their concentration is below that at which destruction of passivity occurs. In an attempt to identify the process affected, subsequent experiments disclosed that the ennobling was not observable when triply distilled water and highly purified reagents were used. It was known that the laboratory supply of distilled water contains about 10^{-6} / copper ions, and the ennobling effect was immediately obtained when small concentrations of copper sulfate were added to the very pure system.

Further studies have been concerned with the mechanism whereby thiocyanate ion affects the reduction of cupric species on passive stainless steel in 1×10^{-4} / H_2SO_4 + 9×10^{-4} / Na_2SO_4 at 67°C. Potentiostatic techniques demonstrated that, in the dilute concentration range of interest, the most important interaction is the formation of the 1:1 complex between cupric and thiocyanate ions, in agreement with a recent spectrophotometric analysis.[17] The electrochemical specific rate constant of the thiocyanato complex is considerably larger than that of uncomplexed cupric ion. Tafel-type plots of the logarithm of the electrochemical specific rate constants of each species

[13] Summer employee, Ohio University, Athens.

[14] R. F. Sympson and G. H. Cartledge, *J. Phys. Chem.* 60, 1037 (1956).

[15] G. H. Cartledge and R. F. Sympson, *Chem. Semiann. Prog. Rep. Dec. 20, 1955*, ORNL-2046, p 10.

[16] G. H. Cartledge, *Chem. Semiann. Prog. Rep. June 20, 1956*, ORNL-2159, p 66.

[17] N. Tanaka and T. Takamura, *J. Inorg. & Nuclear Chem.* 9, 15 (1959).

against electrode potential are identical in form with those reported elsewhere[18,19] for the reduction of cupric ion on passive stainless steel in 0.1 *N* H_2SO_4 at 85°C. Further studies will also consider the equilibrium aspects of the competition between sulfate and thiocyanate ions for complex formation with cupric ion, as well as the kinetics for reaction of each important species at the interphase of passive stainless steel.

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[18] F. A. Posey, *Chem. Ann. Prog. Rep. June 20, 1957*, ORNL-2386, p 110.

[19] F. A. Posey, G. H. Cartledge, and R. P. Yaffe, *J. Electrochem. Soc.* 106, 582 (1959).

NONAQUEOUS SYSTEMS AT HIGH TEMPERATURES

HETEROGENEOUS ISOTOPIC EXCHANGE REACTIONS OF FLUORINE-CONTAINING COMPOUNDS

W. H. Christie

The study of the fluorine exchange between gaseous fluorocarbons and solid metal fluorides was extended. The exchange of F^{18}-labeled perfluoropropene gas with solid CsF was examined as a function of the pretreatment of the crystalline CsF phase. For grossly defective CsF crystals, prepared by rapid recrystallization from water, the exchange was found to consist of a very rapid initial phase followed by a slow logarithmic one. Annealing the CsF crystals at approximately two-thirds of the melting point eliminated the rapid initial exchange. Only slow exchange was observed in this case.

The rate and extent of exchange of perfluoropropene with CsF were correlated with the catalytic properties of CsF. Cesium fluoride when properly activated is a catalyst for the polymerization and oxidation of perfluoropropene.

The mechanism of the exchange probably involves the formation of an unstable olefin π-bond complex with the metal fluoride. The rapid exchange with the bulk of the crystal was facilitated by the defect structure of the solid.

VAPOR PHASE ASSOCIATION OF ALKALI HALIDES

S. Datz Wm. T. Smith, Jr.[1]

In attempting to reconcile the vapor pressures of some alkali halides measured by effusion[2] with other thermodynamic data, it became apparent that the degree of association of these substances in the vapor is uncertain. A measurement of the vapor density was therefore undertaken, and the first published results[3] are abstracted here.

"A technique has been developed for the determination of the molecular weight of vapors at high temperatures by measurement of the pressure at constant vapor density, the pressure measuring device being a molten gold manometer. For the dissociation of Na_2I_2 into NaI, measurements from 1175° to 1350°K indicated a ΔE^0 of 40.2 kcal. mol.$^{-1}$ and a ΔS^0 of 27.0 e.u. at 1260°K."

MOLTEN SALT–METAL SOLUTIONS

Electrical Conductivity of Solutions of Potassium Metal in Molten Potassium Fluoride

H. R. Bronstein M. A. Bredig

In earlier reports,[4,5] the strong dependence of the equivalent conductance at infinite dilution of the alkali metal dissolved in its molten halide, Λ_M^∞, on the nature of the anion of the salt was demonstrated. It was possible to conclude that in the fluoride melt, Λ_M^∞ would reach a very low value. A first series of measurements on solutions of potassium metal in molten potassium fluoride at 905°C carried out with the use of an MgO single-crystal cell (Fig. 27) shows this to be the case, with Λ_M^∞ approximating 750 ohm^{-1}·cm^2, which is about one-fourth the next higher Λ_M^∞ of 3000 ohm^{-1}·cm^2 for the chloride system. As proposed earlier,[4,5] this strong anion effect is believed to be connected with the polarizability of the anion which promotes electronic conductance and which is very low for the fluoride compared with that of the chloride, bromide, or iodide.

In Fig. 27 the square root of the concentration expressed in metal equivalents per liter is plotted as the abscissa because it was observed that for the potassium metal–iodide system, the log Λ_M when plotted against the square root of c gave a straight line ending in the equivalent conductance of pure metal. The significance of this relationship is not clear, and Fig. 27 shows that it does not seem to hold true for the other three halide systems, whose curves appear to cross the iodide curve and to approach the conductivity

[1]Consultant, University of Tennessee Chemistry Department.

[2]S. Datz and R. E. Minturn, *Chem. Ann. Prog. Rep. June 20, 1957*, ORNL-2386, p 125.

[3]S. Datz and Wm. T. Smith, Jr., *J. Phys. Chem.* 63, 938 (1959).

[4]H. R. Bronstein and M. A. Bredig, *J. Am. Chem. Soc.* 80, 2077–81 (1958).

[5]H. R. Bronstein and M. A. Bredig, *Chem. Ann. Prog. Rep. June 20, 1957*, ORNL-2386, p 124; *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 75.

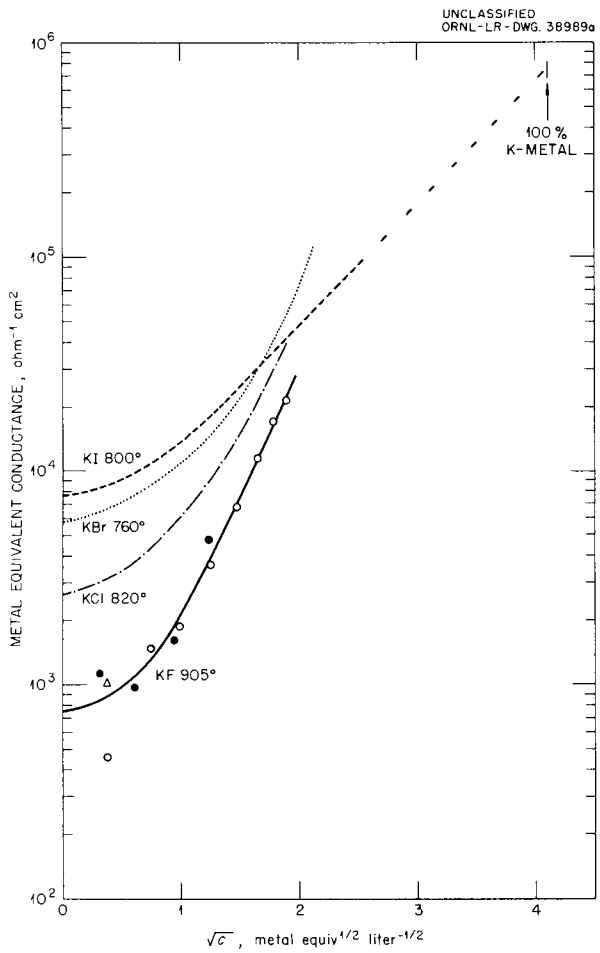

Fig. 27. Equivalent Conductance of Potassium Metal Dissolved in Molten Potassium Fluoride as a Function of Metal Concentration.

of the pure metal in a manner different from a straight line. Somewhat similar behavior of the iodide system was also observed in the sodium systems. To clarify the significance of these observations, measurements of the conductivity in the metal-rich portions of the systems are planned.

A plot of log Λ_M vs the mole fraction of the metal shows a lack of order, with all curves crossing each other. The greater order in Fig. 27, where a simple function (the square root) of the metal concentration expressed in equivalents per liter was chosen as the independent variable, is thought to reflect the importance of the separation of the metal molecules in space, which depends on the molar volume of the salt as well as on its mole fraction, and the decrease of which leads to the gradual establishment of truly metallic conductance.

Finally, it may be pointed out that a value of 3.77 ± 0.07 $ohm^{-1}\cdot cm^{-1}$ for the specific conductance of pure molten KF at 905°C found during this investigation must replace a value of 4.48 $ohm^{-1}\cdot cm^{-1}$ derived from an earlier experimental equation[6] which was found to be in error most probably because of a distortion of the potential probe arrangement used in the earlier work. The new value is in agreement with a value of 3.80 ± 0.05 $ohm^{-1}\cdot cm^{-1}$ reported by Yim and Feinleib.[7]

Transport of Color in Cadmium and Sodium Metal Solutions in Their Molten Bromides

A. S. Dworkin M. A. Bredig

An experiment was designed to follow the movement of color through a metal–metal halide solution when electrical current is passed through the solution.

A quartz tube containing the salt was placed in a furnace with a viewing port. Two smaller-bore tubes, the ends of which were closed with porous alundum plugs about 2 cm in length, extended into the salt. The salt was melted, and some of it was drawn up through the plugs into the tubes. Metal was added to each of the tubes in excess of the amount necessary to form saturated solutions above the plugs. Electrodes were inserted into the saturated solutions, current was passed, and a visual observation of the direction of the movement of color through the porous plugs was made.

The nature of the Na-NaBr solution necessitated more complex apparatus than did the $Cd\text{-}CdCl_2$. Synthetic sapphire was used for the inner tubes rather than quartz, and the method of inserting the sodium and keeping it in solution was more complicated. The electrodes were graphite for the $Cd\text{-}CdCl_2$ and stainless steel for the Na-NaBr system.

In the $Cd\text{-}CdCl_2$ experiments, about 0.7 amp caused the color boundary to move the length of the plug in about 30 min toward the negative

[6] I. S. Yaffe and E. R. Van Artsdalen, *Chem. Semiann. Prog. Rep. June 20, 1956*, ORNL-2159, p 79, Table 24.

[7] E. W. Yim and M. Feinleib, *J. Electrochem. Soc.* 104, 626 (1957).

electrode, during which time the color boundary in the other plug remained stationary. Reversing the electrodes caused a reversal in the direction of the moving boundary. This can be interpreted to indicate the presence of a positively charged complex, probably Cd_2^{++} (ref 8). In the Na-NaBr experiment the color migrated toward the positive electrode, indicating the absence of colored positive complexes and the presence of electronic conductance previously found in our electrical conductance measurements.

Heat of Fusion Measurements

A. S. Dworkin M. A. Bredig

Many of the values of the heats of fusion of the alkali halides which appear in the literature are of questionable validity, especially when they have been derived by means other than calorimetric. Since these values are of importance in connection with our metal–metal halide studies, a calorimeter was built to obtain values of greater reliability.

A copper block calorimeter was chosen as the simplest to build and operate to obtain the desired accuracy. The heat content of the sample and container was measured over a sufficient temperature range above and below the melting point of the salt to allow extrapolation to the melting point. The difference in heat content at the melting point is equal to the heat of fusion. The calorimeter was calibrated with an NBS sample of synthetic sapphire (Al_2O_3). The precision of the heat content measurements is better than 0.2%, leading to heat of fusion results which are good to about 1%. This was checked by determining the heat of fusion of KCl, which agreed with the NBS value[9] to about 1%.

The alkali-metal salts measured were LiCl, LiBr, LiI, NaBr, NaI, KCl, KBr, KI, CsBr, and CsI. The lithium and sodium salts were dried by slowly heating them under vacuum and then melting under argon and filtering while molten. The potassium and cesium salts were Harshaw single crystals which were taken to be dry except for surface moisture which was removed by pumping. The salts were sealed in Inconel containers under argon.

In Table 17 are the currently measured values of the heats of fusion (ΔH_m) together with previously measured acceptable calorimetric heats of fusion by other investigators. Also listed are the entropies of fusion (ΔS_m) calculated from these values and the entropies of fusion currently found in Brewer's tabulation,[10] most of which have been derived from noncalorimetric methods.

It is noteworthy that the entropy of fusion ranges from 6.26 in cesium iodide to 4.7 in lithium iodide, while the older, erroneous values ranged from 6.7 to as low as 2.0 e.u./mole. It is believed that the greater constancy of the entropy of fusion is also in better agreement with present ideas about the process of melting in the alkali halides. It is worth noting that among the cesium halides, as was predictable,[11] the two groups having different crystal structures, CsF-CsCl (NaCl type) and CsBr-CsI (CsI type), are distinguished by different entropies of fusion, approximately 5.3 and 6.2 e.u./mole, respectively.

The heat of fusion of BiI_3 has also been measured and was found to be 9.41 kcal.

Nonideality and Metal Association in the Sodium–Sodium Halide Systems

M. A. Bredig H. R. Bronstein
A. S. Dworkin

Earlier measurements[12] of these systems had left considerable uncertainty with regard to the degree of deviation from Raoult's law for the salt component in the vicinity of its melting point. A redetermination of the difference between the melting point of the pure salt and the monotectic temperature yielded new values for this difference, the error in the earlier data being due to a slight contamination by oxide.

In addition, in the course of the electrical conductivity measurements,[13] it also became

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[8] Cf. K. Grjotheim, F. Grönwold, and J. Krogh-Moe, *J. Am. Chem. Soc.* 77, 5824 (1955).

[9] T. B. Douglas, NBS, private communication.

[10] L. Brewer, *Natl. Nuclear Energy Ser., Div. IV* 19B, 196–97 (1950).

[11] J. W. Johnson, P. A. Agron, and M. A. Bredig, *J. Am. Chem. Soc.* 77, 2734 (1955).

[12] M. A. Bredig, J. W. Johnson, and W. T. Smith, Jr., *J. Am. Chem. Soc.* 77, 307 (1955).

[13] H. R. Bronstein and M. A. Bredig, *J. Am. Chem. Soc.* 80, 2077 (1958).

Table 17. Entropy of Fusion of the Alkali Halides

Alkali Halide	ΔH_m (kcal) (Calorimetric)	ΔS_m (e.u.)	ΔS_m (e.u.) (Brewer)[a]
LiF	6.47[b]	5.79	2.1
LiCl	4.76[c]	5.39	3.6
LiBr	4.22[c]	5.13	3.5
LiI	3.50[c]	4.72	2.0
NaF	8.03[d]	6.33	5.5
NaCl	6.85,[e] 7.01[f]	6.38, 6.53	6.7
NaBr	6.24[c]	6.10	6.0
NaI	5.64[c]	6.03	5.6
KF	6.75[e]	5.98	5.8
KCl	6.27,[g] 6.34[c]	6.00, 6.07	6.2
KBr	6.10[c]	6.05	4.9
KI	5.74[c]	5.99	4.3
CsF	5.19[c]	5.32	2.6
CsCl	4.84[c]	5.27	3.9
CsBr	5.64[c]	6.20	3.0
CsI	5.60,[c] (5.98[h])	6.26, (6.6[h])	3.0

[a] L. Brewer, *Natl. Nuclear Energy Ser., Div. IV* 19B, 196–97 (1950).
[b] T. B. Douglas and J. L. Dever, *J. Am. Chem. Soc.* 76, 4826 (1954).
[c] This work.
[d] C. J. O'Brien and K. K. Kelley, *J. Am. Chem. Soc.* 79, 5616 (1957).
[e] K. K. Kelley, *U.S. Bur. Mines Bull.* 476, 166, 142 (1949).
[f] M. Tashiro, *Glass Ind.* 37, 549 (1956).
[g] T. B. Douglas, NBS, private communication.
[h] D. F. Smith, University of Alabama, private communication.

apparent that the composition of the monotectic salt-rich liquid phase was in error due to incomplete separation of the liquid metal and the salt phases in the early sampling method. It is now believed that the earlier solubility values for the metal in the molten salt were too high because metal phase present in the salt sampling chamber during equilibration was retained therein. The new data obtained by a different sampling method[13] and summarized in Table 18 and Fig. 28 show a considerable positive deviation from Raoult's law, indicating that in the monotectic salt-rich liquid, similarly as in the potassium systems, approximately 60 to 70% of the dissolved metal is present in the form of diatomic molecules. A more detailed discussion has been submitted for publication in the *Journal of Physical Chemistry* under the title "Miscibility of Liquid Metals with Salts. IV. The Sodium–Sodium Halide Systems at High Temperatures."

Table 18. Nonideality and Metal Association in the Sodium–Sodium Halide Systems

	Systems of Na with			
	NaF	NaCl	NaBr	NaI
T_m, mp of pure salt, °C	995[a]	800[b]	747[a]	660.1[c]
ΔH_f, heat of fusion (salt), cal	8000	7000	6260[c]	5620[c]
T_{mon}, monotectic temperature, °C	990[a]	795.3[b]	740[a]	656.7[c]
Monotectic salt-rich liquid phase				
X_{solute} (calc)[d]	0.012	0.014	0.020	0.011
X_{Na} (analyt)		0.021	0.029	0.016
α(approx)[e]		0.3	0.4	0.4

[a]H. R. Bronstein and M. A. Bredig, *J. Am. Chem. Soc.* 80, 2077 (1958).

[b]J. W. Johnson and M. A. Bredig, 1956.

[c]A. Dworkin and M. A. Bredig, 1959.

[d]Ideal (Raoult's law) mole fraction of solute: $X_{solute}\,(\text{calc}) = \frac{\Delta H_f}{R} \cdot \frac{T_m - T_{mon}}{T_m \cdot T_{mon}}$.

[e]Estimate of degree of dissociation of Na_2 molecules: $\alpha = \frac{2X_{solute}\,(\text{calc})}{X_{Na}\,(\text{analyt})} - 1$, where X_{solute} (calc) = total moles ($Na + Na_2$) after dissociation of Na_2, and $\frac{1}{2}X_{Na}$ (analyt) = moles of Na_2 before dissociation, both per 1 mole of metal-salt mixture.

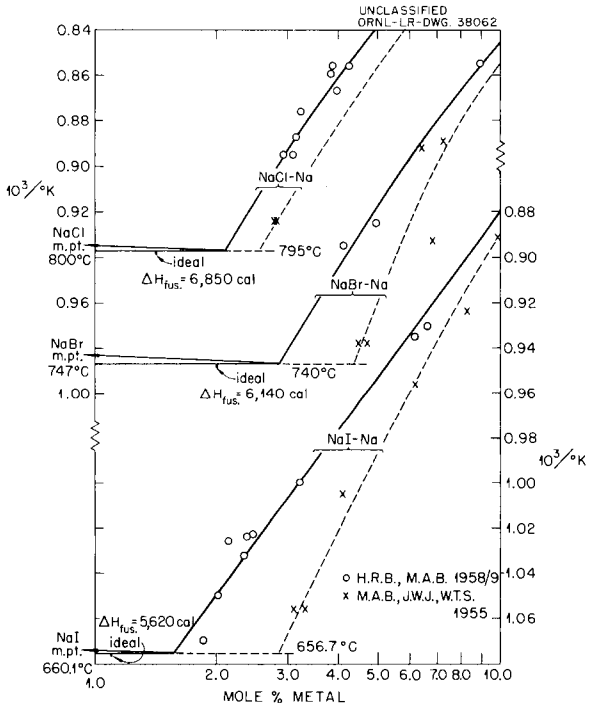

Fig. 28. Derivation of Monotectic Liquid Salt-Rich Phase Composition from Intersection of Solubility Curves with Monotectic Horizontals. Comparison with "ideal" composition (positive deviation from Raoult's law).

Dimeric Bismuth(I) Ion, $(Bi_2)^{++}$, in Molten Bismuth Trihalides

M. A. Bredig

Vapor pressure measurements by Cubicciotti *et al.*[14] of bismuth halides over solutions of bismuth metal in its halides were interpreted semiquantitatively through Oracle calculations by assuming the formation of two solute species, namely, a bismuth subhalide, Bi_2Cl_2, and diatomic metal molecules, Bi_2. Also, the melting-point depression produced by the addition of Bi to $BiCl_3$ was explained by the formation of Bi_2Cl_2, after a correct value for the heat of fusion of $BiCl_3$ had become available through direct calorimetric determination. Details of the discussion are found in a paper just published.[15]

[14]D. Cubicciotti, F. J. Keneshea, Jr., and C. M. Kelley, *J. Phys. Chem.* 62, 463 (1958); 62, 999 (1958).

[15]M. A. Bredig, *J. Phys. Chem.* 63, 978 (1959).

CHEMICAL PHYSICS

MICROWAVE AND RADIO-FREQUENCY SPECTROSCOPY

Hydrogen Gas and Atomic Hydrogen Yields from Irradiated Acids

R. Livingston A. Weinberger

In earlier reports[1,2] results of assays for atomic and molecular hydrogen in irradiated acids were summarized. In this work aqueous solutions of sulfuric, phosphoric, and perchloric acids were irradiated at 77°K with Co^{60} gamma rays and then melted and assayed for molecular hydrogen and oxygen by conventional vacuum-line techniques. The frozen irradiated acids were also examined in a paramagnetic resonance spectrometer to determine the concentration of atomic hydrogen present. All the atomic hydrogen values reported were relative values obtained by making comparisons with one reference concentration of sulfuric acid. An accurate absolute assay of the reference sample was to be attempted at a later date. This program is now nearing completion and will soon be prepared for publication. The measurements of the gas yields and relative atomic hydrogen yields in the three acids are complete. Preliminary results on the absolute assay of atomic hydrogen from 0.129 mole fraction sulfuric acid, irradiated at 77°K as a glass, are close to twice the molecular yield, $G_{H_2} = 0.62$, found by warming similarly irradiated acids. This indicates a direct correspondence between the stably trapped atomic intermediate and the final chemical product.

Paramagnetic Resonance Studies of Irradiated Systems

H. Zeldes R. W. Holmberg
R. Livingston

Previous mention has been made[3] of a study of calcium tungstate single crystals irradiated at 77°K with gamma rays. Two groups of lines were found, and the g-tensors describing their behavior have been deduced. The rates at which the two groups of lines disappeared when the crystal was warmed have been studied and have been found to be second order, with the same rate for each group of lines. Moreover, the concentrations of the species giving rise to the two groups of lines are about the same. This strongly indicates that the two species are formed in the same elementary process during the irradiation and that their disappearance is by back reaction with each other. Single crystals prepared in two different ways have given greatly different yields of the two species, which suggests the role of impurities or defects to be important. The lines of one group show a striking width anisotropy which is not understood. As mentioned earlier,[3] each group of lines contains weak hyperfine lines. Anomalies in their appearance have also been found and are now being studied in greater detail.

Single crystals of calcite (calcium carbonate) have been obtained from several natural sources and examined before and after irradiation at 77°K. A number of the samples contained paramagnetic impurities, particularly manganese, and their spectra could be seen before irradiation. All samples after irradiation had one characteristic very sharp line at the free electron g value. This line became power-saturated very easily and showed essentially no anisotropy. Other lines formed by irradiation seemed to be attributable to impurities. One crystal, for example, showed a six-line spectrum which was characteristic for a species located in a lattice site of threefold multiplicity and with the electron coupled to a nucleus of spin $\frac{1}{2}$.

New components have been built and put into operation for enhancing spectrometer sensitivity. These include a device to stabilize the klystron frequency by locking it on the measuring cavity, and a new chart recording system. This apparatus will be used for the Van de Graaff experiment on liquids mentioned in the last progress report.[4]

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[1] A. Weinberger and R. Livingston, *Chem. Ann. Prog. Rep. June 20, 1957*, ORNL-2386, p 128.

[2] R. Livingston and A. Weinberger, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 89.

[3] H. Zeldes, R. Livingston, and R. Holmberg, *Chem. Ann. Prog. Rep. June 20, 1957*, ORNL-2386, p 129.

[4] R. Livingston and R. Holmberg, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 89.

Diluted Single Crystals of α,α-Diphenyl-β-picrylhydrazyl

R. W. Holmberg R. Livingston

Diphenylpicrylhydrazyl (DPPH) is a stable free radical that is commonly used as a test material in paramagnetic resonance spectrometers and has been the object of a large number of paramagnetic studies.[5] The spectrum of a dilute benzene solution of the radical consists of five lines that are only moderately well resolved. The five lines result from hyperfine interaction of the unpaired electron with the two (hydrazyl) nitrogen nuclei, and it appears that the isotropic parts of the couplings to the two nitrogen nuclei are about equal. Only the isotropic contribution to the hyperfine interaction is observed in solution. A single crystal of the undiluted radical shows only a single sharp absorption line; exchange interactions in the undiluted material are very large, and no hyperfine effects are observed.

In the present research single crystals of diamagnetic α,α-diphenyl-β-picrylhydrazine ($DPPH_2$) containing small amounts of DPPH have been grown from benzene solution. This scheme for achieving magnetic dilution greatly reduces the exchange interaction as well as electron magnetic dipole-dipole interactions. The spectrum from a single crystal, instead of being a single sharp line, is found to be a multiplet of anisotropic hyperfine lines. A study of this more complex spectrum gives much more detailed information on the electron probability distribution; effects from both the isotropic and anisotropic terms of the hyperfine interaction are seen.

In order to study the spectrum most effectively, it was necessary to know something of the structure of the crystals. X-ray diffraction studies were made (see the following section of this Annual Report), and the mixed crystal was found to have the same structure as $DPPH_2$. It is monoclinic with space group $P2_1$ and with two molecules per unit cell. Benzene is also incorporated, and from density measurements it appears that there are probably two benzene molecules per unit cell.

The spectra have been measured for many orientations of a single crystal, but usable data were obtained for only a limited number of these orientations since the line spacings were often not large compared with the line widths. In addition, for many orientations two partly superimposed spectra were seen, one spectrum from each of the two molecules in the unit cell. By orienting the applied magnetic field parallel to the *ac* plane of the crystal, however, the two molecules behaved in an equivalent manner, and greatly simplified spectra were seen. These spectra were consistent with an unpaired electron interacting anisotropically with two nitrogen nuclei (spin = 1); for some orientations, for example, the expected nine-line spectrum was seen. The measurements thus far show the interactions to be anisotropic, as would be expected, since the electron has mostly *p*-orbital character. Moreover, the interaction is noticeably stronger with one nitrogen. The maximum splittings observed in the *ac* plane were 24 gauss for one nitrogen and 15 for the other. An examination of the data for other planes indicates the true maxima to be roughly 8% larger than these numbers. From the partial analysis of the data it also appears that the principal axes of the two tensors describing the hyperfine interactions will have different directions within the crystal. The data are not sufficient to elucidate these two tensors completely. It is hoped that a more detailed analysis can be made with data from molecules having incorporated N^{15} (spin = $\frac{1}{2}$). DPPH has been synthesized with the nitrogen closest to the picryl group replaced by N^{15}. A single crystal is now being prepared. Successful experiments will enable a positive statement to be made with respect to an assignment of which nitrogen has which hyperfine interaction. Moreover, with reduced multiplicity of lines it is hoped that a larger amount of valid data can be obtained for various crystal orientations. This will allow firmer statements to be made about the hyperfine tensors, which in turn will give new evidence on the structure of the radical.

[5] See, for example, G. Berthet, *La Résonance Paramagnétique Electronique, et la Structure des Radicaux Libres Organiques Stables*, thesis, Faculté des Sciences de l'Université de Paris, Feb. 1957, and the references contained therein.

CELL SIZE AND SPACE GROUP OF α,α-DIPHENYL-β-PICRYLHYDRAZINE

R. D. Ellison R. W. Holmberg

In connection with a study described in the preceding section, the crystallographic unit cell size and space group of diphenylpicrylhydrazine ($DPPH_2$) were determined for crystals grown from a benzene solution. The crystals were sufficiently stable to the atmosphere to allow powder diffraction patterns to be taken on a diffractometer without difficulty, but rather special handling was required to preserve small individual crystals for a time period long enough to take single-crystal patterns. The single crystals were mounted on glass wool fibers and were enclosed in, but not touching the walls of, 0.5-mm thin-wall glass capillary tubes that also contained small wads of cotton soaked with benzene. Precession camera data for two zones were obtained in addition to powder diffraction data.

From the single-crystal data, it is seen that $DPPH_2$ as grown from benzene solution is monoclinic with a cell size of

$$a = 9.20\ \text{Å}, \qquad b = 10.66\ \text{Å},$$

$$c = 11.71\ \text{Å}, \qquad \beta = 110°43'.$$

The powder patterns were indexed on the basis of this cell and found to confirm the cell size.

The systematic absence of the $0k0$ reflections when k is odd, together with a readily observable pyroelectric effect, indicates the noncentrosymmetric space group $P2_1$. The density, calculated on the basis of two molecules of diphenylpicrylhydrazine plus two benzenes of crystallization per cell, is 1.46 g/cc, which is in good agreement with a preliminary pycnometric density measurement of 1.40 g/cc.

NEUTRON DIFFRACTION STUDY OF THE AMMONIUM AND HYDRONIUM PERCHLORATES

H. G. Smith H. A. Levy

It is known from x-ray work[6] that perchloric acid monohydrate is isomorphous with ammonium perchlorate, which strongly suggests that the compound is actually the "salt" $(OH_3)^+(ClO_4)^-$. This has been verified, at low temperatures at least, by proton magnetic resonance.[7]

Since there is considerable interest in the structure of the hydronium ion, a neutron diffraction study of hydronium perchlorate was undertaken to determine as accurately as possible the configuration of the OH_3^+ ion. A similar investigation of ammonium perchlorate also was made in order to compare the two structures in detail.

Room-temperature intensity data of the $(h0l)$ and $(hk0)$ zones were obtained for NH_4ClO_4. Nuclear density maps indicated that the protons in the ammonium ion were disordered and very likely undergoing a high degree of reorientation. A least-squares analysis based on a freely rotating NH_4^+ ion gave satisfactory agreement between the observed and calculated structure factors. These results are in accord with a recent investigation[8] of the infrared spectrum of NH_4ClO_4.

The ammonium ion is surrounded by 12 oxygen atoms of neighboring perchlorate groups with an average N-O distance of about 3.1 Å. The perchlorate ion is slightly distorted from a perfect tetrahedron, the Cl-O bonds being 1.46, 1.43, and 1.42 Å (±0.014 Å). The thermal parameters of the oxygen atoms are highly anisotropic, indicating a rotary oscillation of the perchlorate ion.

Intensity data of the $(h0l)$ and (hkh) zones were obtained for hydronium perchlorate, and of the $(h0l)$ zone for 83% deuterated hydronium perchlorate. The environment of the hydronium ion is similar to that of the ammonium ion in the ammonium perchlorate, but the hydronium ion is disordered in a different way. A likely model is one with the protons directed toward three neighboring ClO_4^- ions while in several disordered positions.

SINGLE-CRYSTAL NEUTRON DIFFRACTION STUDY OF HYDROGEN PEROXIDE

W. R. Busing H. A. Levy

Single-crystal neutron diffraction studies of H_2O_2 have been previously reported by the authors.[9,10] In this earlier work, which was

[6] M. Volmer, *Ann. Chem., Liebigs* 440, 200 (1924); F. S. Lee and G. B. Carpenter, *J. Phys. Chem.* 63, 279 (1959).

[7] R. E. Richards and J. A. S. Smith, *Trans. Faraday Soc.* 47, 1261 (1951).

[8] T. C. Waddington, *J. Chem. Soc.* 1958, 4340.

[9] W. R. Busing and H. A. Levy, *Chem. Ann. Prog. Rep. June 20, 1957*, ORNL-2386, p 137.

[10] W. R. Busing and H. A. Levy, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 90.

based on intensity measurements of *hk*0 and *hhl* reflections, there was some overlapping of the hydrogen atoms, and, consequently, the hydrogen parameters were not very accurately determined. This work has now been supplemented by the measurement of the intensities of 65 reflections of the *h*0*l* zone in which the hydrogen atoms are well resolved.

The crystal structure parameters were refined by the method of least squares using the data from all three zones, but omitting five strong reflections which were thought to be affected by extinction. These calculations were performed on the IBM-704 computer using a program which is described elsewhere.[11,12] The final discrepancy factor, R, based on F^2 was 7.5%, and the refined coordinates and temperature factor coefficients are given below with their standard errors.[13]

	Oxygen	Hydrogen
x	0.0730 ± 0.0004	0.2180 ± 0.0009
y	0.1672 ± 0.0005	0.4524 ± 0.0012
z	0.2213 ± 0.0002	0.3818 ± 0.0005
$4a^2B_{11}$	1.57 ± 0.07	2.64 ± 0.16
$4a^2B_{22}$	1.66 ± 0.07	3.11 ± 0.15
$4c^2B_{33}$	1.51 ± 0.06	2.28 ± 0.09
$4a^2B_{12}$	0.12 ± 0.05	−0.33 ± 0.12
$4acB_{13}$	−0.11 ± 0.06	−0.62 ± 0.12
$4acB_{23}$	−0.04 ± 0.06	−0.20 ± 0.12

The molecular geometry of H_2O_2 is shown in Fig. 29 with some of the interatomic distances and angles which have been computed[14] from the above parameters. Of particular interest is the fact that the dihedral angle defined by the molecule is essentially a right angle. In a theoretical treatment of the structure Penney and Sutherland[15] predicted that the predominant factor determining this angle would be the repulsion of nonbonded electrons in the *p*-orbitals on each oxygen. While this would tend to make the angle 90°, it was estimated that the repulsion between the two O-H dipoles would increase the angle to about 100°. The present results seem to indicate that the latter effect is of much less importance than was previously supposed.

[11] "A Crystallographic Least-Squares Program for the IBM-704," this report.

[12] W. R. Busing and H. A. Levy, *Acta Cryst.* 12, 351 (1959).

[13] See refs 9 and 10 for the definitions of these parameters.

[14] For the method of computation see W. R. Busing and H. A. Levy, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 91.

[15] W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.* 2, 492 (1934).

A SINGLE-CRYSTAL NEUTRON SPECTROMETER FOR A HIGH FLUX REACTOR[16]

S. W. Peterson H. A. Levy

A small lightweight single-crystal neutron spectrometer has been developed from a General Electric SPG x-ray spectrogoniometer as the basic unit. The design of this unit has been altered to adapt it for step scanning of diffraction peaks. Novel features of the over-all arrangement include provision for utilization of a single beam hole for simultaneous operation of two diffraction units, and for operation of one of the units as a horizontal axis instrument with the detector swinging in a vertical plane. This latter arrangement was chosen to allow selection of a large scattering angle (90°) from the monochromator to take advantage of the higher wavelength resolution available at large angles. Additional novel features include a rotatable steel disk shutter penetrated by several channels, which provides convenient cutoff of the main beam, and a wavelength changer, which consists of a movable channel in the solid shielding surrounding the monochromating crystal. The design of the latter feature is one in which a small stepped cylinder containing an off-axis channel, which, however, looks at a common center, is mounted off axis in a hollow in a larger stepped cylinder. By means of suitable geared rotations of the two cylinders the channel can be rotated in a horizontal plane about the center at the monochromator, and thus the channel opening at the shield surface is effectively translated in a horizontal plane.

Data collection is based on a monitored step scanning scheme. At the present stage automatic step scanning of a diffraction peak is provided

[16] Details of the design were developed by D. L. Holcomb, Engineering and Mechanical Division.

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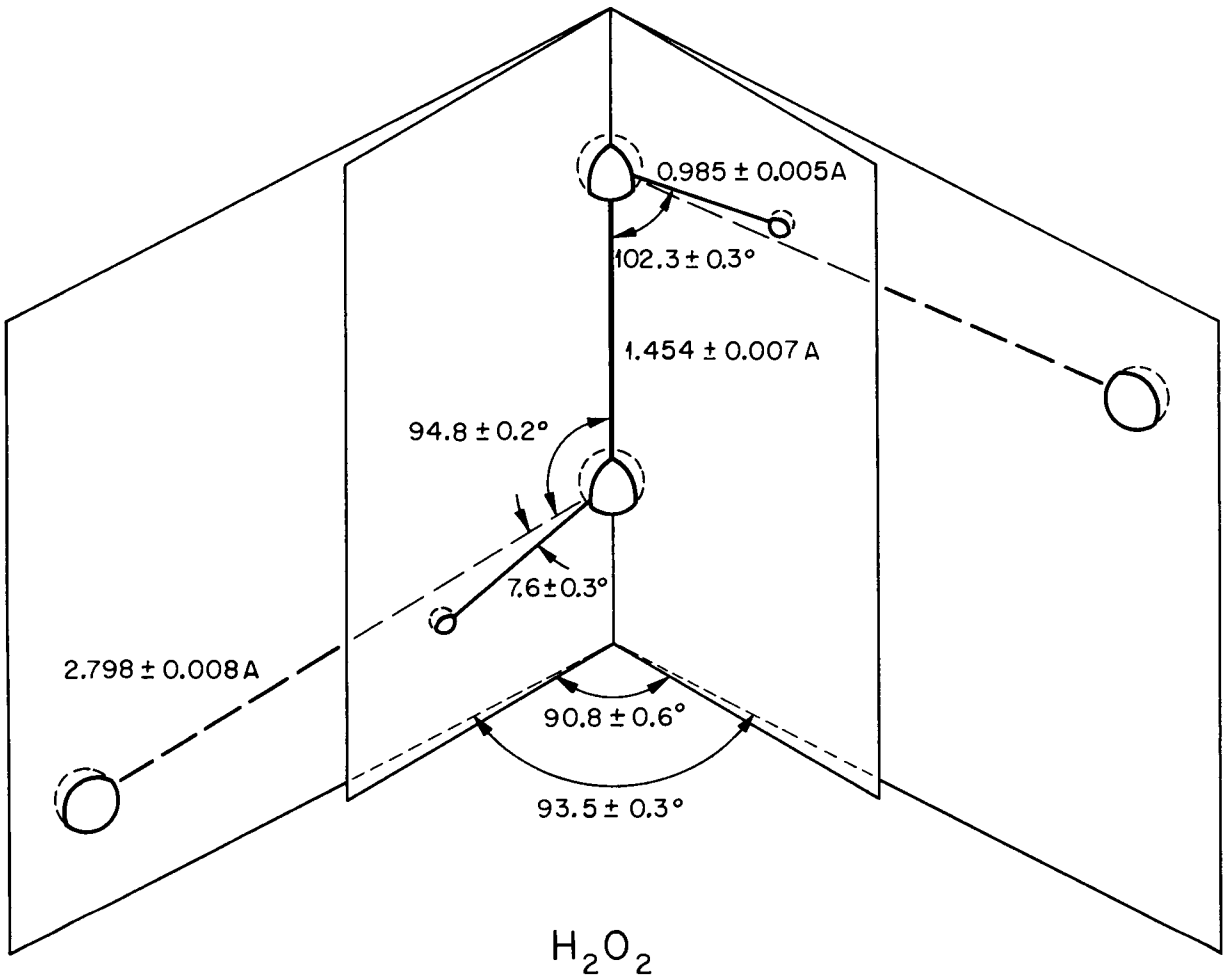

Fig. 29. Molecular Geometry of H_2O_2.

for, but crystal and counter start positions must be preset manually. The operation is controlled by a sequencing system which provides for continuous cycling through the counting cycle, data printout, and motor advance of a preset increment. Data recording is available as a cumulative digital printout of the scaler count and also in analog chart record form by means of a pump circuit coupled to a chart recorder. A G-E crystal orienter whose angle setting must be made manually provides for collection of three-dimensional data. Completely automatic data collection can be incorporated by utilizing digitizer control of crystal angle settings, and this is planned for a later date.

Preliminary results with this equipment at the ORR indicate that the new design features have worked out very successfully. A high-intensity monochromatic beam with good wavelength resolution seems to have been obtained by utilizing the 90° scattering angle. Compared with the ORNL Graphite Reactor an increase in diffracted beam intensity of the order of 5–10 has been achieved along with a reduction of wavelength

spread by a factor of 4. A very satisfactory alignment of the spectrometer has been completed, and the instrumentation is in preliminary working order.

HYDROGEN POSITIONS IN ACETAMIDE HEMIHYDROCHLORIDE

S. W. Peterson J. E. Worsham[17]

Acetamide hemihydrochloride is a rather unstable compound in which two acetamide molecules are associated with a molecule of HCl. An x-ray investigation[18] established a structure in which two acetamide molecules related by a center of symmetry are closely linked through the oxygen atoms. This bond is due presumably to a very short O–H–O contact of 2.40 Å in which the hydrogen atom or nucleus from HCl serves as the link atom. The x-ray analysis yielded approximate locations of five of the six crystallographically distinct hydrogen atoms but no evidence was found for a hydrogen joining the oxygen atoms. This compound thus presented a unique opportunity to study a structure containing presumably the shortest O–H–O bond known from x-ray observations in which the linking hydrogen may be a proton and to discover whether this might be another example[19] of a centered hydrogen bond.

The present neutron study is based on data of two zones ($h0l$ and $hk0$), 187 reflections in all, collected at −150°C to reduce the effect of thermal oscillation. The analysis was carried out by Fourier projections and least-squares refinement with starting parameters based on the x-ray determination. The results are given in the form of a difference Fourier projection of the $h0l$ data shown in Fig. 30, which displays the contours of the six hydrogen atoms. It is at once clear that a hydrogen atom or nucleus does indeed link oxygen atoms of adjacent molecules. The nearly circular contours of this hydrogen atom indicate that it may be in an ordered location determined by a single-minimum potential well. However, the present data do not allow discrimination to be made between such a model and a disordered one with closely spaced sites. The lack of x-ray evidence for the electron cloud of this hydrogen atom would seem to justify describing it as a bare proton; however, a more accurate x-ray study will probably be required to settle this point.

Further results of this study are given in Table 19, which lists the interesting bond distances and angles with their error.

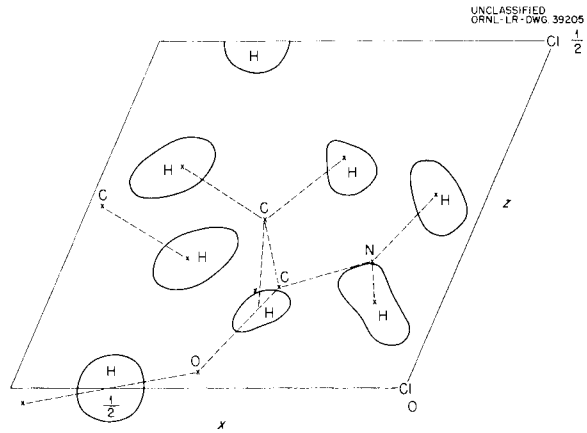

Fig. 30. Acetamide Hemihydrochloride Hydrogen Difference Projection.

Table 19. Bond Distances and Angles in Acetamide Hemihydrochloride

Bond	Length (Å)	Angle	Value (deg)
C-C	1.488 ± 0.008	C-C-O	121.3 ± 0.5
C-O	1.269 ± 0.007	C-C-N	118.9 ± 0.4
C-N	1.309 ± 0.007	N-C-O	119.7 ± 0.5
O---O	2.418 ± 0.011	H-N-H	123.2 ± 0.7
N-H	1.012 ± 0.011	C-N-H	117.6 ± 0.5
N-H[1]	1.023 ± 0.008	C-N-H[1]	119.1 ± 0.6
C-H_1	1.080 ± 0.012	C-C-H_1	110.6 ± 0.5
C-H_2	1.072 ± 0.041	C-C-H_2	100.9 ± 1.1
C-H_3	1.073 ± 0.044	C-C-H_3	120.4 ± 1.4
N---Cl	2.232 ± 0.008		
N---Cl	2.280 ± 0.010		

[17] Summer research participant, 1958, University of Richmond.

[18] W. Takei, thesis, California Institute of Technology, 1958.

[19] S. W. Peterson and H. A. Levy, *J. Chem. Phys.* **29**, 948 (1958).

A CRYSTALLOGRAPHIC LEAST-SQUARES PROGRAM FOR THE IBM-704[20,21]

W. R. Busing H. A. Levy

Given the parameters which define a crystal structure, it is possible to calculate the structure factor, $F(hkl)$, which is simply related to the intensity of x-ray or neutron diffraction from the crystal plane with indices hkl. In the experimental determination of crystal structures the inverse calculation is desired, and if the structure is known approximately, the method of least squares provides a straightforward way of adjusting the parameters to improve the agreement of the calculated with the observed F's.[22] Because F is a nonlinear function of the parameters, an iterative procedure must be used in which their values are adjusted repeatedly until no further improvement occurs.

The number of parameters to be adjusted may be as many as nine per independent atom, so that the method of least squares requires the solution of simultaneous equations of rather high orders. For this reason it has been common practice in crystallographic work to neglect the off-diagonal terms of these equations, and several computer programs[23,24] still use this approximation. The difficulties which are introduced in this way include slow convergence (or sometimes nonconvergence) and the underestimation of the errors of the resulting parameters.[25] The experience of the authors based on the refinements of some 17 crystal structures is that these difficulties are minimized when the full matrix is used. These calculations were made with several versions of a program for the Oracle and more recently with a program prepared for the IBM-704.

Some of the features of this new program are (1) choice of over-all, symmetric, or anisotropic temperature factors, (2) refinement on F or F^2, (3) use of x-ray or neutron diffraction data, and (4) arbitrary selection of parameters to be varied. The maximum number of such variables is 120 for an 8192-word memory or 251 for a 32,768-word memory. The program allows the symmetry and choice of origin to be specified easily and usually automatically so that any space group may be accommodated.

[20] W. R. Busing and H. A. Levy, *Acta Cryst.* **12**, 351 (1959).

[21] W. R. Busing and H. A. Levy, *A Crystallographic Least Squares Refinement Program for the IBM 704*, ORNL CF-59-4-37 (April 19, 1959).

[22] E. W. Hughes, *J. Am. Chem. Soc.* **63**, 1737 (1941).

[23] D. Sayre and V. Vand, "The Least-Squares Program NYXRI for Refinement of Crystal Structures," Conference on the Use of the IBM 704 Computer for Crystal Structure Analysis, Washington, D. C. (Nov. 1957).

[24] W. M. MacIntyre, "A General Least Squares Program for the Refinement of Anisotropic Thermal Parameters on the IBM 704," American Crystallographic Association Annual Meeting, Milwaukee, Wisconsin (June 1958).

[25] R. A. Sparks and K. N. Trueblood, "The Importance of Interatomic Cross-Terms in Least Squares Refinement," American Crystallographic Association Annual Meeting, Milwaukee, Wisconsin (June 1958).

POLARIZATION CORRECTION FOR UPPER LEVEL WEISSENBERG GEOMETRY USING CRYSTAL MONOCHROMATIZED RADIATION

H. A. Levy R. D. Ellison

Several presentations[26–28] of the form of the polarization correction factor for upper level Weissenberg geometry when crystal monochromatized radiation is used have left unspecified the orientation of the instrumental polar axis with respect to the plane of incidence at the monochromator, although a special orientation was, in each case, assumed. This work is a presentation of the polarization factor for the general case.

Azaroff[29] has given the following general expression for the polarization correction P when crystal monochromatized radiation is used:

$$(1 + \cos^2 2\theta_m) P = (\cos^2 2\theta_m \cos^2 \rho + \sin^2 \rho) \cos^2 2\theta_s + \cos^2 2\theta_m \sin^2 \rho + \cos^2 \rho \ ,$$

where θ_m is the Bragg angle of the monochromator, θ_s that of the sample reflection, and ρ is the angle between the normals to the planes of incidence at the monochromator and at the sample.

Application of this expression to any experimental method is essentially the task of evaluating ρ in terms of convenient variables. For inclined-axis Weissenberg measurements, these may be

[26] E. J. W. Whittaker, *Acta Cryst.* **6**, 222 (1953).

[27] L. V. Azaroff, *Acta Cryst.* **9**, 315 (1956).

[28] W. L. Bond, *Acta Cryst.* **12**, 375 (1959).

[29] L. V. Azaroff, *Acta Cryst.* **8**, 701 (1955).

taken as the angles μ and ν, defined in the usual way,[30] and θ_s. The orientation of the instrumental axis may be specified by means of a single angle σ, the angle between the normals to the plane of incidence at the monochromator and to the plane generated by the Weissenberg axis and the primary monochromatic beam. The sign of σ is to be taken so that the relation $\rho = \sigma + \tau$ holds for the acute angles σ and τ. Here τ is the angle between normals to the planes generated by the primary monochromatic beam with the Weissenberg axis and with the reflected beam. The evaluation of τ, together with the knowledge of the value of σ, will yield ρ.

If the unit vectors $\mathbf{s}_0$, $\mathbf{s}$, and $\mathbf{z}$ lie along the directions of the primary monochromatic beam, the reflected beam, and the Weissenberg axis, respectively, and if the positive direction of $\mathbf{z}$ is such that $\mathbf{z}$ makes an obtuse angle with $\mathbf{s}_0$, then

$$\cos \tau = \frac{(\mathbf{s} \times \mathbf{s}_0) \cdot (\mathbf{z} \times \mathbf{s}_0)}{|\sin (\mathbf{s}, \mathbf{s}_0)||\sin (\mathbf{z}, \mathbf{s}_0)|} = \frac{(\mathbf{s} \times \mathbf{s}_0) \cdot (\mathbf{z} \times \mathbf{s}_0)}{\sin 2\theta_s \cos \mu} .$$

By means of a vector identity, the numerator may be written

$$\begin{aligned}(\mathbf{s} \times \mathbf{s}_0) \cdot (\mathbf{z} \times \mathbf{s}_0) &= (\mathbf{s}_0 \cdot \mathbf{s}_0)(\mathbf{s} \cdot \mathbf{z}) - (\mathbf{s}_0 \cdot \mathbf{z})(\mathbf{s} \cdot \mathbf{s}_0) \\ &= \cos (\mathbf{s}, \mathbf{z}) - \cos (\mathbf{s}_0, \mathbf{z}) \cos (\mathbf{s}, \mathbf{s}_0) \\ &= \sin \nu - \sin \mu \cos 2\theta_s .\end{aligned}$$

Then the relations

$$\cos \tau = \frac{\sin \nu - \sin \mu \cos 2\theta_s}{\cos \mu \sin 2\theta_s}$$

and

$$\rho = \tau + \sigma$$

yield the desired angle ρ.

The special cases most frequently encountered are those that arise from combinations of the two conditions

$$\sigma = \frac{\pi}{2} \quad \text{or} \quad \sigma = 0 ,$$

$$\mu = 0 \quad \text{or} \quad \mu = -\nu .$$

The expressions for ρ and P in these cases have been worked out.

X-RAY AND NEUTRON DIFFRACTION BY LIQUIDS

H. A. Levy M. A. Bredig
P. A. Agron M. D. Danford

Development of the x-ray diffractometer for liquids has continued. Refinements have been made on the alignment procedure and slit system. Techniques have been further developed for containing molten salts, including the alkali fluorides, at high temperature. A theoretical treatment to correct observed intensities for penetration effects in the samples has been developed and tested.

Molten Salts

Final results for eight molten alkali halide salts have been obtained by x-ray diffraction. Three of these were also studied by neutron diffraction.[31] The first coordination shell, which is interpreted as an M^+X^- approach, is a band of about 0.5 Å half width, with most frequent interatomic distance smaller than that in the solid at room temperature. It corresponds to an *average* coordination of about four to five neighboring ions. A neutron diffraction study of molten Li^7Cl has confirmed that the first coordination shell involves unlike ions. The scattering factor of Li^7 for neutrons is negative, while that for Cl is positive. As a result, the peak arising from Li^7-Cl interactions is inverted in the radial distribution function. The breadths of the first peaks show that ion pairs are to be found significantly closer (and also more widely separated) than the most frequent separation. The "closest distances" are comparable with those found in the monomeric vapor molecules. In Table 20 these gas distances are compared with distances read from the leading edge of the first peaks in the radial distribution functions at one-quarter maximum height. Table 21 summarizes the observations on the short-distance interactions for the eight salts studied. Comparison is made with

[30] M. J. Buerger, *X-Ray Crystallography*, Wiley, New York, 1942.

[31] Results were presented before the New York Academy of Sciences on April 13, 1959, and will appear in the Transactions of the Academy.

the corresponding solids at their melting points and also at room temperature.

The second shell, which corresponds to seven or more ion neighbors, is less well defined than the first. It is most prominent in LiI and most obscure in CsI; this variation is at least partly a consequence of the relative magnitudes of the scattering factors. Table 22 lists the "most frequent" distances for this interaction, and the "coordination numbers" based on areas interpreted as composite M^+-M^+ and X^--X^- interactions. It is seen that these distances are comparable with, usually somewhat greater than, the corresponding distances in the solid at the melting point. Again, the great breadth (~2 Å), particularly to the long-distance side, shows that a great variety of individual configurations occur, and more caution is required in their interpretation.

Table 20. Comparison of Short Cation-Anion Distances in Molten Salts with Corresponding Distances in Gases

Distance	Liquid* (Å)	Gas** (Å)
Li-I	2.48	2.39
Na-I	2.70	2.71
K-Cl	2.69	2.67
Cs-Cl	3.03	2.91
Cs-Br	3.14	3.07
Cs-I	3.35	3.32

*Obtained arbitrarily from the value of *r* at one-quarter peak maximum.

Obtained from microwave results: A Honig, M. L. Stitch, and M. Mandel, *Phys. Rev.* **92, 901 (1953); C. A. Lee *et al.*, *Phys. Rev.* **91**, 1395 (1953); A. M. Honig *et al.*, *Phys. Rev.* **96**, 629 (1954).

Aqueous Solutions

Further results for $BiCl_3$ solutions have been obtained. Two solutions, 3.27 *M* $BiCl_3$–4.14 *M* HCl and 3.20 *M* $BiCl_3$–9.43 *M* HCl, have been studied by x-ray diffraction. The results show a significant increase in the Bi-Cl interatomic distance with increasing HCl concentration. In the two solutions the Bi-Cl interatomic distances are 2.60 and 2.70 Å, respectively. Models with Cl atoms in square-planar, tetrahedral, and trigonal

Table 21. Cation-Anion Distances and Coordination Numbers in Molten and Crystalline Salts

Salt	Liquid			Solid*		
	Distance (Å)	Number	Method**	Melting-Point Distance (Å)	Number	Room-Temperature Distance (Å)
LiCl	2.47	4.0	X	2.66	6	2.57
	2.45	3.5	N			
LiBr	2.68	5.2	X	2.85	6	2.75
LiI	2.85	5.6	X	3.12	6	3.00
NaI	3.15	4.0	X	3.35	6	3.23
KCl	3.10	3.7	X	3.26	6	3.14
	3.10	3.5	N			
CsCl	3.53	4.6	X	3.57	6	(3.47)
				(3.70)	8	3.57
CsBr	3.55	4.6	X	(3.72)	(6)	(3.62)
	3.55	4.7	N	3.86	8	3.71
CsI	3.85	4.5	X	(3.94)	(6)	(3.83)
				4.08	8	3.95

*Values for metastable forms (parentheses) were calculated from molar volumes estimated by J. W. Johnson, P. A. Agron, and M. A. Bredig, *J. Am. Chem. Soc.* 77, 2734 (1955).

**X: x-ray diffraction.
N: neutron diffraction.

Table 22. Anion-Anion or Cation-Cation Distances and Coordination Numbers in Molten and Crystalline Salts

Salt	Liquid			Solid* (Melting Point)	
	Distance (Å)	Number	Method**	Distance (Å)	Number
LiCl	3.85	12.0	X	3.76	12
	3.80	8.3	N		
LiBr	4.12	12.8	X	4.03	12
LiI	4.45	11.3	X	4.41	12
NaI	4.80	8.9	X	4.74	12
KCl		<12	X	4.61	12
	~4.7	7.4	N		
CsCl	4.87	7.1	X	5.05	12
				(4.27)	(6)
CsBr	~5.4	8.3	X	(5.26)	(12)
	~5.2	7.9	N	4.46	6
CsI	~5.5	7.2	X	(5.57)	(12)
				4.72	6

*Values for metastable forms (parentheses) are those estimated by J. W. Johnson, P. A. Agron, and M. A. Bredig, *J. Am. Chem. Soc.* 77, 2734 (1955).

**X: x-ray diffraction.
N: neutron diffraction.

bipyramid arrangements around a central Bi atom have been examined. Of these, the square-planar and trigonal bipyramid arrangements are better. There is no evidence for polynuclear complex formation. Raman studies of two solutions, 2 *M* $BiCl_3$–4 *M* HCl and 2 *M* $BiCl_3$–8 *M* HCl, have shown a shift to lower frequencies with increasing acid concentration, paralleling the increase in the Bi-Cl distance above.

X-ray diffraction studies of UO_3-HCl solutions, with stoichiometries ranging from

$$UO_2(OH)_{0.84}Cl_{1.16} \text{ to } UO_2(OH)_{1.018}Cl_{0.982},$$

have given evidence for polynuclear complexes containing two or more uranium atoms. Ultracentrifugation results (R. M. Rush, unpublished) have indicated that these systems are not monodisperse; for this reason, a complete interpretation of the x-ray data has not been attempted. The U-U interatomic distance is about 3.96 Å and is similar to the shortest U-U distance[32] in crystalline UO_3. The uranium atoms at this separation in crystalline UO_3 are bridged by two oxygen atoms, and the similarity suggests that the uranium atoms in solution may be identically bridged. The U-O distance observed here for the UO_2^{++} ion in solution (~1.9 Å) is shorter than the closest U-O distance in anhydrous UO_3 (2.18 Å). The results also indicate that the cations in solution are hydrated, with each uranium atom having approximately six oxygen neighbors at about 2.4 Å.

A study of UO_2F_2 aqueous solutions indicates a polynuclear complex which may be a dimer, while studies of UO_2Cl_2, $UO_2(ClO_4)_2$, and $UO_2(NO_3)_2$ solutions have indicated no polynuclear complex formation. Further studies of aqueous uranium(VI) solutions are in progress.

CALORIMETRY

Low-Temperature Heat Capacity Calorimeter

R. B. Bevan, Jr. R. A. Gilbert
R. H. Busey

The error in previously reported[33] preliminary measurements made with the liquid-helium-cooled

[32] W. H. Zachariasen, *Acta Cryst.* 1, 265 (1948).

[33] R. B. Bevan, Jr., and R. A. Gilbert, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 95.

calorimeter on a Calorimetry Conference standard sample of benzoic acid was found to be due to contamination of the sample by solder in sealing the calorimeter. A better designed calorimeter was constructed to eliminate the possibility of contamination. New measurements on benzoic acid are represented in Fig. 31 by a graph of the deviations between heat capacities as measured in this research and a smoothed heat capacity curve given by National Bureau of Standards investigators.[34] The agreement is quite satisfactory and compares favorably with previous measurements.[35,36]

High-Temperature Heat Content Calorimeter

R. A. Gilbert R. H. Busey

Preliminary determinations of the enthalpy of a Calorimetry Conference standard sample of synthetic sapphire over the range 0 to 500°C using the high-temperature drop calorimeter[37] have led to improvements in technique and equipment. At present, however, deviations from results reported by investigators[38] at the National Bureau of Standards average approximately 0.4%. The Bunsen ice calorimeter was tested by introduction of accurately measured quantities of electrical energy and found to give results accurate to within 0.05% or better, indicating that the source of error was arising from the furnace or from faulty (non-reproducible) dropping of the sample from the furnace to the ice calorimeter. It is believed that the difficulty has been found in the alignment of the furnace. This condition has been corrected, and measurements on the standard sample are continuing.

[34] G. T. Furukawa *et al.*, *J. Research Natl. Bur. Standards* **57**, 67 (1956).

[35] D. W. Osborne, E. F. Westrum, Jr., and H. R. Lohr, *J. Am. Chem. Soc.* **77**, 2737 (1955).

[36] R. H. Busey, *J. Am. Chem. Soc.* **78**, 3263 (1956).

[37] R. A. Gilbert, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 96.

[38] G. T. Furukawa *et al.*, *J. Research Natl. Bur. Standards* **57**, 67 (1956).

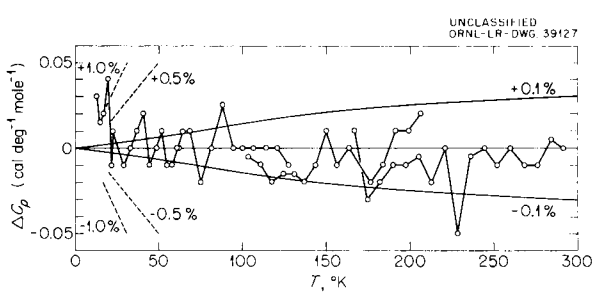

Fig. 31. Comparison Between Experimental Heat Capacities of This Research and the NBS Smoothed Curve for Heat Capacity of Calorimetry Conference Standard Sample of Benzoic Acid. ΔC_p represents experimental C_p minus NBS smoothed curve.

SURFACE IONIZATION

R. E. Minturn S. Datz
E. H. Taylor

Because the positive-ion noise from tungsten filaments limits the sensitivity of the surface ionization gage for the detection of molecular beams, some effort has been devoted to a study of the phenomenon. Two papers describing the results have been prepared and are abstracted below:

1. "The spontaneous emission of positive ions from a heated tungsten filament occurs as pulses, a single pulse releasing as many as 10^6 ions in less than 100 μsec. The pulses are composed mainly of potassium ions, present as impurities in the tungsten lattice. It is suggested that these impurities concentrate in minute cavities resulting from the pinning of many edge dislocations at a single point. The concentrated impurities are released from the heated filament as a burst of positive ions when the cavity is propagated to the surface by strains introduced into the crystal. At temperatures where the formation of an adsorbed layer is possible, oxygen has a very pronounced effect upon the rate of emission of positive ion pulses. Several possible reasons for this effect are discussed."

2. "Among the sources of noise in vacuum tubes is the 'anomalous flicker effect,' which was recently ascribed by Lindemann and Van der Ziel to the interaction of positive ion bursts from a filament with an electron space charge. Since the postulated characteristics of such positive ion pulses in a particular commercial diode (Sylvania 5722) did not agree with direct measurements upon a surface ionization gage in this Laboratory, further measurements, both of positive ion bursts and of variations in electron current, were undertaken with the 5722 and the surface ionization gage.

"The measurements with the 5722 confirmed the electron measurements of Lindemann and Van der Ziel, but the positive ion measurements showed pulses like those previously observed in the surface ionization gage at the same filament temperature, rather than the faster and larger pulses suggested by Lindemann and Van der Ziel to explain the flicker noise.

"It is shown that the observed positive ion pulses should give rise to flicker pulses of the observed size and shape under the usual theories of electron tube operation."

MASS SPECTROMETRY AND RELATED TECHNIQUES

Two-Stage Mass Spectrometer

G. F. Wells C. R. Baldock

The two-stage mass spectrometer previously described[39] is now being utilized in the neutron cross-section program for which it was designed. The two associated high-purity chemistry laboratories have recently been completed and put in operation.

Formation of NO^- in Nitric Oxide and Nitrous Oxide by Electron Impact[40]

P. S. Rudolph C. E. Melton
G. M. Begun

The negative ion NO^- was observed in a previous study of ion-molecule reactions using a mixture of nitric oxide and formic acid.[41] The NO^- ion has been postulated by Bradbury[42] to explain the results of some electron attachment studies in nitric oxide. Williams and Essex[43] suggested that NO^- might be an intermediate in the radiation chemistry of nitrous oxide. However, in a recent paper[44] on negative ion formation by electron impact in N_2O and NO, it was reported that O^- was formed but that NO^- was not. It seemed worth while, in view of this disagreement, to repeat the mass spectroscopic experiments using isotopically labeled compounds. Results from these experiments conclusively demonstrated that NO^- is formed in both NO and N_2O by electron impact. In the case of nitrous oxide, NO^- is shown by isotopic labeling to be formed almost exclusively by cleavage of the N-N bond.

Negative Ion Mass Spectra of Hydrocarbons and Alcohols[45]

C. E. Melton P. S. Rudolph

The relative abundance of the negative ions formed by electron impact in methane, the C_2 hydrocarbons, *n*-butane, and all the alkyl alcohols through the butyl alcohols was determined. Data for four of the more interesting of these compounds are shown in Table 23. It is well known that as the alkyl radical increases in length in a homologous series of alcohols, the reactivity of the hydroxyl group becomes less pronounced. Hence it is not surprising that the negative ion spectra of *n*-butyl alcohol and *n*-butane show much greater similarity

[39] G. F. Wells, C. E. Melton, and C. R. Baldock, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 98.

[40] P. S. Rudolph, C. E. Melton, and G. M. Begun, *J. Chem. Phys.* 30, 588 (1959).

[41] C. E. Melton and G. A. Ropp, *J. Am. Chem. Soc.* 80, 5573 (1958).

[42] N. E. Bradbury, *J. Chem. Phys.* 12, 827 (1934).

[43] N. T. Williams and H. Essex, *J. Chem. Phys.* 16, 1153 (1948).

[44] B. E. Knox and B. P. Burtt, *J. Chem. Phys.* 28, 1256 (1958).

[45] C. E. Melton and P. S. Rudolph, submitted to *J. Chem. Phys.*

Table 23. Relative Abundance of Negative Ions from Some Alkanes and Corresponding Alcohols

m/e	Ion	Ethane	Ethanol	*n*-Butane	*n*-Butyl Alcohol
12	C^-	20	31	3	3
13	CH^-	29	51	13	7
14	CH_2^-	8	18	7	4
15	CH_3^-		28	2	1
24	C_2^-	100	61	29	31
25	C_2H^-	100	100	100	100
26	$C_2H_2^-$	3	3	5	3
36	C_3^-			3	6
37	C_3H^-			2	4
38	$C_3H_2^-$				2
48	C_4^-	1		1	1
49	C_4H^-			3	2

than do the spectra of ethyl alcohol and ethane, as shown in this table.

The mass spectra for the C_2 hydrocarbons showed a linear increase in the relative abundance of C_2H^- with increasing saturation.

A comparison of the tendencies toward the formation of negative and positive ions shows that a maximum of 5 negative ions are produced per 100,000 positive ions. These results suggest that positive ions are much more abundant in the radiolysis of hydrocarbons and alcohols. Further evidence for this conclusion appears in studies of the alpha-particle radiolysis of the C_2 hydrocarbons,[46] in which negative ions were not observed.

GAS PHASE RADIOLYTIC STUDIES IN THE MASS SPECTROMETER

P. S. Rudolph C. E. Melton

Mass Spectrum of Acetylene Produced by 5.1-Mev Alpha Particles[47]

Ions induced in polyatomic gases by alpha particles have been measured with the research mass spectrometer. For this measurement, the ion source (Fig. 32) was modified by covering the

[46] P. S. Rudolph and C. E. Melton, *J. Phys. Chem.* 63, 916 (1959).

[47] C. E. Melton and P. S. Rudolph, *J. Chem. Phys.* 30, 847 (1959).

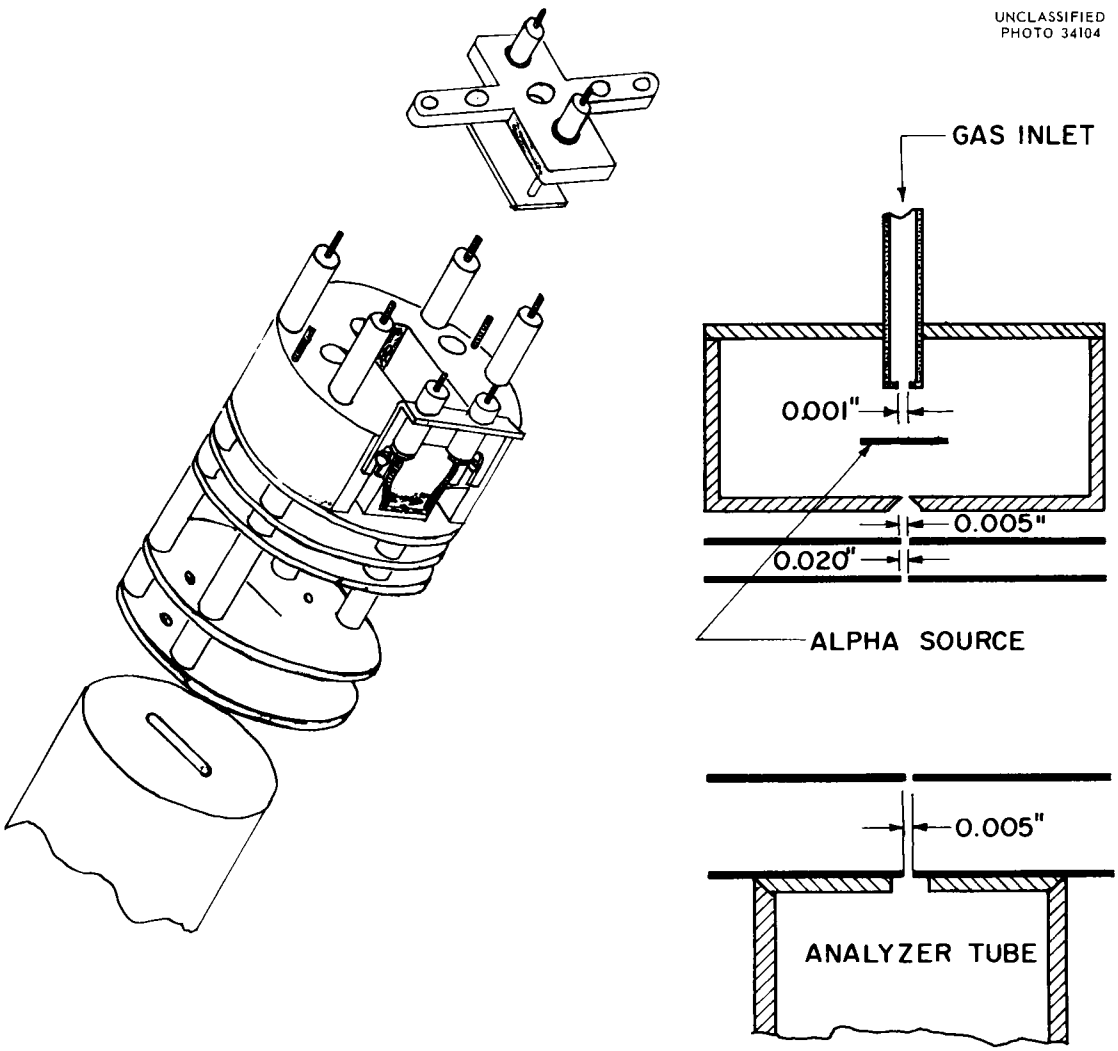

Fig. 32. Source for Alpha Ionization Studies.

ion repeller with an alpha emitter (Po^{208}) having a decay rate of 2×10^6 d/sec. This modification permitted the study of (1) ions produced by alpha particles alone or (2) ions produced by both electrons, from a thoria-iridium filament,[48] and alpha particles in combination.

A comparison of acetylene mass spectral data (Table 24) clearly shows the striking differences between the mass spectra produced by alpha particles and by 75-ev electrons. These results indicate that the use of alpha particles to produce ions in a mass spectrometer may be useful for mass spectral analysis, in addition to its obvious application to radiation chemistry studies.

Mass Spectrometric Studies of Ionic Intermediates in the Alpha-Particle Radiolysis of Acetylene[49]

Ionic intermediates from the alpha-particle radiolysis of acetylene were systematically studied as a function of pressure by magnetic mass separation of the ions. "Polymeric" ions, $C_4H_n^+$ and $C_6H_n^+$, have been identified and their per cent abundance determined. The most probable mechanisms for the formation of the observed "polymeric" ions are ion-molecule reactions involving parent ion ($C_2H_2^+$) or secondary ions (e.g., $C_4H_3^+$) and neutral molecules. These "polymeric" ions are formed without the elimination of carbon, but with the elimination of hydrogen, except for $C_4H_4^+$. The pressure dependence of five of the nine ions observed and the mechanisms for their formation are given in Fig. 33.

[48]C. E. Melton, *Rev. Sci. Instr.* **29**, 250 (1958).

[49]P. S. Rudolph and C. E. Melton, *J. Phys. Chem.* **63**, 916 (1959).

Table 24. Mass Spectra of Acetylene

m/e	Prabable Ion	Relative Abundance: Electron Impact Reaction,* 75-ev Electrons	Relative Abundance: Alpha-Induced Reaction, 5.1-Mev Alpha Particles
12	C^+	1	
13	CH^+	4.4	
24	C_2^+	5.7	
25	C_2H^+	20.7	7.3
26	$C_2H_2^+$	100	100
27	$C^{13}C^{12}H_2^+$	2.2	2.2

*C. E. Melton, M. M. Bretscher, and R. Baldock, *J. Chem. Phys.* **26**, 1302 (1957).

Ion-Molecule Charge-Transfer Reactions in the Alpha Radiolysis of Various Hydrocarbons in a Mass Spectrometer[50]

The separation of energetically possible charge-transfer reactions into probable and improbable reactions has been effected by employing mixtures in the alpha-particle mass spectrometer at pressures as high as 0.11 mm Hg. Binary mixtures of the C_2 hydrocarbons and of acetylene and benzene were studied. Alpha-particle-induced charge-transfer reactions were shown to be very probable in the radiolysis of a mixture of C_2H_2 and C_6H_6,

[50]Submitted to *J. Chem. Phys.*

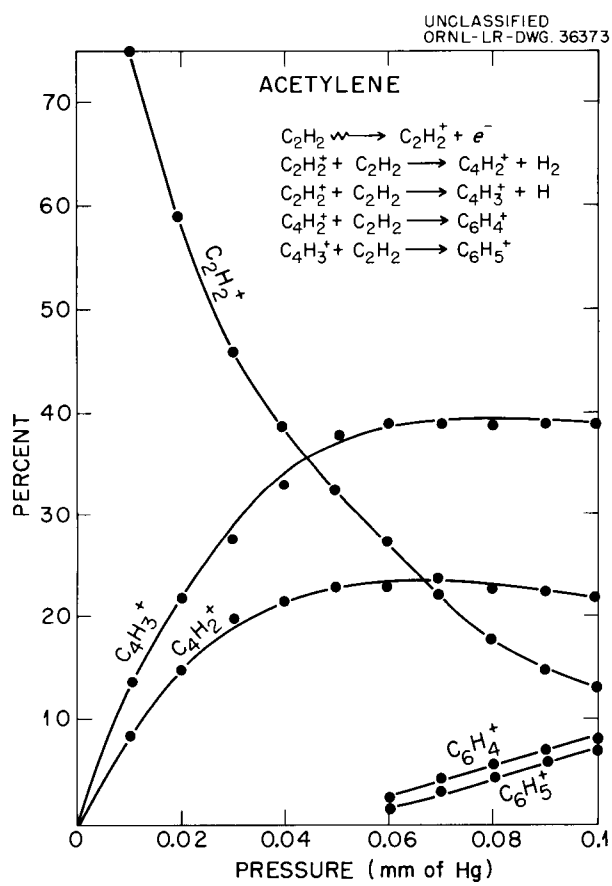

Fig. 33. Per Cent Abundance of Various Ionic Species from C_2H_2 as a Function of Pressure.

but improbable in the radiolysis of binary mixtures of C_2H_4 with C_2H_2 and C_2H_6. The results from the C_2H_2 and C_6H_6 mixture corroborate the earlier postulates of Lind and Rudolph[51] that the retardation of the polymerization of C_2H_2 by C_6H_6 can be explained on the basis of ion-molecule charge-transfer reactions.

A RAPID METHOD OF DIRECT ESTIMATION OF A DEUTERIUM KINETIC ISOTOPE EFFECT

G. A. Ropp C. E. Melton

During mass spectrometric studies of the photochemical oxidation of formic acid by chlorine,

$$HCOOH + Cl_2 \xrightarrow{h\nu} 2HCl + CO_2$$

first studied by West and Rollefson,[52] it was found that the determination of the over-all rate by measurement of the ratio of the peak heights of CO_2 and HCOOH was sufficiently reproducible to be used to measure a deuterium isotope effect. Since this method proved convenient and rapid, it may have rather general interest.

The measurements were carried out in the expansion bulb of a modified 6-in.-radius mass spectrometer[53] in a darkened room. With a mixture of chlorine and formic acid flowing at a steady rate through the leak into the ionization chamber, light from a projector was focused on a spot on the expansion bulb just behind the leak. After a steady state was attained with the light on, the per cent reaction was computed from the ratio of the peak height at mass 44 (carbon dioxide) to the peak height at mass 46 (formic acid). Under the same conditions of light and pressure, the per cent reaction was computed for the reaction of formic-*d* acid. The deuterium isotope effect was calculated as the ratio of the two percentages of reaction, a satisfactory approximation below about 15% reaction. Four independent pairs of experiments gave a mean value of $k_H/k_D = 1.6$. The temperature in the reaction zone was estimated to be at least 70°C due to conduction of heat from the hot filament. Since isotope effects are well known to decrease with increasing temperature, the agreement of the measured deuterium isotope effect, $k_H/k_D = 1.6$, with that predicted from the C^{13} fractionation factor,[54] $k_H/k_D = \sim 2$, is reasonable.

[51] S. C. Lind and P. S. Rudolph, *J. Chem. Phys.* **26**, 1768 (1957).

[52] H. West and G. K. Rollefson, *J. Am. Chem. Soc.* **58**, 2140 (1936).

[53] C. E. Melton, G. A. Ropp, and P. S. Rudolph, *Chem. Ann. Prog. Rep. June 20, 1958*, ORNL-2584, p 101.

[54] G. A. Ropp, C. J. Danby, and D. A. Dominey, *J. Am. Chem. Soc.* **79**, 4944 (1957).

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