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QUARTERLY PROGRESS REPORT

FOR PERIOD ENDING DECEMBER 31, 1951

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CHEMISTRY DIVISION

QUARTERLY PROGRESS REPORT

for Period Ending December 31, 1951

S. C. Lind, Acting Director

G. E. Boyd, M. A. Bredig, Associate Directors

DATE ISSUED

MAY 20 1952

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ABSTRACT

INORGANIC CHEMISTRY

The preparation of solid thorium perchlorate by fuming thorium nitrate to dryness with perchloric acid at 200 to 215°C gives a partly hydrolyzed product, which is white, microcrystalline, highly hygroscopic, and completely soluble in water. Further studies of the composition and stability of the solid will include x-ray examination, which may decide between the two structures:

$$Th(OH)_2(ClO_4)_2 \text{ or } ThO(ClO_4)_2.H_2O.$$

By use of the ultracentrifuge method, the polymerization of thorium perchlorate in 1 *M* NaCl solution was studied. The thorium is primarily monodisperse with apparent molecular weight of about 1200. The value 1700 obtained by estimating a "charge" correction is in fair agreement for a tetramer $(ThO(ClO_4)_2)_4$. Evidence of yet higher polymers was also found.

In the determination of freezing-point lowering of salt solutions, a "thermistor" has been found to be reliable, sensitive, and adaptable to continuous measurements. A Western Electric thermistor with a resistance of about 365,000 ohms was used in series with a standard resistor of about 1,000,000 ohms. The temperature coefficient of the standard resistor was about 0.015%, and therefore it was mounted in a vessel that was thermostatically controlled at 25 ± 0.1°C. The voltage drop of 1.5 across the two resistors is measured by a vibrating-reed electrometer. The opposing potential, supplied by a Rubicon potentiometer in series with a Brown Electronik recorder, indicates to 0.01°C for a distance of 2.5 cm on the recorder. The instrument has proved reliable and stable during several months of use.

By using carefully purified and analyzed uranyl fluoride, freezing-point depressions were determined for several series of solutions. The result generally confirms the earlier one of Secoy, although it now appears that both molecular association and electrolytic dissociation are smaller than previously thought.

The adsorbability of zinc, cadmium, and mercury(II) in Dowex-1 was studied in hydrochloric acid solutions 0.01 to 12 *M* at 25°C. Zinc and cadmium show maximum adsorption near 2 *M* HCl, with decreasing values at higher concentrations, whereas mercury(II) shows only decreasing adsorption in the region studied. Yttrium was separated from scandium by adsorption from 12 *M* HCl in Dowex-1. Gallium was easily separated from aluminum in 3.5 *M* HCl by adsorption in Dowex-1.

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The adsorption of indium is several orders of magnitude smaller than that of $GaCl_4^-$, from which it is inferred that indium forms a complex with negative charge >1. Thallium(III) was found to be strongly adsorbed, especially at low concentrations of hydrochloric acid, whereas thallium(I) showed only moderate adsorption.

By using Zn^{65} as a tracer in studying the exchange of zinc and hydrogen ions in Dowex-50 at 25, 60, and 87°C, data were obtained to calculate equilibria and to evaluate ΔF, ΔH, and $T\Delta S$. By using Cd^{115} as a tracer, similar data were obtained in the exchange of cadmium and hydrogen at 25 and 60°C. The separation of zinc and cadmium by ion exchange should be simple, particularly in the range 0.5 to 1 *M* Cl^-. Activity coefficients of zinc perchlorate and of cadmium perchlorate were also calculated (Table 8).

Preliminary studies are being made on adsorption of hydrochloric acid by the anion-exchange resin Dowex-1 to gain some concept of the internal ion equilibrium within the resin phase.

The purification of uranyl sulphate and fluoride solutions by electromigration is being undertaken in a two- or three-compartment cell in which the cells are separated by suitable membranes. Owing to its unionized and uncharged state, the uranyl salt remains in the middle compartment, and the undesired cations (fission products) and anions are separated by migration.

Study of the physical, thermodynamic, and magnetic properties of Tc_2O_7 and $HTcO_4$ has continued. Comparison with corresponding rhenium compounds disclosed similarities and some surprising differences.

A study of the kinetics (including intermediate steps) of the reaction between HBr and $HBrO_3$ using Br^{82} as a tracer is continuing. Data are being applied to four simultaneous differential equations with four unknowns by using an IBM computer. An analysis is also being made on the MADDIDA digital analogue computer in California.

NUCLEAR CHEMISTRY

In the decay scheme for Ga^{67}, 12 additional transitions have been found that indicate at least six excited levels in Zn^{67}. A decay scheme has been fitted to the data for energy and gamma-gamma coincidence. Branching ratios and conversion coefficients were determined. Assignment of spins to the Zn^{67} levels will be undertaken.

A tentative value for the melting point of technetium element is 2140

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± 20°C, which was obtained by using a microvacuum furnace and optical pyrometry.

RADIO-ORGANIC CHEMISTRY

Radiation Chemistry

Radiation Experiments. Experimental investigations of the effect of gamma radiation on dilute aqueous solutions of acetic-1-C^{14} acid and acetic-2-C^{14} acid have shown the only important reactions to be decarboxylation and coupling at the alpha position to form succinic acid. The carboxyl carbon of acetic-1-C^{14} acid was found to be converted to carbon dioxide or to become a carboxyl carbon of succinic acid. A part of the alpha-carbon atom of acetic acid was found in the alpha position of succinic acid. The portion of alpha-position carbon released by the decarboxylation of acetic-2-C^{14} acid was present in the form of nonvolatile acidic material, the constituents of which have not been determined. Experiments have shown the absence of many of the likely products.

No succinic acid was obtained by the action of hydrogen peroxide on dilute aqueous acetic acid, alone, or in the presence of ferrous sulfate. Irradiation of dilute aqueous acetic acid in the presence of excess ferrous sulfate led to the elimination of the coupling reaction. Only a trace of succinic acid was formed when dilute aqueous acetic acid solution swept with oxygen and containing hydrogen peroxide was irradiated. The only nonvolatile acidic product formed by gamma radiolysis of aqueous butyric acid was 2,3-diethylsuccinic acid. The principal reactions were decarboxylation and coupling in the alpha position. Similar results were indicated for valeric acid. Irradiation of a solution of benzene, water, and acetic acid apparently led to the formation of phenylacetic acid.

Analytical Developments. Partition chromatographic methods have been developed for the separation of acetic acid and propionic acid in dilute aqueous solution. Solvent systems for the paper-chromatographic identification of 2,3-diethylsuccinic acid were developed.

Preparative Methods. 2,2-Dimethylpropionic-1-C^{14} acid has been prepared for use in radiation experiments. The preparation of 2,2-dimethylpropionic-3-C^{14} acid has been attempted. These compounds will be used to determine the course of gamma radiolysis with acids containing a blocked alpha position.

Isotope Effect Studies

Measurement of the Carbon^{13} Isotope Effect in the Dehydration of Formic Acid. Preliminary values for the C^{13} isotope effect [expressed as $(k_{12} - k_{13})/k_{12}$] in the sulfuric acid

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dehydration of formic acid of normal C^{13} abundance are 5.8% at 0°C and 5.7% at 24.04°C. These results were obtained by the use of an apparatus in which successive samples of evolved carbon monoxide were collected, measured, and burned quantitatively to carbon dioxide prior to mass spectrographic analysis.

Measurement of the Isotope Effect in the Decarboxylation of Malonic-2-C^{14} Acid at 154°C. An investigation is under way to determine the values for the isotope effect in the decarboxylations of malonic-1-C^{14} acid and malonic-2-C^{14} acid. The results will be of interest since they offer a comparison of the effects on the rates of reaction of substitution of C^{14} at each of two ends of the affected bond. With malonic-2-C^{14} acid, the isotope effect may be evaluated by determining the specific activity change of the unreacted malonic acid with time as the reaction progresses.

Evaluation of the Isotope Effect in the Saponification of Ethyl p-*Anisate-7-C^{14} at 25°C.* As part of a broad study of the effect of *para*-substituents on the isotope effects in the saponification of substituted ethyl benzoates, ethyl *p*-anisate (labeled with C^{14} in the carbonyl group) has been shown to hydrolyze at 25°C in alkaline solution with isotope fractionation amounting to 0.915 for the ratio k_{14}/k_{12}. The experimental method involved the determination of the specific activity of the first *p*-anisic acid formed and that of the product from complete hydrolysis. Under these conditions, the ratio k_{14}/k_{12} is equal to the ratio of the two respective specific activities.

Evaluation of the Isotope Effect in the Saponification of Ethyl Benzoate-7-C^{14} at Three Temperatures. A study of the variation with temperature of the isotope fractionation in the hydrolysis of ethyl benzoate (labeled with C^{14} in the carboxyl group) has shown very little temperature dependence. The preliminary values for k_{14}/k_{12} are 0.924 at 0°C, 0.929 at 25°C, and 0.931 at 60°C.

Studies on the Mechanisms of Organic Reactions

Migratory Aptitudes from the Rearrangement of Diarylethanols. With the aim of obtaining less ambiguous data on the intrinsic migratory aptitudes of substituted aryl groups, the acid-catalyzed rearrangements of C^{14}-labeled diarylethanols have been investigated. By determination of the C^{14} distribution in the two ethylenic carbon atoms of the symmetrical diarylethylenes produced, the migration percentages of the substituted phenyl groups were found to be: *p*-tolyl, 65%; *m*-tolyl, 61%; *p*-biphenylyl, 57%; and *p*-anisyl, 96%.

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Migratory Aptitudes in the Nitrous Acid Rearrangement of Diarylethylamines. As a comparison with the migration ratios of substituted aryl groups in the diphenylethanol rearrangement, the migration tendencies of the substituted aryl groups in the nitrous acid-induced arrangement of diarylethylamines to phenyl benzyl carbinols have been determined. The migration percentages were found to be strikingly different from the previous case and to indicate a lower degree of selectivity in the rearrangement: *p*-tolyl, 47%; *m*-tolyl, 48%; *p*-biphenylyl, 50%; and *p*-anisyl, 59%.

Wagner Rearrangement of 2-Phenyl-2-(o-tolyl)-ethanol. As a comparison with the results of a study of the migratory preferences in the rearrangement of 1-methyl-9-fluorenemethanol, the migration ratio of phenyl to *o*-tolyl has been shown to be 55:45 in the acid catalyzed rearrangement of 2-phenyl-2-(*o*-tolyl)-ethanol to *o*-methylstilbene.

Reaction of Acetonitrile with Benzoic Acid. Benzoic acid, labeled with C^{14} in the carboxyl group, has been shown to react with acetonitrile in the presence of phosphoric acid at 280°C to give benzonitrile and acetic acid in which no interchange of the carbon positions has occurred. The reaction is postulated to involve acid-catalyzed equilibria in which the —N and —OOH groups are exchanged.

Isotope Exchange Reactions Involving the Carbon-Carbon Bond. The study of the exchange of the benzal moiety in compounds formed in carbonyl methylene condensation reactions has been extended to the Perkin reaction. This reaction has been found to be irreversible.

Further study of a previously reported reaction indicates that the piperidine-catalyzed exchange of 2,4-dinitrostilbene with benzaldehyde-7-C^{14} occurs only in the presence of a small amount of water.

Structure Determination Studies

Structure Determination of C^{14}-Labeled 1-Methylphenanthrene. Additional proof of the structure of the methylfluorenecarboxylic acid from the degradation of 1-methylphenanthrene has been obtained. These studies confirm the equal distribution of radioactivities in the nine and ten positions of the latter compound, which was prepared by the action of phosphorus pentoxide on 1-methyl-9-fluorenemethanol-10-C^{14}.

Structure Determination of Chrysene-5,6-C^{14}_1. Chrysene-5,6-C^{14}_1, degraded according to a previously described scheme, has now been shown to contain a radioactivity distribution in the five and six positions of 76:24. This ratio is significant in view of the lack of selectivity

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previously demonstrated in similar rearrangements.

CHEMISTRY OF SEPARATIONS PROCESSES

Several sieved portions of Dowex-50 resin have been washed and conditioned for the proposed exchange studies. Density gradient tubes have been set up in a temperature-controlled bath for analysis of D_2O-H_2O mixtures by density determination, and calibration of the gradient tubes is now in progress. The construction of four cells for irradiation studies in the Van de Graaff electron beam is nearing completion.

The extraction of uranyl sulfate from organic solvents has been further studied. *n*-Butyl di-*n*-butylphosphinate $(BuO)Bu_2PO$ and tri-*n*-butyl phosphine oxide Bu_3PO, 0.75 *M* in CCl_4 have been found to be very efficient in extracting 0.1 *M* uranium salt from HNO_3 (0.6 to 3.0 *M*). UO_2Cl_2 and UO_2F_2 have also been extracted with high efficiency by Bu_3PO.

A final report on the extraction of zirconium from chloride solutions by using thenoyltrifluoroacetone in benzene is being prepared.

Studies have been made of self-diffusion in cation-exchange systems. Chromium(III) in a cation exchange was equilibrated with 1.4% H_2O^{18}. This preparation was placed in pure water to study the rate of migration. Two rates were observed, a fast one representing migration of the "free" (intergranular) water and a slower rate for the water of hydration. Estimation of $6H_2O$ per chromium(III) substantiated the view that chromic hydration was involved. Self-diffusion of mixed ions (Na^+ and Rb^+) at 0.22 *M* concentrations in the solution showed an influence of rate. By comparison with the individual rates, the faster ion was retarded in the mixture and the slower accelerated; this change was accompanied by a lowering of activation energy of both ions. Analogous results were attained in the mixtures Na^+ with Zn^{++} and in Na^+ with La^{+++}.

The investigation of ion-exchange equilibria has been continued with Dowex-50 and HCl and HBr solutions on the assumption that the permeability is governed by the Donnan equilibrium for membranes.

Exploration of the separation of fission-product elements has been continued by use of Dowex-2 and various eluting agents. Separation of several pairs of elements has been studied in detail. In working with In^{116}, a precision half life of 54.0 ± 0.1 min was determined. The general principles of chromatography are summarized.

CHEMICAL PHYSICS

The crystal structure of ammonium chloride, which has been found by

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neutron diffraction to be entirely like that of NH_4Br, consists of disordered ammonium ions at the body centers of cubes of chloride ions. The hydrogen atoms exhibit oscillatory rotation of half-angle 12 ± 3 deg. in NH_4Cl and 10 ± 3 deg. in ND_4Cl. By examining KN_3 and VN, the neutron coherent cross section has been redetermined at 11.1 ± 0.4 barns for nitrogen and 0.029 and 0.026 barns for vanadium in vanadium nitride and carbide, respectively.

Improvements have been achieved in the technique for the measurement of bromine and potassium in contemplated molecular beam experiments.

The magnetic moment of Tc^{99} was determined in NH_4TcO_4 by nuclear induction. The computed value is $\mu(Tc^{99}) = +5.6805 \pm 0.0004$.

The new type of spectrum exhibited only in piezoelectric crystals has been confirmed by examining several piezoelectric substances. The spectra are the result of mechanical oscillation of individual crystallites. In sea sand the number of lines observed depends on the number of grains of sand.

Quadrupole spectra have been observed in a number of new compounds, including most of the chloroethanes, *cis*- and *trans*-dichloroethylene, isopropyl chloride, and tertiary butyl chloride.

Work on the calorimetry of the radioactivity of C^{14} has been continued. If the computed value of the average energy of radiation is assumed to be correct, a value of about 6000 years is arrived at for the half life of C^{14}.

RADIATION CHEMISTRY

The decomposition of aqueous solutions of UO_2SO_4 and of UO_2F_2 in pile irradiation has been measured as a function of total dose, U^{235} enrichment, concentration, temperature, and added solute. The hydrogen yield is the net result of the forward (decomposition) reaction and the opposing recombination of hydrogen and oxygen. Decomposition is favored by higher enrichment from heavy particle ionization by fission recoil. Recombination is favored by higher temperature and higher concentrations of uranyl ion in solution. Irradiation by Co^{60} was also studied. The effect of Br^- ion in increasing decomposition is greatest for gamma radiation and least for fission recoil.

Incidental to a study of the Szilard-Chalmers reaction of Br^{82} in crystalline $KBrO_3$, it was necessary to know the direct decomposition of $KBrO_3$ by other types of radiation. The total effect was $k_T = k_\gamma + k_n + k_\beta$, as shown by the fact that decomposition in the pile is linear with time and proportional to the power. The effect of shielding was also measured with

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lead, cadmium, and boron. The effect of gamma rays from Co^{60} was also determined.

Continued study of the decrease in catalytic activity of ZnO for the reaction $C_2H_4 + H_2$ by intense and prolonged gamma radiation (12,000 r/min from Co^{60} up to 100 days) gave evidence that the effect is not the result of poisoning by adsorbed reactants or products. A sample of ZnO that had been reduced severalfold in activity by gamma rays was completely restored to its initial activity by overnight evacuation.

CHEMISTRY OF THE SOLID STATE

The investigation of the high-temperature structure of UC_2 by x-ray diffraction has been hampered by the slight surface oxidation, which gives the pattern of UO_2. By raising the temperature to 1850°C, where the reaction $UO_2 + 4C = UC_2 + 2CO$ occurs, the cubic form of UC_2 was for the first time actually observed. The temperature of transition, tetragonal to cubic, will be sought. The change in specific volume is unusually high. LaC_2 was found to possess a cubic structure at 1750°C that reverts to tetragonal at some lower temperature. Lattice constants have been found for both cubic and tetragonal UC_2 and LaC_2.

Work has been suspended on the remote control x-ray diffraction spectrometer until a new Norelco apparatus is received.

As an approach to determining the structure at high temperature of the alkali metal–beryllium fluoride complexes, a study of glaserite $[K_3\ Na(SO_4)_2]$ has been undertaken. Glaserite is isotopic with the alpha forms of the complex beryllium fluorides and has the advantage of retaining its high-temperature structure at room temperature.

The irradiation of lead oxide, which in the Chalk River pile for one month at at exposure to 6.4×10^{19} fast neutrons per cm^2 was converted (25%) to the yellow form, has been repeated in the LITR at 3.6×10^{19} fast neutrons per cm^2 in a water-cooled compartment with a negative result. A possible explanation assumes that the temperature may have risen in the Chalk River experiment above the transition point and produced a temperature rather than a radiation effect. Further tests with the temperature and radiation monitored will be necessary to resolve the discrepancy. No transformation was observed in the LITR with the calcite and aragonite forms of $CaCO_3$.

Preliminary experiments have been made with metals dissolved in their fused salts, since such mixtures might possibly be used as coolants or fuel media in reactors. About 12 mole % of cadmium is soluble in fused $CdCl_2$,

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but again precipitates as metal upon cooling. Calcium was found to dissolve in fused $CaCl_2$ to 40 mole %, which is intermediate between previous determinations. However, it is possible that some $CaCl_2 \cdot 6H_2O$ may have contaminated the $CaCl_2$ to give a reaction $CaCl_2 \cdot 6H_2O + 12\ Ca = CaCl_2 + 6CaO + 6CaH_2$. The product, upon solution in water, would give both alkalinity and H_2 evolution that would be mistaken to indicate calcium. Experiments with sodium in molten NaCl have given two values, 10 mole % and 4 mole %, both of which are lower than a previous value of 15 mole % given in the literature. Further investigation is required.

INSTRUMENTATION

Developmental work on a new linear amplifier for scintillation spectrometry is complete and a model is now in construction. The pulse shaper consisting of two identical shorted delay lines is the novel feature.

A logarithmic sweep circuit for pulse-height analysis has been developed. The radiations from the sample are converted to electrical pulses whose amplitudes are proportional to the energy of radiation. By use of a screen and long time exposure, a photographic method is achieved for determination of the energy distribution from a radioactive source.

The possibility of detecting ionizing events in a gas by the photomultiplier technique has been explored with positive results. A collimated alpha-ray source is passed through the gas at atmospheric pressure. Helium, neon, and argon have shown pulse heights in the order of intensity 1, 2, and 3×. The argon pulse is about 1/500 as high as sodium iodide pulses, for the same energy. Polyatomic gases are dissociated and exert a quenching action quite similar to that in a Geiger-Mueller counter. Therefore they do not scintillate.

REACTOR CHEMISTRY

Work in progress on the stability of plutonium in aqueous UO_2SO_4 solution in the range 100 to 200°C has shown that the hydrolytic equilibrium is not reached in 10 days below 140°C. Further work will be done on reaction rates above 140°C. The stability of plutonium in UO_2F_2 solution at 130°C does not differ appreciably from that of plutonium sulfate.

Complete solubility studies for yttrium and lanthanum sulfates in 0.126 and 1.26 *M* UO_2SO_4 from 150 to 300°C were recently reported. Currently the following solubilities are being determined: Cs_2SO_4 in 1.26 *M* UO_2SO_4 from 170 to 290°C, and in 0.126 *M* UO_2SO_4 from 55 to 180°C. $Ce(SO_4)_2$ in 1.26 *M* UO_2SO_4 is only slightly soluble at room temperature

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and has a negative temperature coefficient of solubility. MoO_3 is appreciably soluble in 1.26 *M* UO_2SO_4 at room temperature. A white precipitate formed upon heating to 75°C, which disappeared at 190°C and reappeared at 115°C, upon cooling, and persisted at room temperature. At 250°C, 1% of MoO_3, or more, is soluble in 1.26 *M* UO_2SO_4. Exploratory samples of $Zr(SO_4)_2$ showed complete solubility below 200°C, but at higher temperatures white precipitates appeared, which persisted upon cooling to room temperature.

Composite samples of Cs, La, Mo, Y, and Zr sulfates were tested in 1.26 *M* UO_2SO_4 with the concentration of each adjusted to 50% (or lower) of the individual solubility. Abnormal precipitation resulted, which was probably caused by complex salt formation with molybdenum and zirconium. The solubility of $CdSO_4$ in 1.26 *M* UO_2SO_4 varied from 31.62 wt % at 23°C to 22.51 at 248°C. Ag_2SO_4 in 1.26 *M* UO_2SO_4 is soluble to 2.36 wt % at 52°C and to 17.25 at 263°C. At 250°C, solubilities greater than 0.19 *M* UO_2 in 0.126 *M* UO_2F_2 and greater than 0.59 *M* in 1.26 *M* UO_2F_2 were observed.

Conductivity data are now available for aqueous solution of UO_2SO_4 from 0.0001 to 6 *N* at 0.25 and 50°C, and for UO_2F_2 from 0.0001 to 1 *N* at 0 and 25°C.

The vapor pressures of UO_2SO_4 solutions (6.84 and 32.82 wt %) have been determined from 200 to 350°C, corrected for dissolved air, and compared with the literature values for water (Table 42).

More accuracy in the analysis of UO_2SO_4 has been attained by removal of UO_2 in a Dowex exchange column and subsequent titration of sulfate ion in the effluent with standard base.

The effect of radiation on aqueous reactor solutions is under active investigation. The results may be summarized as follows:

1. Studies of initial rates of gas production from uranyl solutions exposed to pile radiation have been extended to cover wider ranges of enrichment and concentration.

2. Nonradiation studies of the homogeneous recombination of hydrogen and oxygen in solutions (catalyzed by uranyl, copper, and other ions) have been extended. The reaction appears, experimentally, to be first-order with respect to copper concentration and to be independent of uranyl concentration over a relatively large range of concentration. Techniques for converting experimentally observed values of dP/dt into data useful for kinetic studies have been considerably refined.

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3. The catalytic effect of copper ions on recombination has been demonstrated by inpile experiments at neutron fluxes of up to 1×10^{13}. The kinetics of gas production and recombination at given values of flux, temperature, and copper concentration have been shown to be described satisfactorily by a simple differential equation. Predictions have been made, and checked, for fluxes as high as those expected in small-scale homogeneous reactors.

4. The effect of gamma or pile radiation on the recombination of hydrogen and oxygen in the presence of distilled water at high pressures and temperatures up to 290°C has been shown to be insignificant so far as practical effects in homogeneous reactors are concerned.

An attempt is being made to develop a reference electrode suitable for use at high temperature. It will be used especially in studying passive films on stainless steel. The most promising cell to date is lead in mercury amalgam (with platinum contact lead) in an electrode solution of 0.13 *M* UO_2SO_4 against $Ag\text{-}Ag_2SO_4$. A bomb experiment at 250°C showed that the UO_2SO_4 in solution is reduced by the amalgam. Further attempts will be made.

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CHEMISTRY DIVISION QUARTERLY PROGRESS REPORT FOR PERIOD ENDING DECEMBER 31,1951

INORGANIC CHEMISTRY

CHARACTERIZATION OF SOLID THORIUM PERCHLORATE

W. C. Waggener R. W. Stoughton

Solid thorium perchlorate prepared by fuming thorium nitrate hydrate to dryness with perchloric acid at 200 to 215°C has been found to be partially hydrolyzed.[1] Its composition closely approximates $Th(OH)_2(ClO_4)_2$ or $ThO(ClO_4)_2 \cdot H_2O$, as determined from the analyses of (1) thorium by precipitation and ignition of the oxalate to the dioxide; (2) hydroxyl (or hydroxyl equivalent) by titration with acid; (3) charge of the hydrolyzed cation by exchange of the thorium with hydrogen ions from a cation-exchange resin and titration of the displaced hydrogen ion; and (4) perchlorate by precipitation and weighing as tetraphenylarsonium perchlorate.

Analyses of two preparations of the solid are given in Table 1.

Thorium perchlorate prepared as described is a white, microcrystalline, highly hygroscopic solid that dissolves in water with virtually no residue. At the temperature at which it is prepared (200 to 215°C) it tends to lose weight slowly over a period of days. Studies of the properties of this solid and of its aqueous solutions are aimed at a better understanding of the hydrolytic behavior of the thorium ion. Further data on the composition and stability of the solid are being obtained, and it is planned to obtain structural data through x-ray studies, which may permit a choice to be made between the formulas $Th(OH)_2(ClO_4)_2$ and $ThO(ClO_4)_2 \cdot H_2O$. Aqueous solutions are being studied by pH measurements.

ULTRACENTRIFUGAL STUDIES OF THORIUM PERCHLORATE SOLUTIONS

J. S. Johnson K. A. Kraus

From previous pH measurements[2] of thorium chloride in NaCl and $NaClO_4$ solutions, it became apparent that thorium tends to dimerize at relatively low hydroxyl numbers $n < 0.1$, where n is the number of hydroxide ions per thorium ion. Thus it appeared of interest to see whether further polymerization of thorium would occur at higher hydroxyl numbers. The region in the neighborhood of $n = 2$ was selected for this study. A 0.02 *M* thorium solution of ionic strength $\mu = 1$ ($NaClO_4$) in which the hydroxyl number is approximately 1.9 was used. It was found that the thorium is primarily monodisperse, with an apparent molecular weight of about 1200. Since the polymeric particles must carry a considerable charge in perchlorate solutions, the actual molecular weight of the thorium polymer particles would be higher. This "charge" correction was estimated by assuming that the polymer carries a charge of $+2x$, where x is the number of thorium ions per polymer. Setting $x = 4$ (tetramer), the charge correction is about +500, which yields a molecular weight of 1700 that is in good agreement with the theoretical molecular weight of 1788 for the tetramer

(1) W. C. Waggener and R. W. Stoughton, "Characterization of Solid Thorium Perchlorate," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1951*, ORNL-1153, p. 7.

(2) K. A. Kraus and R. W. Holmberg, *Hydrolytic Behavior of Metal Ions; II. Acidity of Thorium Tetrachloride Solutions*, AECD-2919 (Aug. 29, 1950).

TABLE 1

Analysis of Solid Thorium Perchlorate

	CALCULATED FOR $Th(OH)_2(ClO_4)_2$ (%)		PREPARATION A (%)		PREPARATION B (%)	
Th	49.91	(1.00)*	49.46	(1.00)*	49.40	(1.00)*
OH	7.32	(2.00)	7.39	(2.04)	7.25	(2.00)
ClO_4	42.77	(2.00)	42.84	(2.02)	42.37	(2.00)
Total	100.00		99.69		99.02	
Molecular Weight	465.1		469.5		470.0	

*Values in parentheses are mole ratios based on thorium.

$(ThO(ClO_4)_2)_4$. It is of interest that this species was previously postulated on the basis of data on pH change with dilution.[3] Although this agreement appears excellent, it should be pointed out that the uncertainty in the estimation of the charge correction and the partial specific volume of the thorium species is sufficiently large to make it possible that the polymeric particle could be a trimer or pentamer.

A similar thorium solution of lower concentration (0.015 *M* Th) in 1 *M* $NaClO_4$ and of hydroxyl number 2.1 was also investigated. In this solution considerable dispersity of the apparent molecular weights was found; they ranged from about 1300 to 5700. These numbers would also have to be revised upward considerably because of the charge correction. Unquestionably, higher polymers than tetramers are being formed in these solutions.

USE OF THERMISTOR IN FREEZING-POINT MEASUREMENTS

J. S. Johnson K. A. Kraus

In connection with the measurements of the freezing-point depressions of uranyl fluoride solutions, it was found that a "thermistor" is a reliable and sensitive instrument that can be readily adapted to continuous measurements. A Western Electric thermistor[4] with a resistance of approximately 365,000 ohms was used in series with a standard resistor of approximately 1,000,000 ohms. The temperature coefficient of the standard resistor was determined to be about 0.015%, and therefore it was mounted in a vessel in which the temperature was thermostatically controlled at 25 ± 0.1°C. The two resistors were connected to a "telephone" (1.5-v) battery and the voltage drop across the thermistor was measured by using a vibrating-reed electrometer. The bucking potential was supplied by a Rubicon precision potentiometer in series with a Brown Electronik recorder, which was adjusted for 3-mv full-scale sensitivity. Since the thermistor has a temperature coefficient of approximately 5% per °C, a distance of about 2.5 cm on the Brown recorder was equivalent to 0.01°C.

Before and after a three-month period the thermistor was calibrated

(3) R. Schaal and J. Faucherre, "Variations of pH as a Function of the Dilution. Application to the Study of Soluble Basic Salts," *Bull. soc. chim. France* **1947**, 927-32.

(4) J. A. Becker, C. B. Green, and G. L. Pearson, "Properties and Uses of Thermistors – Thermally Sensitive Resistors," *Bell System Tech. J.* **26**, 170 (1947).

against a Bureau of Standards calibrated platinum resistance thermometer (Mueller Bridge). Ritscher of the ORNL Instrument Division assisted in these calibrations. It was found that the two calibrations checked within experimental accuracy.

The thermistor was mounted inside a 0.6-cm-diameter, 4-cm-long, platinum thimble and held in place with a bismuth-lead-tin alloy (m.p. 150°C). The thimble was sealed to a soft glass tube, which carried the leads, and was filled with ceresin wax for insulation. To illustrate the reproducibility of the instrument, the ice points determined over a 15-day period are shown in Table 2. The standard deviation (σ) of these measurements is ±0.0011°C.

TABLE 2
Ice Point Determinations with Thermistor

DATE	THERMISTOR RESISTANCE ($\times 10^{-5}\ \Omega$)	Δ	Δ^2
Nov. 12, A.M.	3.6520	−2	4
Nov. 12, P.M.	3.6519	−3	9
Nov. 12, P.M.	3.6524	+2	4
Nov. 13	3.6522	0	0
Nov. 15, A.M.	3.6524	+2	4
Nov. 15, P.M.	3.6523	+1	1
Nov. 19, A.M.	3.6521	−1	1
Nov. 19, A.M.	3.6523	+1	1
Nov. 19, P.M.	3.6519	−3	9
Nov. 20	3.6520	−2	4
Nov. 23, A.M.	3.6523	+1	1
Nov. 23, P.M.	3.6524	+2	4
Nov. 24	3.6524	+2	4
Nov. 27	3.6522	0	0
	Mean = 3.65220		46
	σ = 19Ω or ±0.0011°C.		

FREEZING POINTS AND ACTIVITY COEFFICIENTS OF URANYL FLUORIDE SOLUTIONS

J. S. Johnson K. A. Kraus

The freezing-point depressions of several series of uranyl fluoride solutions were determined in an attempt to improve the accuracy of the data previously reported by Secoy[5] and to check the interpretation previously given.[6]

The measurements were carried out with two preparations of uranyl fluoride; one preparation was made by the Harshaw Chemical Company and the other by the Y-12 Chemical Department. Negligible impurities were found in both samples by spectroscopic analysis, supplemented by an activation analysis for sodium that was made by M. Wittels, C. Feldman, and G. W. Leddicotte of the ORNL Analytical Chemistry Division. The fluoride-to-uranium ratios for the two samples were 1.983 and 1.998, respectively, as determined by the Y-12 Analytical Department. The two samples did not show significant differences in the freezing-point depressions.

Solutions were prepared by dissolving the material in distilled water or by diluting aliquots. All solutions were prepared on a weight basis. The stock solutions and a number of the "diluted" solutions were analyzed by determining the uranium content (as U_3O_8) through direct evaporation of the solutions, followed by ignition of the residue, and through ignition after precipitation of ammonium uranate.[7] The two methods agreed to within a few tenths of a per cent and indicated that there was not significant contamination.

The freezing points were determined with the thermistor described in the

(5) C. H. Secoy, "The Mean Activity Coefficients of Uranyl Fluoride in Water Solutions at 25°," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, ORNL-795, p. 28-34.

(6) J. S. Johnson and K. A. Kraus, "Undissociated Species and Dimerization in Aqueous Solutions of Uranyl Fluoride," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951*, ORNL-1116.

(7) The uranate analyses were made by H. Cutcher and P. Thomason of the ORNL Analytical Chemistry Division.

previous section by the following technique: Solutions were placed in an unsilvered Dewar flask. The jacket was not evacuated, since it contained outlet and inlet tubes to admit freezing mixtures. The assembly was placed in a freezing mixture until part of the solution froze. It was then transferred to a bath containing a freezing mixture of the proper temperature to give the desired rate of heating. A continuous record of the temperature during the warming period showed a curve with a practically linear, slowly rising branch while ice was present in the solution and a more rapidly rising branch after the ice melted. The intersections of the extrapolated linear branches of the temperature curves were assumed to be the freezing points of the solutions. In the more concentrated solutions (2.5 to 5 molal), the freezing points could be reproduced to better than ±0.006°C with heating rates differing by a factor of 2 to 3. For the more dilute solutions the reproducibility was usually better than ±0.002°C. The observed freezing points are summarized in Fig. 1 and Table 3.

Nominal activity coefficients were calculated from the freezing-point data by assuming that $\nu = 1$ and $-\ln\gamma = j = 1 - \theta/\lambda\nu m$ at $m = 0.1$, where ν is the number of moles of particles per mole of uranyl fluoride, θ is the freezing-point depression, m is the molality of uranyl fluoride, and λ is the molal freezing-point depression constant. As described in an earlier report,[6] "true" activity coefficients ($\nu = 1$ at infinite dilution) cannot be obtained because the measurements were not extended to sufficiently low concentrations and because the dissociation into ions that will occur at lower concentrations will necessitate the choice of different values of ν. In general, the interpretation follows that described earlier.[6]

TABLE 3

Freezing-Point Depressions of Uranyl Fluoride

m	SOLUTION[a]	θ, °C[b]	θ/m
0.1005	4	0.176	1.75
0.1972	2	0.331	1.678
0.2974	2	0.487	1.638
0.3005	3	0.486	1.617
0.4914	4	0.768	1.563
0.4941	2	0.772	1.562
0.6943	4	1.058	1.526
0.8875	2	1.334	1.503
0.8936	1	1.344	1.504
1.077	1	1.610	1.495
1.341	1	2.003	1.494
1.348	3	2.004	1.487
1.601	3	2.402	1.500
2.077	2	3.189	1.535
2.086	4	3.203	1.535
2.088	3	3.188	1.527
2.554	3	4.033	1.579
3.028	3	4.943	1.632
3.437	3	5.812	1.691
4.027	3	7.143	1.774
4.558	3	8.406	1.844
5.249	3	10.183	1.940

[a] Solutions 1, 2, and 3 were prepared from Harshaw UO_2F_2; solution 4 was prepared from Y-12 UO_2F_2.

[b] Averages of measurements.

As shown in Fig. 2, the activity coefficients calculated from the new freezing-point data are very similar to those from the freezing-point depressions of Secoy, that is, they drop to approximately 0.54 and then rise to approximately 0.61 at 5 m. As discussed earlier, the initial decrease is probably caused by association of uranyl fluoride to a dimer and the rise of γ at high m as a result of changes in the activity coefficients of the monomer and dimer of uranyl fluoride. By using the equations of the earlier quarterly report,[6]

calculations were made of the dimerization constant,

$$K_d = \frac{a_2}{a_1^{\,2}}, \qquad (1)$$

where a_2 and a_1 are the activities of dimer and monomer, respectively, and also of b_1 in the assumed equations for the activity coefficients for the monomer and dimer:

$$\log \gamma_1 = b_1 m$$

and (2)

$$\log \gamma_2 = 2b_1 m .$$

Neglecting possible dissociation at low concentrations, the best fit of the data was obtained with $K_d = 1.5$

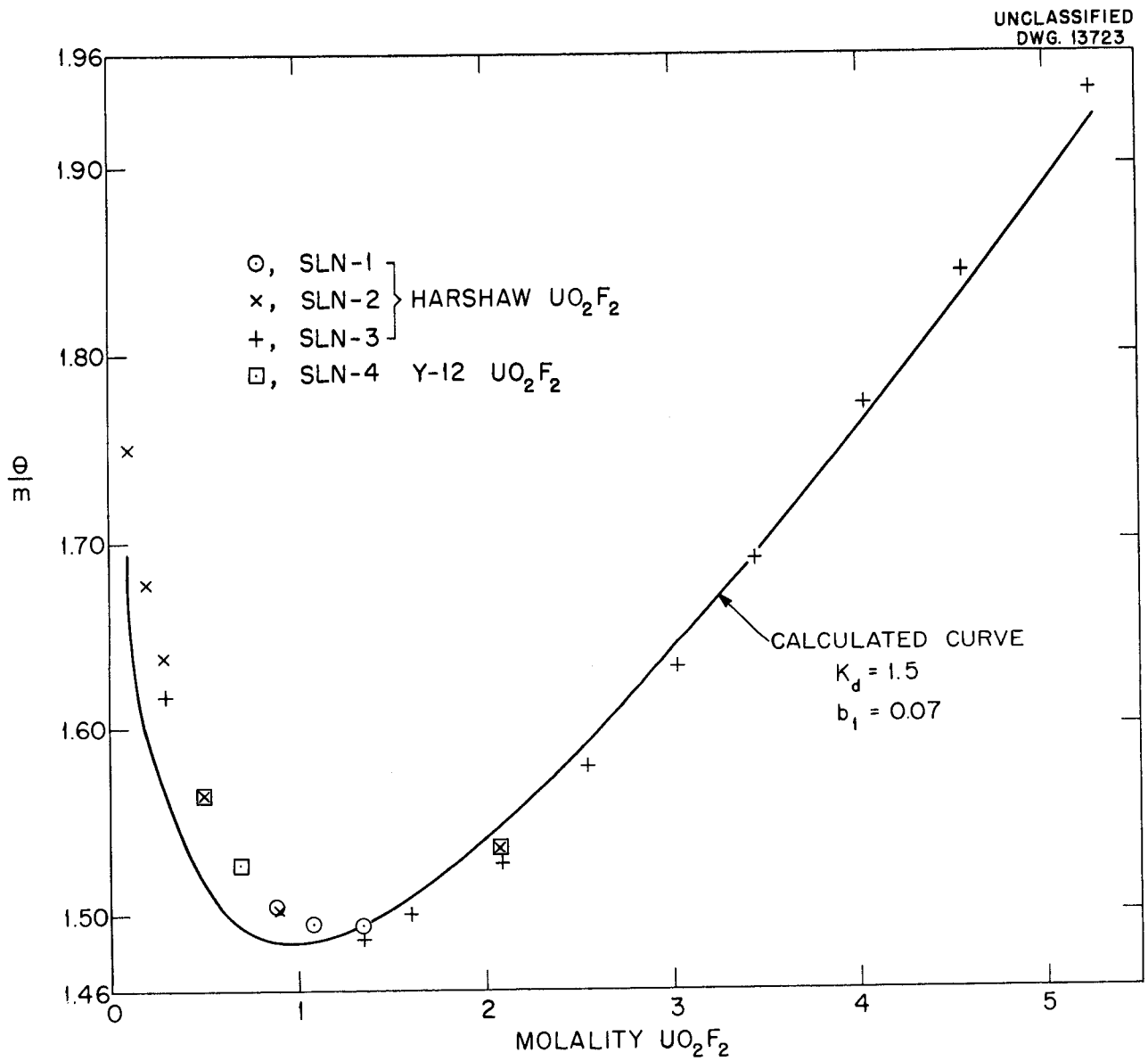

Fig. 1. Freezing Point Depression of UO_2F_2.

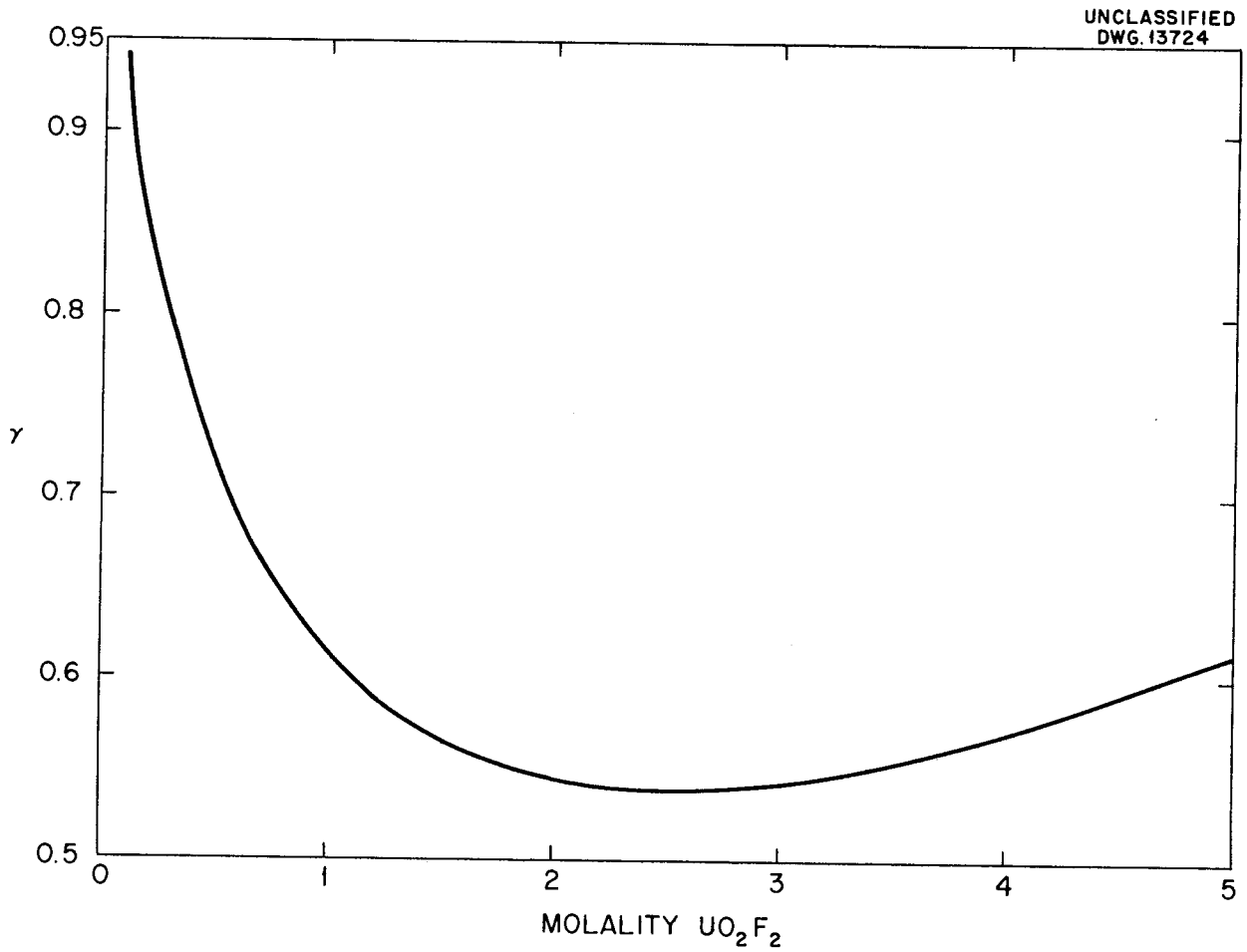

Fig. 2. Nominal Activity Coefficients of Uranyl Fluoride.

and $b_1 = 0.07$, as shown in Fig. 1 This led to small deviations of the theoretical curve from the experimental curve that were definitely outside the experimental error. However, since it was assumed that K_d and b_1 were independent of temperature and that dissociation was negligible, it is not surprising that such deviations from the experimental curve appear. The agreement is sufficiently good to support the assumptions that (1) uranyl fluoride is practically undissociated at low concentrations and largely associated at high concentrations, and (2) the activity coefficients γ_1 and γ_2 follow approximately Eq. 2.

These conclusions are the same as those previously obtained by using the data of Secoy. However, it now appears that the molecular association constant is considerably smaller than originally stated and that electrolytic dissociation is also less important in the region studied.

ANION-EXCHANGE STUDIES

K. A. Kraus F. Nelson
G. W. Smith

Zinc, Cadmium, and Mercury(II) in Hydrochloric Acid Solutions. The adsorbability of zinc, cadmium, and

mercury(II) by the anion-exchange resin Dowex-1 was studied in hydrochloric acid solutions from about 0.01 to 12 *M* HCl at 25°C. The experiments were carried out by a "shaking technique" under conditions in which the amount of metal adsorbed by the resin was negligible (<0.1%) compared with its capacity. The extent of adsorption was calculated from the decrease in the metal concentration after equilibration by using radiochemical techniques and Zn^{65}, Cd^{115}, and Hg^{203} tracers.

The results of the experiment are shown in Fig. 3 in which the logarithm of the observed distribution coefficient *D* (amount per gram of air-dried resin/amount per cubic centimeter of solution) is plotted against the molarity of hydrochloric acid. Zinc and cadmium show maximum adsorbability near 2 *M* HCl and decreasing adsorption above this concentration, whereas mercury(II) shows only decreasing adsorption in the region studied. It is believed that decreasing adsorption with increasing hydrochloric acid concentration occurs in these solutions when negatively charged complex ions (probably $MCl_4^=$) are the predominant species. A more detailed analysis of the curves is in progress.

Separation of Scandium and Yttrium. As reported in an earlier quarterly report,[8] scandium shows small, but appreciable, adsorption on Dowex-1 from relatively concentrated hydrochloric acid solutions. This adsorbability is sufficient to give some separation from nonadsorbable ions, as demonstrated in Fig. 4, which shows a separation of yttrium from scandium. In this experiment, 0.6 mg of scandium (containing Sc^{46}) and 0.1 mg of yttrium (containing Y^{91}) were adsorbed from 12 *M* HCl on a 40-cm by 0.04-cm^2 column. Elution was carried out with 12 *M* HCl. Analysis was performed by counting samples of the eluate. As shown in Fig. 4, satisfactory separation of the two elements can be achieved.

Separation of Gallium and Aluminum. It has been found that gallium can be strongly adsorbed from hydrochloric acid solutions, so it is apparent that it can readily be separated from many positive ions, particularly those showing little or no adsorption. A typical example of separation of gallium and aluminum is described in the following.

A 2.0 *M* $AlCl_3$ solution containing 3.5 *M* HCl and about 10^{-4} *M* Ga (containing Ga^{72}) was passed through a 10-cm by 0.04-cm^2 column. The movement of the gallium was followed by the automatic scanner, and it was found that after passage of approximately 20 ml of solution at a flow rate of 0.45 cc/cm^2, gallium activity could only be detected in the upper 0.9 cm of the column. Thus it appears that large volumes of aluminum solutions containing gallium could readily be processed by using relatively small amounts of resin.

Indium. The adsorbability of indium(III) from 3, 7, and 12 *M* HCl solutions was studied by determining the elution constants, *E*, on a 10-cm by 0.04-cm^2 column. The rate of movement of the indium band was determined by adding In^{114} tracer and following it with the automatic scanner. The results of the experiments are shown in Table 4.

It is interesting that although indium is adsorbable by the anion exchangers from concentrated hydrochloric acid solutions, this adsorbability is several orders of magnitude smaller than for gallium,

[8] K. A. Kraus, G. E. Moore, F. Nelson, and G. W. Smith, "Anion-Exchange Studies in Hydrochloric Acid Solutions," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951*, ORNL-1116, p. 10.

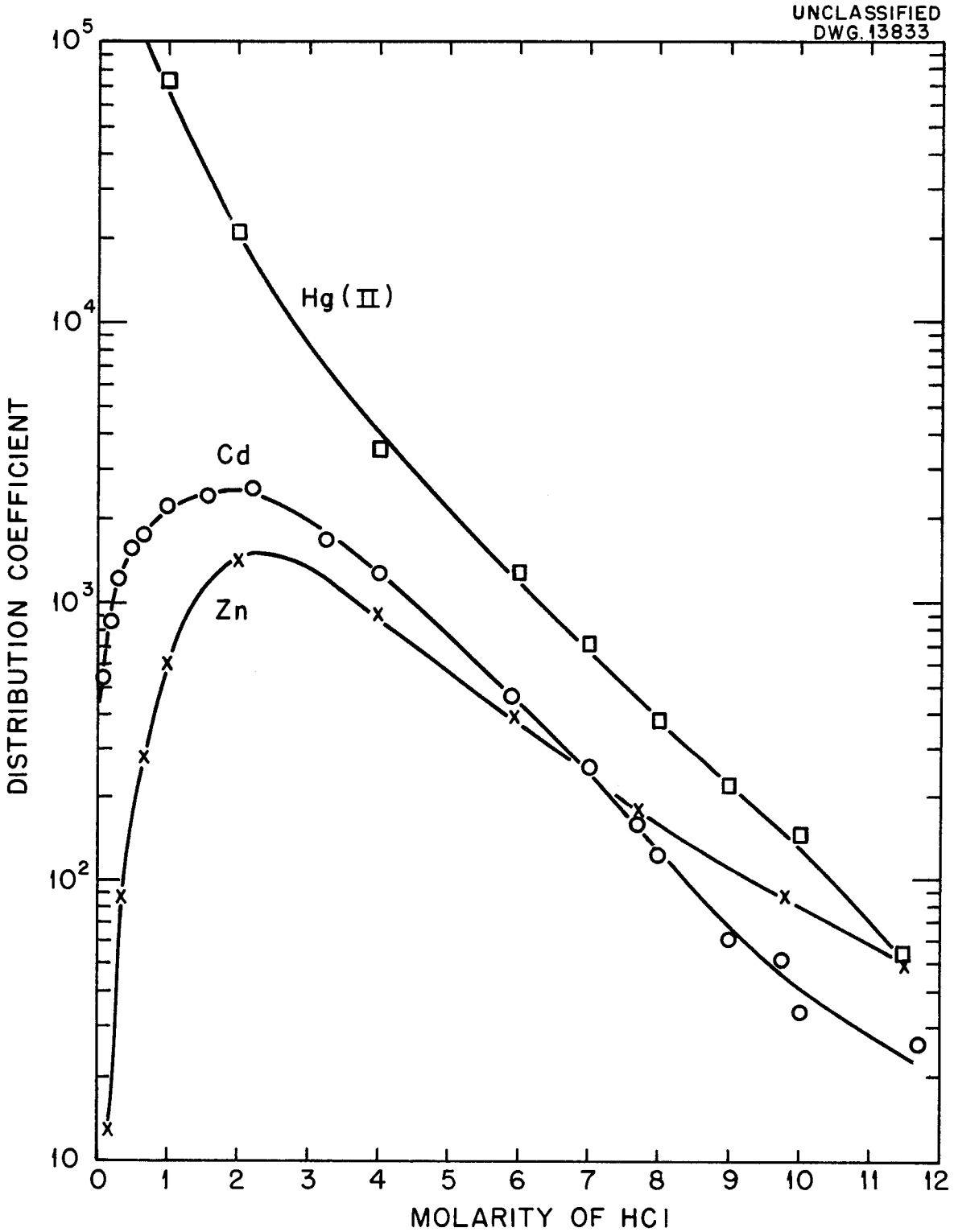

Fig. 3. Adsorption of Zn, Cd, and Hg(II) on Dowex-1 Anion Exchange Resin (Tracer Loading, 25°C).

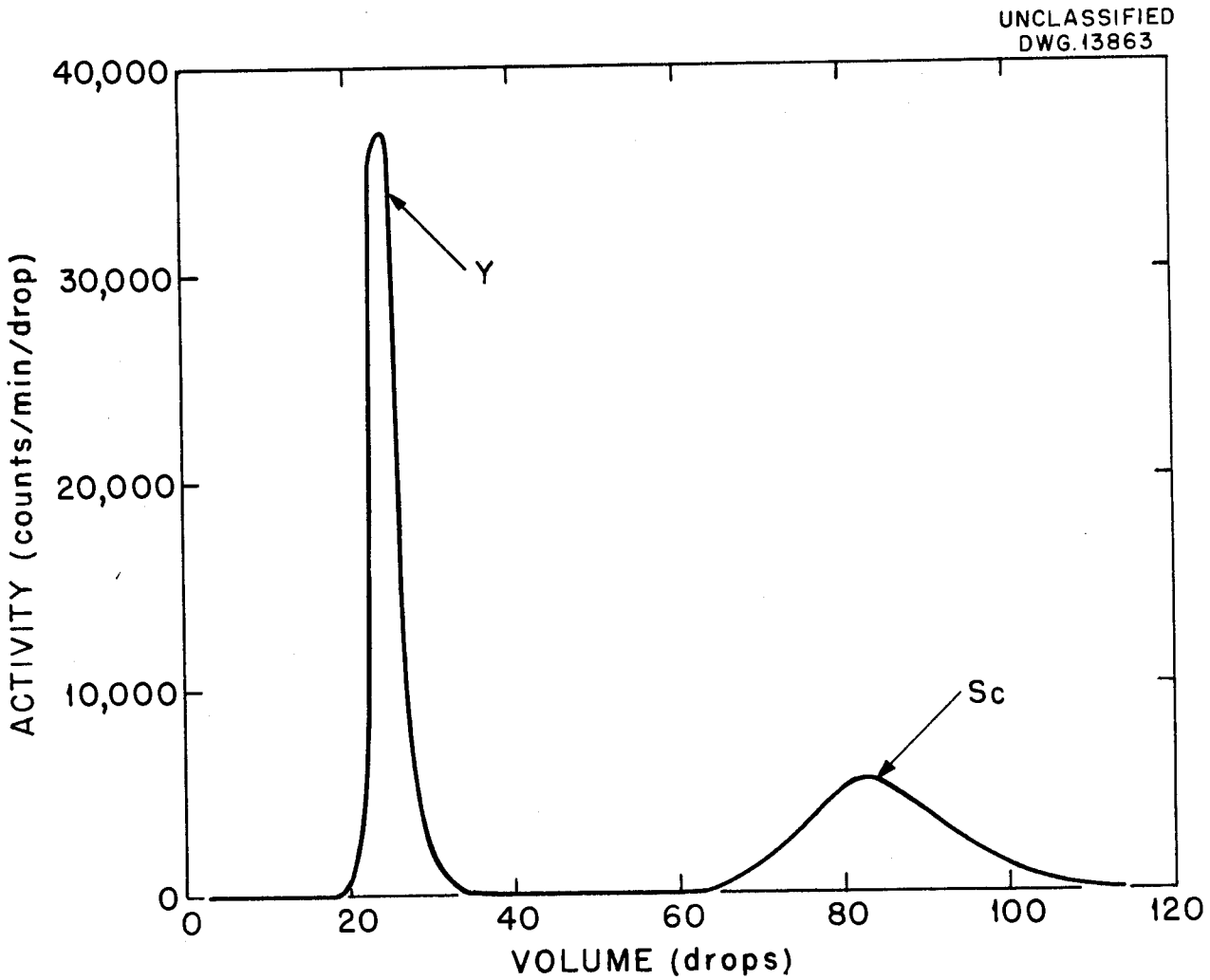

Fig. 4. Separation of Scandium and Yttrium.

TABLE 4

Distribution Coefficients of Indium in Hydrochloric Acid

HCl CONCENTRATION (*M*)	*E*	*D*
3.0	0.095	10.1
7	0.11	8.8
12	0.28	3.2

the element directly above indium in the periodic table. Since gallium is probably adsorbed as $GaCl_4^-$, it might be concluded from this large difference in adsorbability that indium forms a chloride complex of greater negative charge than one.

Adsorption of Thallium(I) and Thallium(III). In an attempt to complete the study of the adsorbability of gallium, indium, and thallium, a series of preliminary experiments was carried out on the adsorbability of thallium(III) from hydrochloric acid solutions. In order to estimate whether possible adsorption of thallium(I) might interfere with this determination, a parallel series of experiments with thallium(I) solutions was carried out. The experiments were

carried out by the shaking technique because thallium is quite strongly adsorbed. Equilibration times of the order of 20 hr were used. All thallium solutions were analyzed polarographically for thallium(I) and thallium(III). The solutions were not found to be significantly contaminated by the other oxidation state. Oxidation of thallium(I) to thallium(III) was achieved by passing chlorine through the solutions. Before equilibration, the chlorine was removed by passing nitrogen through the solutions.

Thallium(I) shows only moderate adsorption, but thallium(III) is very strongly adsorbed, particularly at low hydrochloric acid concentrations. The thallium(I) adsorbability shows a maximum at 4 *M* HCl with *D* (amount per gram of resin/amount per cubic centimeter of solution) equal to about 100.

Thallium(III), in the range studied (above 1 *M* HCl), showed a practically linear logarithmic decrease of *D* from about 20,000 in 1 *M* HCl to about 300 in 12 *M* HCl. Since D_{Tl} in concentrated hydrochloric acid is very much smaller than D_{Ga}, it appears that thallium(III) forms a chloride complex with more than four chloride ions (higher negative charge than −1) in contrast to the tetrachloro complex formed by gallium ($GaCl_4^-$).

DETERMINATION OF THE STABILITY OF COMPLEX IONS BY USING CATION-EXCHANGE RESINS: ZINC AND CADMIUM CHLORIDE COMPLEXES

R. A. Plane K. A. Kraus

As mentioned in the last quarterly report,[9] experiments are under way to determine the feasibility of using cation-exchange resins to determine the stability of *weak* complex ions in aqueous solutions at room temperatures and at elevated temperatures and thus to evaluate, in addition to ΔF, ΔH and $T\,\Delta S$ for the reactions. Data have been obtained on the exchange of zinc and cadmium in perchloric acid solutions, and from these data estimates of the heat of adsorption of the ions have been made. Data are now also available on the adsorption of zinc and cadmium in mixed hydrochloric-perchloric acid solutions at room temperatures and at elevated temperatures, and from these data information on the stability of the chloride complexes and the heats and entropies of the reactions has been gathered.

Zinc-Hydrogen Exchange and Zinc-Chloride Complexes. The exchange of zinc (using tracer Zn^{65}) and hydrogen ions between Dowex-50 cation-exchange resin and aqueous solutions of perchloric acid and hydrochloric acid was measured at 25, 60, and 87°C as a function of ionic strength in the range 0.05 to 5 *M*. The earlier data were reported in the previous quarterly report,[9] and additional data have been obtained that are in good agreement.

From the distribution coefficients in perchloric acid, the equilibrium constant

$$K^m\ (\mathrm{II}) = \frac{(Zn^{++})_r\ (H^+)^2}{(Zn^{++})\ (H^+)_r^{\,2}}$$

$$= K^0\ (\mathrm{II})\ G\ (\mathrm{II}) \quad (1)$$

can be evaluated. In Eq. 1 the parentheses indicate concentrations; the subscript *r*, the resin phase; K^0 (II), the "activity" constant; and *G* (II), the proper activity-coefficient ratio. Neglecting small differences

(9) R. A. Plane and K. A. Kraus, "Cation Exchange of Zinc in Chloride and Perchlorate Solutions," *op. cit.*, ORNL-1153, p. 9.

in the activity-coefficient ratio, G (II), in hydrochloric and perchloric acid solutions, the adsorbability in hydrochloric acid is different from that in perchloric acid since zinc forms a series of complexes $ZnCl_i^{+2-i}$ that differ in their adsorbability from Zn^{++}. In the interpretation it has been assumed that i = 1 to 4 and that the complex $ZnCl^+$ is the only complex adsorbed by the cation-exchange resin. The equilibrium constant for its adsorption can be written as

$$K^m\ (\mathrm{I}) = \frac{(ZnCl^+)_r\ (H^+)}{(ZnCl^+)\ (H^+)_r} = K^0\ (\mathrm{I})\ G\ (\mathrm{I})\ , \qquad (2)$$

where K^0 (I) and G (I) are the activity constant and proper activity-coefficient ratio, respectively. Since the observed distribution coefficient is

$$D_{Zn} = \frac{(Zn^{++})_r + (ZnCl^+)_r}{(Zn_T)}\ , \qquad (3)$$

where (Zn_T) is the total concentration of zinc in the aqueous phase, combination of Eqs. 1, 2, and 3 yields

$$D_{Zn} = \frac{(H^+)_r}{(H^+)\ (Zn^{++}) \sum_{i=0}^{i=4} k_{0i}^m\ (Cl^-)^i} \left[\frac{K^m\ (\mathrm{II})\ (H^+)_r}{(H^+)} + K^m\ (\mathrm{I})\ k_{01}^m\ (Cl^-) \right] . \qquad (4)$$

In Eq. 4, k_{0i}^m is the equilibrium constant for the formation of the complex $ZnCl_i^{+2-i}$ according to the equation

$$k_{0i}^m = \frac{(ZnCl_i^{+2-i})}{(Zn^{++})\ (Cl^-)^i} = k_{0i}^0\ G_{i0}\ , \qquad (5)$$

where, as in Eqs. 1 and 2, k_{0i}^0 and G_{i0} are the activity constants and proper activity-coefficient ratios, respectively. Since the experiments were carried out under conditions of changing ionic strength, it is necessary to estimate the various activity-coefficient ratios.

The activity-coefficient ratios for the resin phase have been assumed constant, since all experiments were carried out under conditions in which the zinc concentration in the resin was very small (less than 0.1% of the resin sites occupied by zinc). Hence, for the estimation of changes in G (II) and G (I), only the activity coefficients of the aqueous phase will be considered. G (II) [or K^m (II)] can be directly obtained from the experimental data in perchloric acid. G (I) was assumed essentially constant in the ionic strength range studied, since the variations of G (II) are relatively small and would be expected to be larger than those of G (I). $G_{0i} = 1/G_{i0}$ was assumed to follow the relation

$$\log G_{0i} = \frac{-0.509\ \Delta Z_i^2\ \mu^{1/2}}{1 + A\mu^{1/2}} + b_{0i}\, m\ , \qquad (6)$$

where ΔZ_i^2 is the difference in the square of the charges of the product and the reactant ions, A is a constant assumed to be equal to 1.5, and m is the molality of the supporting electrolyte. For the linear term, the relationship $b_{0i} = 0.25\ i$ was assumed, which had previously been obtained from anion-exchange studies of ferric chloride complexes.[10] From the data previously reported and the additional

(10) K. A. Kraus and G. E. Moore, unpublished results.

data obtained during the last quarter, the following constants were evaluated at 25°C:

$$k_{01}^{0} = 3.4 \pm 0.2 ,$$

$$k_{02}^{0} = 16 \pm 4 ,$$

$$k_{03}^{0} = 3.5 \pm 2 ,$$

$$k_{04}^{0} = 0.6 \pm 0.5 .$$

These constants are considerably larger than those calculated by Sillén and Liljeqvist[11] from potentiometric measurements. They report no measurable complexing in 0.5 *M* chloride. However, from the cation-exchange studies, it may be concluded that under the above-mentioned conditions approximately 30% of the zinc is complexed. The reason for the discrepancy is not known, although it is suspected that the data of Sillen and Liljeqvist may be in error, since in their work changes in liquid-junction potentials as a function of chloride concentration at constant μ were considered negligible.

Only limited data have been obtained at higher temperatures. From these data it appears that the stability constants increase with temperature, with the ΔH of complexing being of the order of a few kilocalories. Assignment of reliable values of ΔH to each complexing reaction is difficult since in the experimental range of chloride concentrations no single complex predominates.

Values of *K* (II) were determined in the temperature range of 25 to 87°C and ionic strength range of 0.05 to 2 *M*. From the extremely small temperature coefficient, the heat of the adsorption reaction, $\Delta H = 0.15 \pm 0.15$ kcal/mole, was found for the particular batch of resin used. Only very rough estimates of *K* (I) could be obtained from the data, and it appears that *K* (I) is of the same order of magnitude as *K* (II).

Cadmium-Hydrogen Exchange and Cadmium-Chloride Complexes. The exchange of cadmium (using Cd^{115}) and hydrogen ions between Dowex-50 cation-exchange resin and aqueous solutions of perchloric acid and mixed hydrochloric-perchloric acid solutions was studied at 25 and 60°C. Since Cd^{++} forms stronger chloride complexes than Zn^{++}, the experiments could be performed at lower ionic strength and at constant ionic strength. (Values of $\mu = 0.1$, 0.2, and 0.5 were selected.) The results are shown in Fig. 5. In the evaluation of the constants, it was assumed that the activity-coefficient ratios are constant in each series at constant μ. The data could be explained reasonably well by assuming that $CdCl^{+}$ is the only complex formed in the chloride concentration range studied. The values found for k_{01} are shown in Table 5. From the observed temperature coefficient, $\Delta H = \sim 1$ kcal and $\Delta S = \sim 10$ e.u. were found for the reaction $Cd^{++} + Cl^{-} \rightarrow CdCl^{+}$, as also shown in Table 5. These values are in good agreement with those previously reported. A literature survey of the cadmium-chloride complexes is given in Table 6.

From the temperature coefficient of *K* (II), ΔH for the adsorption reaction $Cd^{++} + (2H^{+})_{r} \rightarrow (Cd^{++})_{r} + 2H^{+}$ was found to be 1.4 kcal/mole in the temperature range 25 to 60°C and ionic strength range $\mu = 0.1$ to 2.0 for the particular batch of resin used. It should be pointed out that this value for ΔH cannot be directly compared with that reported for zinc in the previous section since different preparations of resins were used.

[11] L. G. Sillén and B. Liljeqvist, "On the Complex Formation Between Zn^{2+} and Cl^{-}, Br^{-}, and I^{-} Ions," *Svensk. Kem. Tid.* **56**, 85-95 (1944).

TABLE 5

Thermodynamic Functions for the Reaction $Cd^{++} + Cl^{-} \rightarrow CdCl^{+}$

μ	k_{01} 25°C	k_{01} 60°C	ΔF (kcal/mole at 25°C)	ΔH (kcal/mole)	ΔS (cal/mole-deg.)
0.1	40 ± 3	46 ± 7	-2.2	+0.8	+10.0
0.2	34 ± 2	36 ± 4	-2.1	+0.3	+ 8.0
0.5	35 ± 2	46 ± 8	-2.1	+1.5	+12.1

TABLE 6

Literature Survey of Cadmium-Chloride Complexes

k_{01}	k_{02}	k_{03}	k_{04}	μ	T (°C)	REFERENCES
27	180	80		3.0	0	(*a*)
25	150	250		3.0	25	(*a*)
36	130	290		3.0	47.5	(*a*)
99				0	18	(*b*)
100	400	500	1000	0.04 to 0.2	~18	(*c*)
350				0	25	(*d*)
90				0	25	(*e*)
38.5	170	260		3.0	25	(*f*)
			ΔH (25°C)	ΔF (25°C)	ΔS	
$Cd^{++} + Cl^{-} \longrightarrow CdCl^{+}$			0.63	-1.91	8.5	(*a*)
$Cd^{++} + 2\ Cl^{-} \longrightarrow CdCl_2$			-1.10	-3.01	6.4	(*a*)
$Cd^{++} + 3\ Cl^{-} \longrightarrow CdCl_3$			4.62	-3.28	26.5	(*a*)

(*a*) E. L. King, *J. Am. Chem. Soc.* **71**, 319-22 (1949).

(*b*) E. C. Richellato and C. W. Davies, *Trans. Faraday Soc.* **26**, 592-600 (1930).

(*c*) H. L. Riley and V. Gallafent, *J. Chem. Soc.* 1932, 514.

(*d*) L. Brüll, *Gazz. chim. ital.* **64**, 734 (1934).

(*e*) H. Harned and M. Fitzgerald, *J. Am. Chem. Soc.* **58**, 2624 (1936).

(*f*) I. Leden, *Z. physik, Chem.* **A188**, 160-81 (1941).

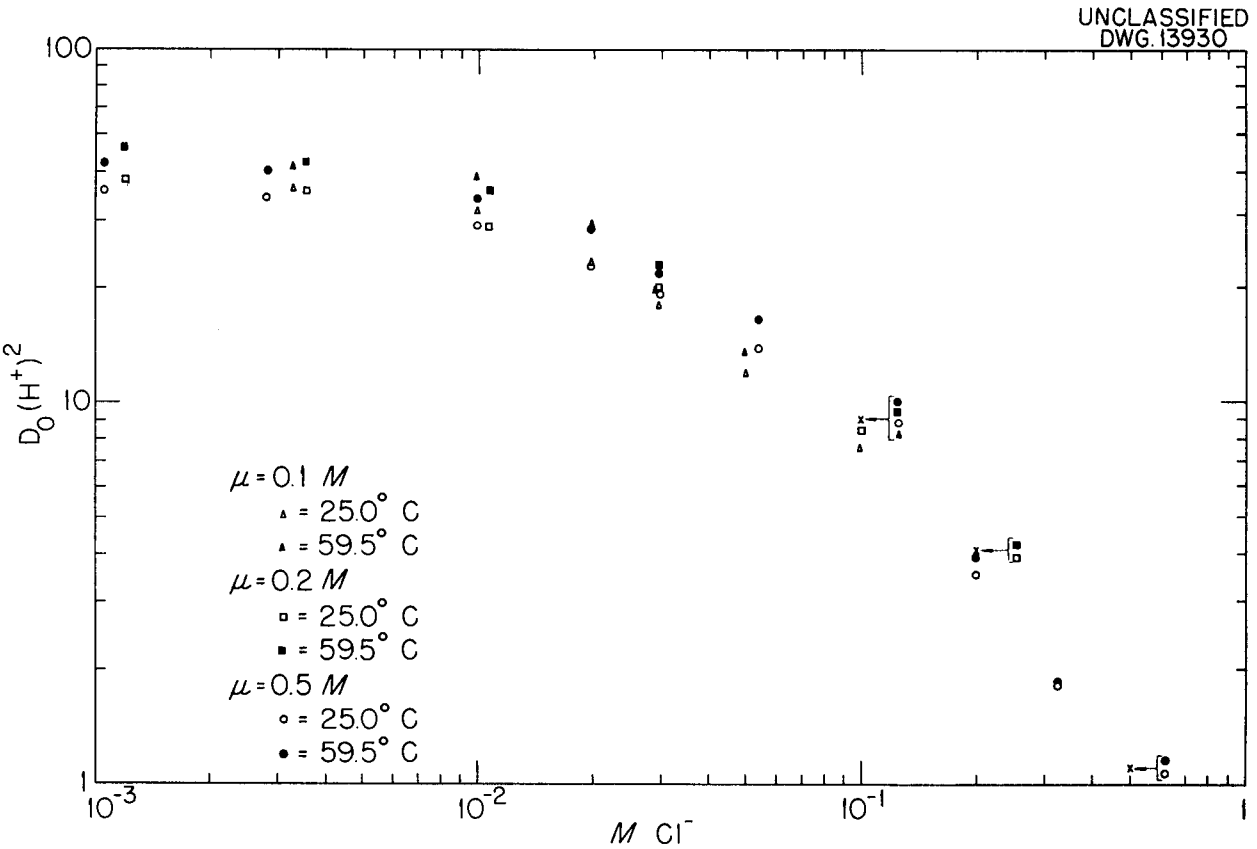

Fig. 5. Exchange of Hydrogen and Cadmium(II) Ions Between Dowex-50 Resin and Aqueous Solutions of HCl and $HClO_4$.

Separation of Zinc and Cadmium by Cation Exchange. Because of the large differences in the stability of the chloride complexes, the adsorbabilities of zinc and cadmium in chloride solutions differ markedly, as shown in Table 7. On the basis of the results shown in Table 7 it is apparent that the separation of zinc and cadmium should be very simple by cation exchange, particularly in the range 0.5 to 1 *M* Cl^-. In all cases cadmium will appear first in the eluate. Although above this concentration the ratio D_{Zn}/D_{Cd} is expected to increase further, the rapid drop-off of the value of D_{Zn} appears to preclude the use of considerably more concentrated chloride solutions for separations.

TABLE 7

Adsorbability of Zinc and Cadmium from Hydrochloric Acid Solutions by Dowex-50 at 25°C

M HCl	D_{Cd}	D_{Zn}	D_{Zn}/D_{Cd}
0.05	5.0×10^3	1.3×10^4	2.6
0.10	8.0×10^2	2.5×10^3	3.1
0.20	1.0×10^2	5.1×10^2	5.1
0.40	10	100	10
0.70	1.4	28	20
1.00	~0.4	10	25

Activity Coefficients of Zinc and Cadmium Perchlorates in Perchlorate Solutions. From the changes of the adsorption constant K^m (II) with ionic

TABLE 8

Activity Coefficients of $Zn(ClO_4)_2$ and $Cd(ClO_4)_2$ in $HClO_4$ Solutions

m_{HClO_4}	G_{Zn} (II) $= \gamma_{Zn}/\gamma_H^2$	G_{Cd} (II)	$\gamma_{\pm HClO_4}$	$\gamma_{\pm Zn(ClO_4)_2}$	$\gamma_{\pm Cd(ClO_4)_2}$
0.05	(1.000)	(1.000)	0.835	0.79	0.79
0.10	1.00	1.00	0.803	0.75	0.75
0.20	0.90	0.98	0.778	0.69	0.71
0.30	0.86	0.94	0.760	0.66	0.68
0.40	0.84	0.95	0.755	0.65	0.68
0.50	0.83	0.96	0.769	0.66	0.70
0.75	0.80	0.98	0.795	0.68	0.73
1.00	0.80	1.00	0.823	0.72	0.77
1.50	0.83	1.03	0.923	0.85	0.91
2.00	0.89	1.10	1.055	1.03	1.11
3.00	1.00	1.53	1.448	(1.64)	(1.89)
5.00	1.53	3.67	3.11	(5.23)	(7.00)

strength, estimates of the pertinent activity-coefficient ratio

$$\frac{\gamma_{Zn}{}^r\ \gamma_H{}^2}{(\gamma_H{}^r)^2\ \gamma_{Zn}}$$

can be made. Assuming that all variations of K^m (II) with μ result from changes in the activity-coefficient ratio of the species in solution $(\gamma_H{}^2)/\gamma_{Zn}$, the latter can be evaluated from the observed values of K^m (II) at μ and its (constant) value at low μ. It was assumed that K^m (II) is constant below $\mu = 0.05$. The assumption that $\gamma_{Zn}{}^r/(\gamma_H{}^r)^2$ is approximately constant was made because all experiments were carried out under conditions in which the concentration of zinc in the resin was very small compared with the capacity of the resin (<0.1% of resin sites occupied by zinc). Appreciable amounts of perchloric acid may, however, penetrate into the resin at high μ, so it is doubtful that the assumption $\gamma_{Zn}{}^r/(\gamma_H{}^r)^2$ is a constant is strictly valid above about 2 *M* $HClO_4$.

From the values $\gamma_H{}^2/\gamma_{Zn}$ the activity coefficient of $\gamma_{\pm Zn(ClO_4)_2}$ was evaluated by noting that

$$\frac{\gamma_H{}^2}{\gamma_{Zn}} = \frac{\gamma^4{}_{\pm HClO_4}}{\gamma^3{}_{\pm Zn(ClO_4)_2}}$$

and using the values of $\gamma_{\pm HClO_4}$ given by Harned and Owen.[12] The results of the calculations for both zinc and cadmium are shown in Table 8.

[12] H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 2d Ed., p. 601, Reinhold, New York, 1950.

ADSORPTION OF HYDROCHLORIC ACID BY THE ANION-EXCHANGE RESIN DOWEX-1

G. E. Moore K. A. Kraus

In earlier studies of the adsorption of metal complexes on the anion-exchange resin Dowex-1 it was found that for many elements adsorption was significant only at hydrochloric acid concentrations considerably above 1 *M*. In order to calculate from these data the stability constants of the complexes, estimates of the possible changes of the activity coefficients of the ions in the resin phase are necessary. Some simplification in these estimations can be achieved by either operating with one ion at tracer concentrations in the resin or by maintaining its concentration constant in the resin phase. Under these conditions it might be assumed that the activity-coefficient ratio in the resin phase is constant provided there are no significant changes in the resin phase resulting from its immersion in media of drastically changing ionic strength. Two such changes in the resin phase might be expected: (1) the water concentration of the resin might change, and (2) the main electrolyte of the aqueous phase might also appear at significant concentrations in the resin phase.

Experiments have been carried out that give information concerning both points. Samples of resin were equilibrated in various concentrations of hydrochloric acid in the range 0.002 to 12.1 *M*. Before use, the resin was thoroughly washed with distilled water and dilute and concentrated hydrochloric acid and then extensively washed with ethyl alcohol. The acid and water washes were then repeated. The samples were centrifuged in a sintered glass funnel in a clinical centrifuge until constant weight was obtained.[13] After noting the volume and weight of the samples, they were washed repeatedly with water, and the resulting wash solutions were titrated with sodium hydroxide until no titer was obtained upon further washing. It was noted that the volume of the centrifuged resin bed after equilibration with 0.002 to 12.1 *M* HCl solutions was constant to about ±2.5%, which suggested that the water content of the resin is practically independent of the ionic strength of the surrounding medium. The results of the titrations are shown in Fig. 6. In order to estimate the amount of hydrochloric acid solution held interstitially, similar experiments were carried out with samples of sand and with a sample of spherical glass beads of the same mesh size (-200 + 230). These results are also included in Fig. 6. With the spherical glass beads it was found that the number of millimoles adsorbed per cubic centimeter of beads varied linearly with the molarity of hydrochloric acid and resulted in a straight line plot of unit slope of log *A* vs. log *M*, where *A* is the number of millimoles adsorbed per cubic centimeter and *M* is the molarity of the hydrochloric acid. Such a linear plot was to be expected if a constant volume of hydrochloric acid adhered to the particles. The (interstitial) volume was estimated to be 0.050 cc per cubic centimeter of beads.

Similar results were obtained with the sea sand, which was rather dark in color and probably contained a considerable amount of iron oxides. The particles were largely nonspherical. A linear plot of unit slope of log *A* vs. log *M* was obtained only above 0.2 *M* HCl. At lower concentrations the slope was less than unity, which indicated that in addition to the interstitially held hydrochloric acid some hydrochloric acid was adsorbed, probably on the surface of the sand or the iron oxide particles.

(13) K. W. Pepper, "Sulphonated Cross-Linked Polystyrene: A Monofunctional Cation-Exchange Resin," *J. Applied Chem.* (London) **1**, 124 (1951).

The volume of interstitially held hydrochloric acid was calculated from the portion of the curve above 0.2 *M* and was found to be 0.065 cc per cubic centimeter of sand. This value for the volume is in fair agreement with the value found for spherical glass beads.

As shown in Fig. 6, the linear portion of unit slope in the case of Dowex-1 is obtained only at hydrochloric acid concentrations above 4 *M*. The curve has an S shape and does not approach unit slope even at very low concentrations of hydrochloric acid. The "adsorbed" hydrochloric acid was evaluated by assuming that the amount of water held interstitially by the resin is the same as for the spherical glass beads; the results are shown in Fig. 7. The curve of Fig. 7 is

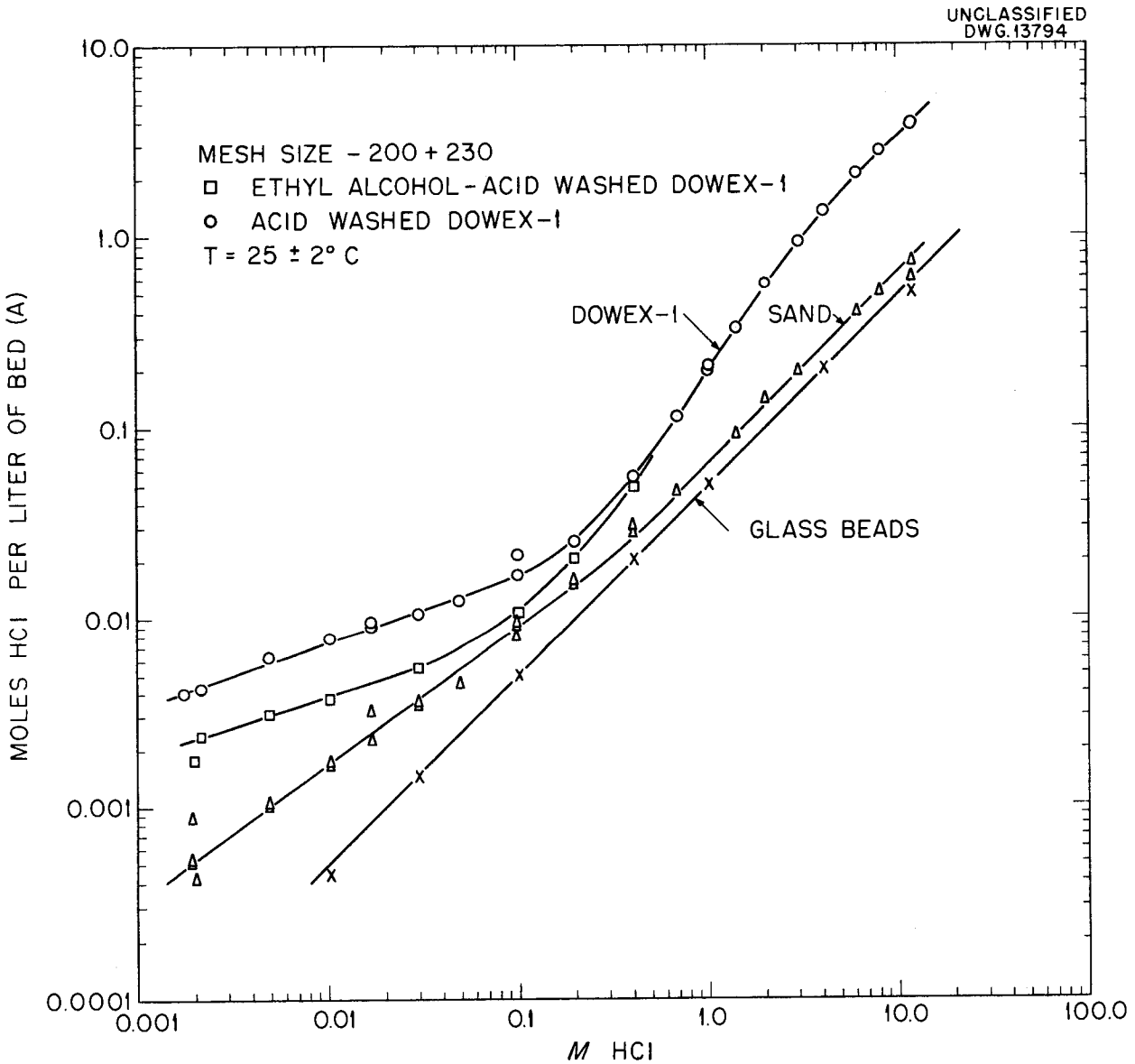

Fig. 6. Retention of HCl by Dowex-1, Sand, and Glass Beads.

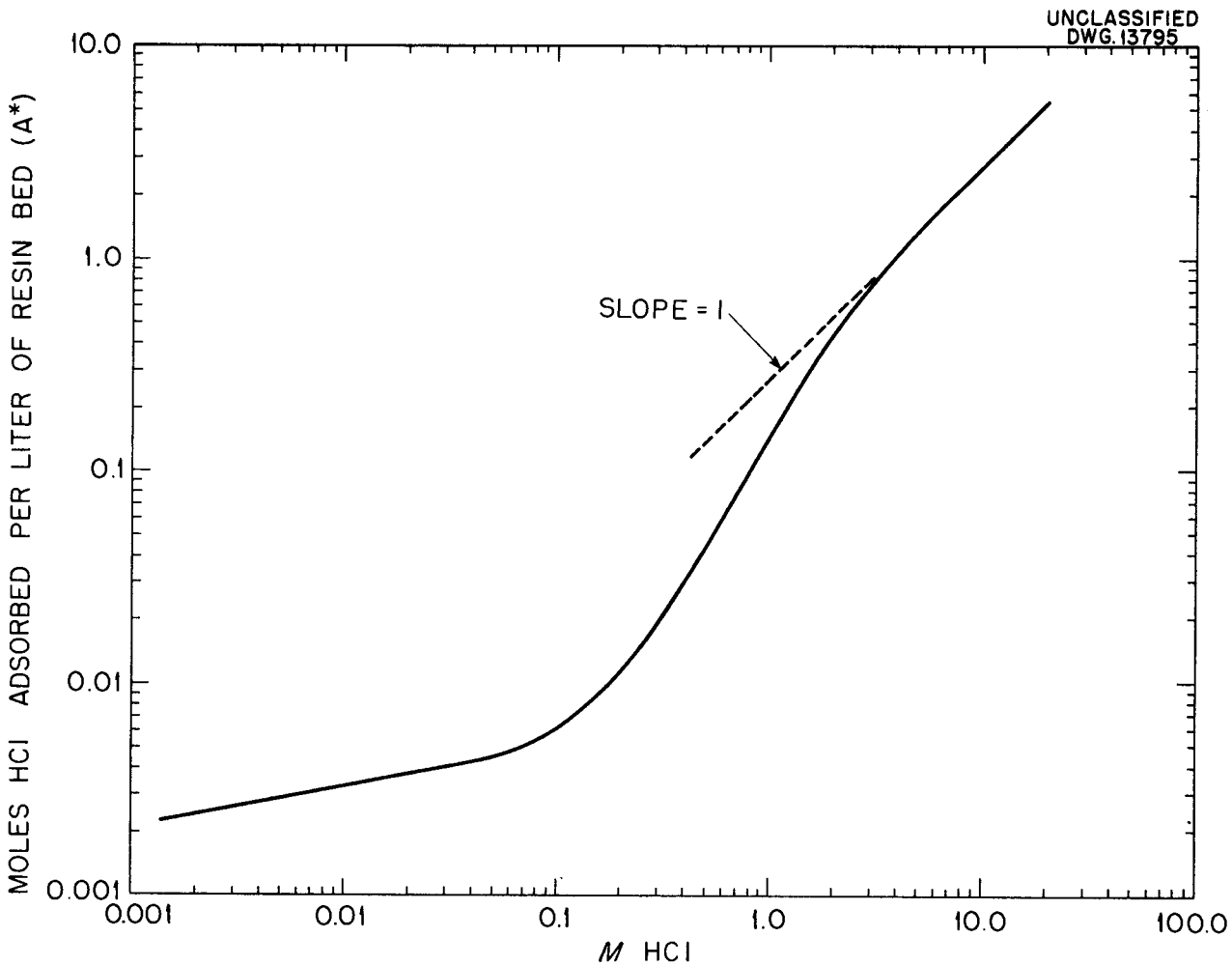

Fig. 7. Adsorption of HCl by Dowex-1 (corrected for interstitial HCl).

apparently composed of three branches, a region of relatively slowly rising *A* below 0.1 *M* HCl, a region of rapidly rising *A* between 0.1 and about 3 *M* HCl, and a region of approximately unit slope above 3 *M* HCl. The volume of hydrochloric acid corresponding to the region of linear slope was 0.275 cc per cubic centimeter of resin bed. The intermediate branch is probably closely related to the Donnan effect, on the basis of which increasing electrolyte content of the resin with increasing molarity on the outside could be predicted. The slowly rising region of *A* below 0.1 *M* HCl probably results from a reaction of the resin or an impurity within the resin with hydrochloric acid. Adsorbability in this region is quite sensitive to the purification treatment to which the resin has been subjected, since resin not washed with alcohol, but only with water and acid, shows in this region values of *A* approximately twice those found with this particular batch of resin, as also shown in Fig. 6.

PURIFICATION OF URANYL SULFATE AND URANYL FLUORIDE SOLUTIONS BY ELECTROMIGRATION

K. A. Kraus F. Nelson

Uranium(VI) forms strong complexes with sulfate and fluoride ions.

Estimates of the stability constants of these complexes indicate that in uranyl sulfate solutions of moderate and high concentrations more than 50% of the uranium is present as the species UO_2SO_4 and that the concentrations of UO_2^{++} and $UO_2(SO_4)_2^{=}$ are approximately equal. Since the mobility of UO_2^{++} and $UO_2(SO_4)_2^{=}$ are probably approximately equal, uranium in uranyl sulfate solutions might be expected to migrate only slightly in an electric field. On the basis of these considerations it appeared profitable to investigate the possibility of purifying uranium(VI) solutions by an electromigration method. Uranyl fluoride should be even more ideally suited for such a method, since it is practically undissociated and known to be a poor conductor (see also previous section on "Freezing Points and Activity Coefficients of Uranyl Fluoride Solutions"). Uranium(VI) appears to occupy a unique position from the point of view of complexing, since it combines a large tendency for complexing with a low initial charge so that only very few ligands are necessary to make neutral or negatively charged species. Hence, an electromigration method should permit separation of uranium from a large number of metal ions.

The main problem in perfecting such an electromigration method appears to be the proper selection of membranes to separate the compartments and the selection of the electrolyte for the cathode compartment of a two-compartment cell. The electrolyte should have a sufficiently high concentration of complexing ions to maintain the uranium at an average neutral or negative charge. If the uranium is placed in the central compartment of a three-compartment cell, proper choice of the electrolytes of the anode and cathode compartments should produce an average positive or negative charge, respectively, for the uranium.

Some preliminary experiments using Cs^{137} and La^{140} tracers as representative fission products have been completed, and it was shown that 75 to 90% of the cesium or lanthanum could be separated from the bulk of the uranium in the UO_2SO_4 solutions (30 g of UO_2SO_4 per liter of solution) in a single stage. Most of the experiments were carried out in cells that were not ideally suited for the purpose; for example, the path through which the ions had to migrate was very long (up to 10 cm), and hence excessively long electrolysis times were required. Since migration experiments can be arranged in a multistage process and they can also be easily used in a continuous process, it is felt that this technique may prove of considerable value in the purification of uranium solutions.

EXPERIMENTAL

The preliminary electromigration studies were carried out with two types of cells.

Two-compartment Cell. The UO_2SO_4 (or UO_2F_2) solution was the anolyte in a U-shaped cell in which the catholyte H_2SO_4 (or NaF) was separated from the anolyte by a sintered glass disk. The anode compartment was approximately 10 cm long and had a volume of about 5 milliliters. Currents of the order of 1 to 5 ma were passed through the cell for several hours. The relative migration of uranium and Cs^{137} was determined from samples taken at various times during the electrolysis. No migration experiments with La^{140} were carried out in this cell.

Three-compartment Cell. A lucite cell with three compartments was constructed in which the compartments were separated by 8-mil cellophane membranes. The cathode and anode compartments had volumes of 3 to 4 ml and were filled with sulfuric acid solutions. The central compartment, which had a thickness of ¼ in. and a volume of about 1 ml, contained the UO_2SO_4 solutions. Electrolyses were

carried out for 30 min at about 3 to 5 v and current densities of 25 to 50 ma/cm^2.

Relative migration of uranium and Cs^{137} (or La^{140}) to the cathode and anode compartments was determined by radiochemical analyses for La^{140} and Cs^{137} and polarographic analysis for uranium.

Results. The results of the experiments are summarized in Tables 9 and 10. In the experiments with the two-compartment cell, some uranium appeared in the cathode compartment only at low sulfuric acid concentrations (0.1 *M* or less), indicating that under these conditions uranium may carry a slight excess positive charge. In all cases, however, the purification from Cs^{140} appeared to be considerable. Similar results were obtained with uranyl fluoride, as shown in Table 10. It should be pointed out, however, that in this cell the anode compartment was very long and relatively long times were required for the removal of the tracer. In the three-compartment cell in which the distance of migration of Cs^{137} and La^{140} was considerably smaller, results comparable with those in the two-compartment cell could be obtained in 30 minutes. Again in 0.1 *M* H_2SO_4 some uranium appeared in the cathode compartment and a smaller

TABLE 9

Purification of Uranium(VI) Solutions by Electromigration in a Two-compartment Cell

ANOLYTE	CATHOLYTE	TIME (hr)	CATHODE		ANODE	
			Cs^{137} (%)	U (%)	Cs^{137} (%)	U (%)
UO_2SO_4 + Cs^{137} (30 g U/l)	0.1 *M* H_2SO_4	19	85	3.5	15	96.5
	2.0 *M* H_2SO_4	9	84	0	16	~100
	4.0 *M* H_2SO_4	4.7	48	0	52	~100
	17.8 *M* H_2SO_4	28.5	20	0	80	~100
UO_2F_2 + Cs^{137} (91 g U/l)	0.1 *M* NaF	67	90	5	10	95

TABLE 10

Purification of Uranium(VI) Solutions by Electromigration in a Three-compartment Cell

30 min electrolysis; anolyte and catholyte 0.1 *M* H_2SO_4

CENTRAL COMPARTMENT	CENTRAL COMPARTMENT		CATHODE		ANODE	
	Cs^{137} (%)	U (%)	Cs^{137} (%)	U (%)	Cs^{137} (%)	U (%)
UO_2SO_4 + Cs^{137} (30 g U/l)	6	81	85	13	9	6
	La^{140} (%)	U (%)	La^{140} (%)	U (%)	La^{140} (%)	U (%)
UO_2SO_4 + La^{140} (30 g U/l)	24	76	75	20	1	4

amount in the anode compartment. It is believed that the amount of uranium in the anode compartment is indicative of the extent of diffusion during the electromigration. The use of higher voltages (faster electromigration) should decrease the net amount of diffusion.

CHEMISTRY OF TECHNETIUM

Thermodynamic Properties of Technetium Compounds (J. W. Cobble, W. T. Smith, Jr.,[14] G. E. Boyd). Vapor pressures of solid and liquid technetium oxide, pertechnic acid ($HTcO_4$), and of a saturated solution of pertechnic acid have been measured as a part of a general program on the determination of the thermodynamic properties of technetium compounds. Conclusions regarding the stability of pertechnic acid and its solutions were reached by combining the vapor pressure data with the heat of solution for technetium oxide, which was determined calorimetrically. Comparisons between the melting and boiling points and between the enthalpies and entropies of fusion, vaporization, and sublimation for the analogous compounds of technetium and rhenium revealed the anticipated similarities as well as some unexpected differences.

The vapor pressure measurements were made using an all-glass sickle gage (Bourdon gage) as a null-point indicator in the conventional manner. A sample of about 100 mg of technetium oxide, the formula for which was demonstrated to be Tc_2O_7,[15] was twice distilled into the evacuated gage. The gage (contained in a pressure jacket) was immersed in an oil thermostat, the temperature of which could be varied, and the absolute pressure necessary to compensate for the technetium heptoxide pressure was read on an external mercury manometer or McLeod gage. Direct observations showed the melting point of the heptoxide to be 120°C; however, the vapor pressure at this temperature (i.e., triple point) was only 0.83 mm, in contrast to rhenium heptoxide, which shows a pressure of 173 mm at its melting point (298 ± 1°C). The technetium heptoxide vapor pressure data (Fig. 8) could be fitted to a two-term Clausius-Clapeyron equation:

$$\log p \text{ (mm)} = -7205/T + 18.28 \text{ (solid-vapor)} , \quad (1)$$

$$\log p \text{ (mm)} = -3571/T + 8.999 \text{ (liquid-vapor)} . \quad (2)$$

Thermodynamic quantities derivable from Eqs. 1 and 2 are summarized in Table 11, which also affords a comparison with corresponding values for rhenium heptoxide.

It is evident that the enthalpies for fusion, vaporization, and sublimation for technetium and rhenium heptoxides are very similar. Also, both show abnormally large entropies of fusion and sublimation. The values for technetium heptoxide are larger than those for any other inorganic compound found and appear to be responsible for its unexpectedly low melting point as well as for the wide temperature interval between its melting and boiling points. If in the molten state technetium heptoxide dissociated to give ion pairs such as $TcO_3^+TcO_4^-$, large entropies might result. This hypothesis also accounts for the rather high Trouton constant ($\Delta H_v/T$) observed.

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[14] Professor, Department of Chemistry, University of Tennessee; Consultant, ORNL.

[15] G. E. Boyd, J. W. Cobble, C. M. Nelson, and W. T. Smith, Jr., "Preparation of Technetium Heptoxide from Technetium Metal; Absorption Spectrum of Pertechnetate Ion," *op. cit.*, ORNL-1116, p. 32.

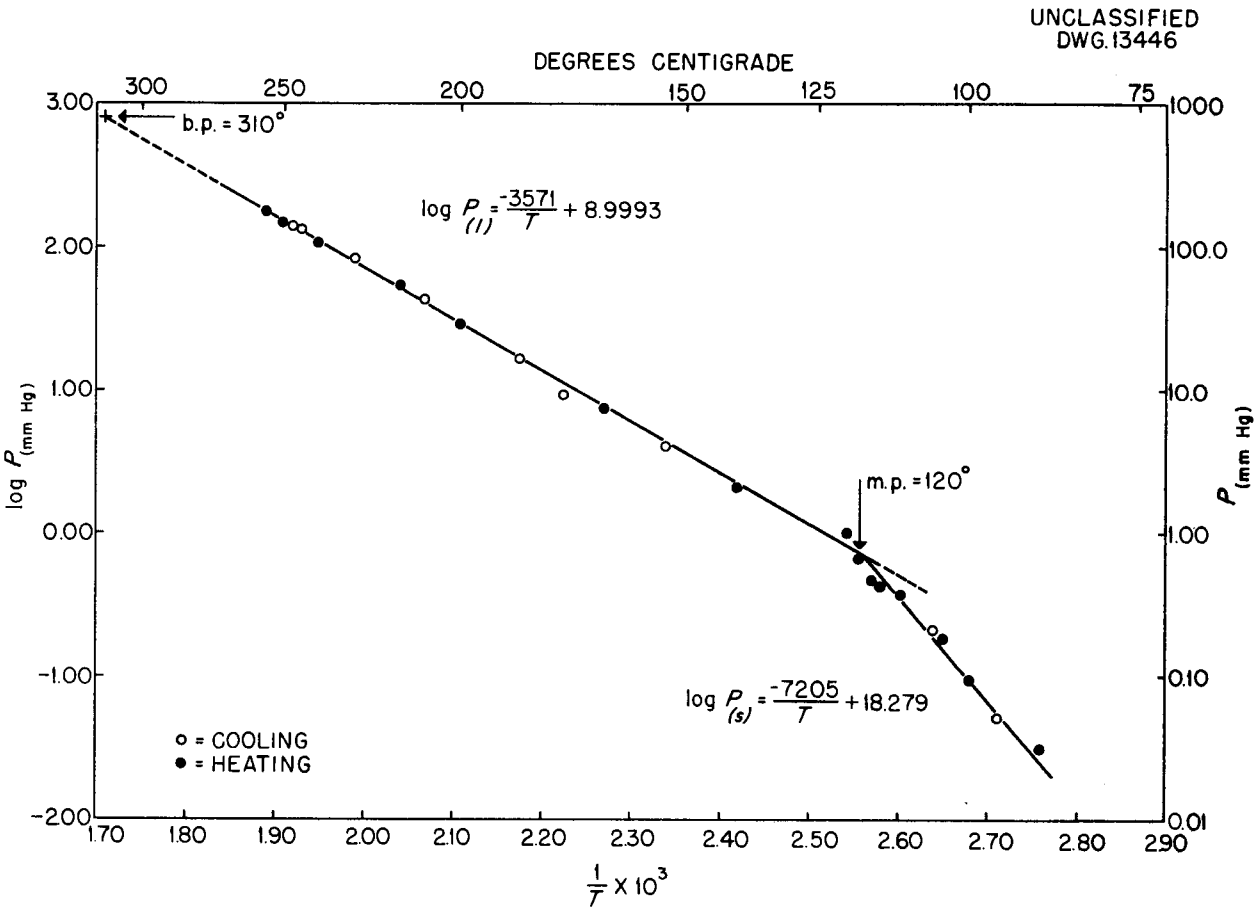

Fig. 8. Vapor Pressure of Technetium Heptoxide.

TABLE 11

Thermodynamic Properties of the Heptoxides of Technetium and Rhenium

	Tc_2O_7	Re_2O_7*
ΔH_{subl}	+33.0 ± 2.6 kcal/mole	+33.5 ± 0.3 kcal/mole
ΔH_v	+16.3 ± 0.2	+17.7 ± 0.2
ΔH_f	+16.7 ± 0.5	+15.8 ± 0.1
Melting point	120 ± 1°C	298 ± 1°C
ΔS_{subl}	84 ± 6 e.u.	58.5 ± 0.5 e.u.
ΔS_v	280 ± 0.3	28.0 ± 0.3
ΔS_f	42 ± 2	27.5 ± 0.3

*Values for rhenium from W. T. Smith, Jr. and L. Line, January 1952 (to be published).

Slow, isothermal evaporation of an aqueous solution of technetium heptoxide leads to the formation of a deep-red, crystalline solid whose composition has been shown[15] to correspond to anhydrous pertechnic acid ($HTcO_4$). This solid shows a vapor pressure by reason of its dissociation into heptoxide and water vapor:

$$2HTcO_4\ (s) = Tc_2O_7\ (s) + H_2O\ (v)\ . \qquad (3)$$

Measurements of the temperature variation of the vapor pressure may be described by

$$\log p\ (\text{mm}) = -2395/T + 8.2074\ , \qquad (4)$$

from which the following thermodynamic quantities may be computed:

$$\Delta H_{298} = 10{,}950 \pm 50\ \text{cal/mole}\ Tc_2O_7\ ,$$

$$\Delta F^\circ_{298} = 3686 \pm 18\ \text{cal/mole}\ Tc_2O_7\ .$$

Values for the enthalpy and standard free-energy changes for

$$2HTcO_4\ (s) = Tc_2O_7\ (s) + H_2O\ (l) \qquad (5)$$

may be found by adding the known values for the vaporization of water to Eq. 3.

$$\Delta H = 430 \pm 50\ \text{cal/mole}\ Tc_2O_7\ ,$$

$$\Delta F^\circ = 1632 \pm 18\ \text{cal/mole}\ Tc_2O_7\ ,$$

$$\Delta S = -4.03 \pm 0.22\ \text{e.u.}$$

The smallness of these ΔH and ΔF° values strongly suggests that the compound ($HTcO_4$) formed by water with Tc_2O_7 is a hydrate rather than a true acid. An analogous statement may be made for $Re_2O_7 + H_2O$.

Measurements of the temperature dependence of the vapor pressures of saturated pertechnic acid solutions give

$$\log p\ (\text{mm}) = -2375/T + 8.2006\ , \qquad (6)$$

from which enthalpies, standard free energies, and entropies for the following equilibrium may be calculated:

$$HTcO_4\ (sat) = HTcO_4\ (s) + \text{aq.}\ , \qquad (7)$$

$$\Delta H = 340 \pm 100\ \text{cal/mole}\ HTcO_4\ ,$$

$$\Delta F^\circ = 1551 \pm 18\ \text{cal/mole}\ HTcO_4\ ,$$

$$\Delta S = 4.06 \pm 0.40\ \text{e.u.}$$

The heat of solution of Tc_2O_7 (s) in water was determined by using a microcalorimeter.[16]

$$Tc_2O_7\ (s) + \text{aq.} = 2HTcO_4\ (aq)\ , \qquad (8)$$

$$\Delta H_{298} = -11{,}590 \pm 80\ \text{cal/mole}\ Tc_2O_7.$$

Combining Eqs. 5 and 8 gives the heat of solution of anhydrous pertechnic acid.

$$HTcO_4\ (s) + \text{aq.} = HTcO_4\ (aq)\ , \qquad (9)$$

$$\Delta H_{298} = -5580 \pm 32\ \text{cal/mole}\ HTcO_4\ .$$

This value is consistent with the conclusion, drawn from the observed electrometric pH titration curve, that in aqueous solution pertechnic acid is a strong acid. Perrhenic acid is known to be a strong acid.

Measurements on the heat of combustion of metallic technetium and rhenium and of ReO_3 are now being conducted. Further efforts to prepare TcO_3 and to make measurements of the electric conductivity of fused Tc_2O_7 and Re_2O_7 are planned.

Magnetic Studies on Technetium Compounds (C. M. Nelson, W. T. Smith, Jr.,[14] G. E. Boyd). A number of technetium and rhenium compounds have

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[16] J. W. Cobble, G. E. Boyd, and W. T. Smith, Jr., "Chemistry of Technetium," *op. cit.*, ORNL-1153, p. 9.

been prepared and measured over a temperature range of 78 to 406°K in the magnetic susceptibility apparatus. This apparatus, previously described, performed satisfactorily except that the sensitivity for diamagnetic compounds was not so good as desired. Greater sensitivity would be necessary for accurate measurements on diamagnetic and weakly paramagnetic substances. However, since the present work was intended as a survey of the magnetic properties of technetium and rhenium compounds, the apparatus was sufficient. Various concentrations of aqueous nickel chloride solutions, solid sodium chloride, and pure water were used in the calibration. Samples ranging from 50 to 300 mg were contained in quartz containers. The magnetic force acting on a sample is given by $f = m \chi H \, dH/dz$, where m = mass of sample in grams, χ = mass susceptibility, H = magnetic field strength in gauss, and dH/dz = magnetic field gradient in the z direction. For a given magnetic field, the quantity $H \, dH/dz$ may be written as K. Since the force measurements are made as a function of the current flowing through the electromagnet, values of K are listed (Table 12) corresponding to the ampere readings. The values given are the average of ten different samples, including duplicates that agreed usually within 2 to 3%. When K is plotted with H^2 as the abscissa, the points are found to fall almost on a straight line.

Atomic susceptibility values, χ_A, for rhenium, technetium, and manganese are given in Table 13. It is observed that χ_A for technetium lies between those for rhenium and manganese. Various compounds of rhenium(VII) and technetium(VII) were prepared and their χ_M measured and calculated (Table 14).

TABLE 12

Calibration of Magnetic Susceptibility Apparatus

CURRENT (amp)	$K \times 10^{-7}$
1	0.14
2	0.54
3	1.11
4	1.78
5	2.33
6	2.75
8	3.43
10	4.02

TABLE 13

Atomic Susceptibilities of Rhenium, Technetium, and Manganese

	$\chi_A \times 10^6$		
	AT 406°K	AT 298°K	AT 78°K
Rhenium[a]	69 ± 1	68	65
Rhenium[b]	74 ± 2	76	69
Technetium	250 ± 10	270	290
Manganese[c]		527	

[a] Rhenium metal prepared by reduction of $KReO_4$.

[b] Rhenium metal prepared by reduction of NH_4ReO_4.

[c] P. W. Selwood, *Magnetochemistry*, Interscience, New York, 1943.

TABLE 14

Molar Susceptibilities of Compounds of Rhenium and Technetium

	$\chi_M \times 10^6$		
	AT 406°K	AT 298°K	AT 78°K
$KReO_4$	−30 ± 1	−26	−18
NH_4ReO_4	−35 ± 1	−32	−29
NH_4TcO_4	decomposition	+9 ± 2	+14
Re_2O_7	−16 ± 1	−15	−10
Tc_2O_7	−50 ± 2 (350°K)	−40	−22

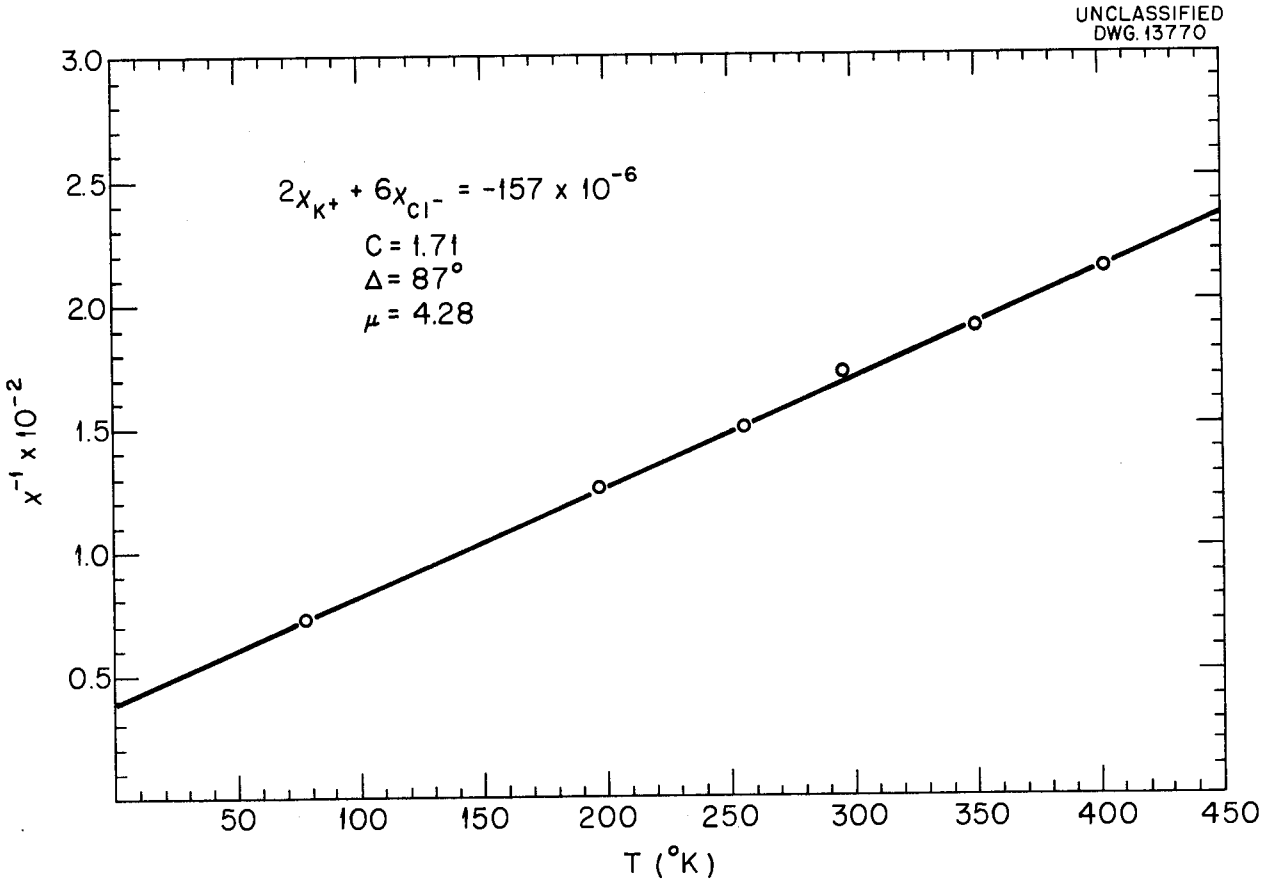


Fig. 9. Temperature Variation of χ for K_2TcCl_6.

In Figs. 9, 10, and 11 are plots of $1/\chi$ for technetium(IV) and rhenium(IV) in complex compounds. Values[17] for the diamagnetic ions K^+, Tl^+, Cl^-, and CNS^- were used to calculate χ for the paramagnetic ion. Using the Curie-Weiss equation, $\chi = C/(T + \Delta)$, values of Δ and C were calculated from these plots. The magnetic moments were calculated from the equation

$$\mu = 2.83 \sqrt{\chi(T + \Delta)} \ .$$

For three unpaired electrons,

$$\mu = \sqrt{n(n + 2)} = 3.87 \ ,$$

if the contribution to the paramagnetism is considered as coming only from the spin of the electrons and the orbital contribution is completely neglected. A comparison of the experimental values of μ with the theoretical moment shows that the agreement is fairly good. The rhenium compounds have lower moments than technetium compounds, whereas compounds of manganese have values of μ ranging around 4.[18]

Other compounds of rhenium and technetium are being investigated, including TcO_2, ReO_2, Ag_2TcCl_6, Ag_2ReCl_6, $K_2Re(SCN)_6$, $Ag_2Re(SCN)_6$, and

(17) V. C. G. Trew, "Ionic Diamagnetic Susceptibility and Diamagnetic Correcting Constants, *Trans. Faraday Soc.* **37**, 476 (1941).

(18) P. W. Selwood, *Magnetochemistry*, Interscience, New York, 1943.

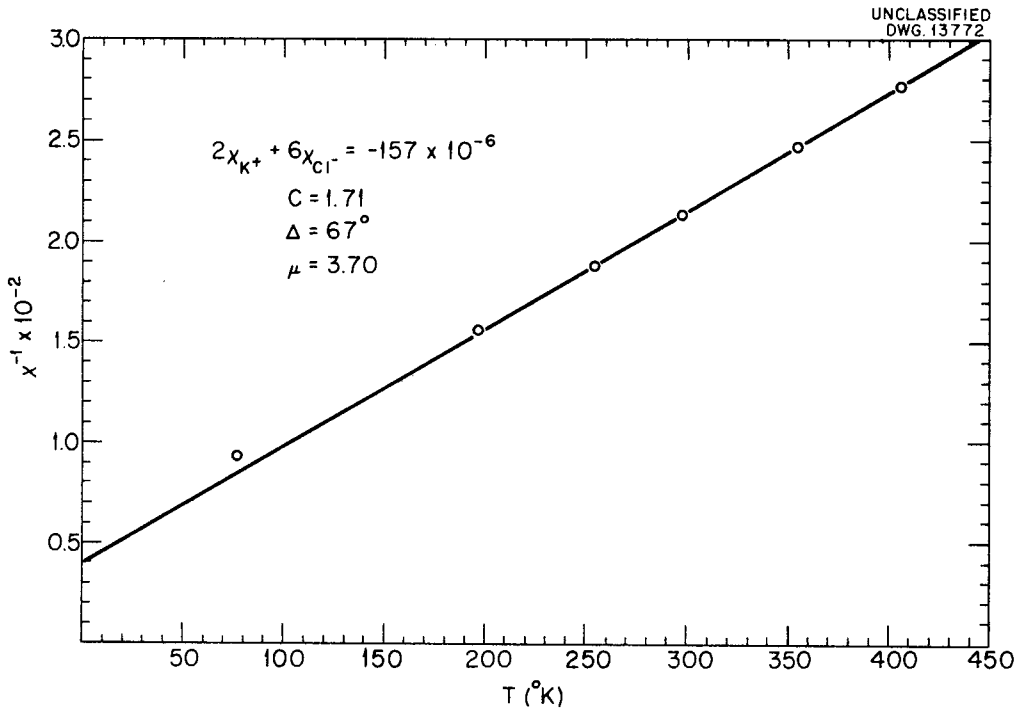


Fig. 10. Temperature Variation of χ for K_2ReCl_6.

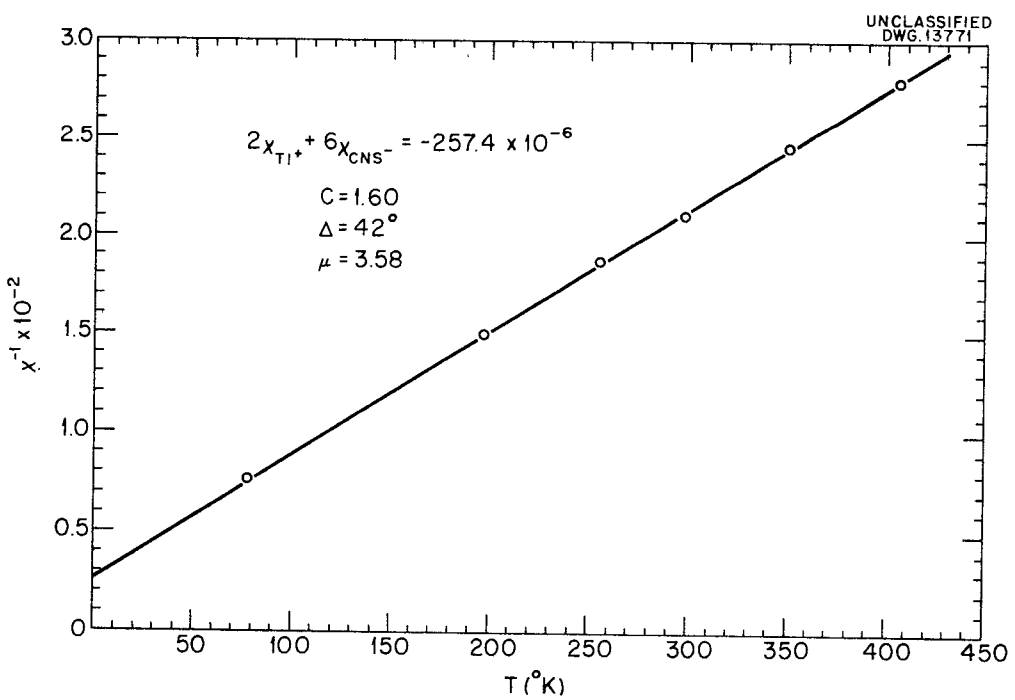


Fig. 11. Temperature Variation of χ for $Tl_2Re(CNS)_6$.

ReO_3. The preparation of $ReCl_3$, $TcCl_3$, and TcO_3 will be attempted.

Br_2-BrO_3 EXCHANGE IN ACID MEDIA USING Br^{82} AS TRACER

O. E. Myers

It was previously reported that the isotopic exchange work was complicated by the slowness of the formation of hypobromous acid in the system studied[19] and that an assumed mechanism consistent with all known facts had been developed:[20]

$$HBr + HBrO_3 = HBrO_2 + HBrO \quad (1)$$

$$HBr + HBrO_2 = 2HBrO \quad (2)$$

$$HBr + HBrO = Br_2 + H_2O \quad (3)$$

The corresponding set of simultaneous nonlinear differential equations is:

$$\dot{x} = A - B ,$$

$$\dot{y} = A + 2B - C ,$$

$$-\dot{z} = A + B + C ,$$

$$\dot{w} = C$$

where

$$A = az - k_1xy \qquad a = k_1' (H^+)^2 (BrO_3^-) \Gamma_1$$

$$B = bxz - k_2y^2 \qquad b = k_2' (H^+) \Gamma_2$$

$$C = cyz - k_3w \qquad c = k_3' (H^+) \Gamma_3$$

$$x = (HBrO_2) \qquad x_0 = x(0) = 0$$

$$y = (HBrO) \qquad y_0 = 0$$

$$z = (Br^-) \qquad z_0 = 0$$

$$w = (Br_2) \qquad w_0 = 0$$

and

k_i = reverse rate constant for ith reaction

k_i' = forward rate constant for ith reaction

Γ_i = activity-coefficient factor for ith reaction

for

$i = 1, 2, 3.$

The constant a may be estimated from other work,[21] and k_2 is fairly well established.[22] Values of k_3 and k_3' are unknown; however, it is known that $k_3/k_3' = (5.8 \pm 0.6) \times 10^{-9}$,[23] and $k_3' > 10^5$ because of the rapidity of Br_2-HBrO exchange. It is believed that for large k_3' only the ratio k_3/k_3' is important for the analysis. There is now no good evidence for the existence of $HBrO_2$, and therefore no values of k_1 and k_2' have been determined. In the present mathematical treatment, the final equilibrium concentration of $HBrO_2$, x_∞, becomes a parameter, and for any chosen value k_1 and k_2' are fixed.

The above mathematical formulation has been set up for analysis on the IBM computer at K-25, and J. H. Fishel of ORNL is currently working on the first solution. C. L. Perry of ORNL has supplied J. D. Whitehurst of ARO, Inc. with a thorough set of initial conditions for analysis on the MADDIDA digital analog computer. The results of these computations are expected to

(19) O. E. Myers and R. W. Stoughton, "Br_2-BrO_3 Exchange Using Radioactive Br^{82}," *op. cit.*, ORNL-1116, p. 24.

(20) O. E. Myers, "Br_2-BrO_3^- Exchange Using Bromine-82 as Tracer," *op. cit.*, ORNL-1153, p. 12.

(21) M. Sclar and L. C. Riesch, "The Kinetic Salt Effect in the Fourth Order Reaction $BrO_3^- + Br^- + 2H^+ \rightarrow$," *J. Am. Chem. Soc.* **58**, 667 (1936).

(22) R. H. Betts and A. N. MacKenzie, "Isotopic Exchange Reactions in the System Bromine-Bromate-Hypobromous Acid," *Can. J. Chem.* **29**, 655-666 (1951); also from work in this Laboratory.

(23) H. A. Liebhafsky, "The Equilibrium Constant of the Bromine Hydrolysis and Its Variation with Temperature," *J. Am. Chem. Soc.* **56**, 1500 (1934).

permit an approximation to k_1, k_2', b, and x_∞.

Growth and decay curves for HBrO in $HBrO_3$-Br_2-$HClO_4$ systems are being obtained spectrophotometrically[24] in order to ascertain the rate constant for disproportionation of HBrO and to supplement the mathematical analysis. It turns out that the previous approximate mathematical treatment[24] is subject to large errors. The approximations are not required, and a more accurate least-square method, suggested by A. S. Householder of ORNL, is being used to interpret the data.

The following conclusions may be drawn: (1) the equilibrium concentration of HBrO in a dark system at 25°C [initially 0.0825 f in $HBrO_3$, 1.66 f in H^+ (as $HClO_4$ and $HBrO_3$) and 0.004167 f in HBr] is less than 2.0×10^{-3} f, rather than 2.4×10^{-3} f;[24] (2) the primary product of the reaction with low-intensity light (photodecomposition of $HBrO_3$) is not Br^-, Br_2, or Br; (3) during 893 hr, 0.95% of the $HBrO_3$ decomposed because of imperfect light shielding.

[24] For checking and extending the work of Betts and MacKenzie.[22]

NUCLEAR CHEMISTRY

DECAY OF GALLIUM^{67}

B. H. Ketelle H. Zeldes
A. R. Brosi

A tentative *K*-capture decay scheme for Ga^{67}, which is useful for radiation dosage calculations, was given in the last quarterly report. This scheme showed five transitions between four levels above the ground state in Zn^{67}. In further work evidence for 12 additional transitions has been found; thus, at least six excited levels in Zn^{67} are indicated.

A more complex decay scheme has been found that is consistent with the transition energies and gamma-gamma coincidence rate data. Branching ratio and conversion coefficient measurements were made, and an attempt to assign to the Zn^{67} levels spins that are consistent with the experimental data will be undertaken.

DETERMINATION OF THE MELTING POINT OF TECHNETIUM METAL

G. W. Parker G. E. Creek
W. J. Martin G. M. Hebert
P. M. Lantz

The obvious value of a direct measurement of the melting point of the new synthetic element technetium has been the object of extended effort involving the construction and calibration of a high-temperature microvacuum furnace.

The currently supplemented supply of the element[1] together with the stepped-up characterization program of others[2] somewhat assured the availability of highly purified and well-characterized specimens of the metal and thereby afforded a reasonable opportunity to obtain a measurement of some consequence.

Although the present data cannot be considered as conclusive because of the incomplete calibration of the apparatus, a final value should soon be available for publication. The present tentative value of 2140 ± 20°C is the result of a limited number of determinations.

Microvacuum Furnace Design. The temperature range first expected (2200 to 2600°C) indicated the general difficulty of the problem, dictated a minimum design of vacuum-type equipment, and indicated the need for reliance upon optical pyrometry. It was also evident that a systematic calibration with pure, known materials would be valuable.

The type of furnace constructed (Fig. 12) is of fairly common design,[3] although this particular unit was purely the result of a trial-and-error procedure. In some respects it is believed to be superior to the type of furnace described in the literature. The variac-controlled 0- to 150-v input to a salvaged filament transformer (5-v, 200-amp output) and the handy current transformer (60 to 1) used as a shunt for the ammeter are of particular value. The large main-line packless valve and the secondary

(1) G. W. Parker and W. J. Martin, "Results of the First Large-scale Separation of Technetium," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951*, ORNL-1116, p. 26.

(2) C. M. Nelson, G. E. Boyd, and W. T. Smith, "Chemistry of Technetium: Measurement of Magnetic Susceptibilities," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1951*, ORNL-1053, p. 53; and subsequent progress reports.

(3) W. O. Stratton, "The Phase Diagram of the $BaO-TiO_2$ System," *J. Chem. Phys.* **19**, 33 (January 1951).

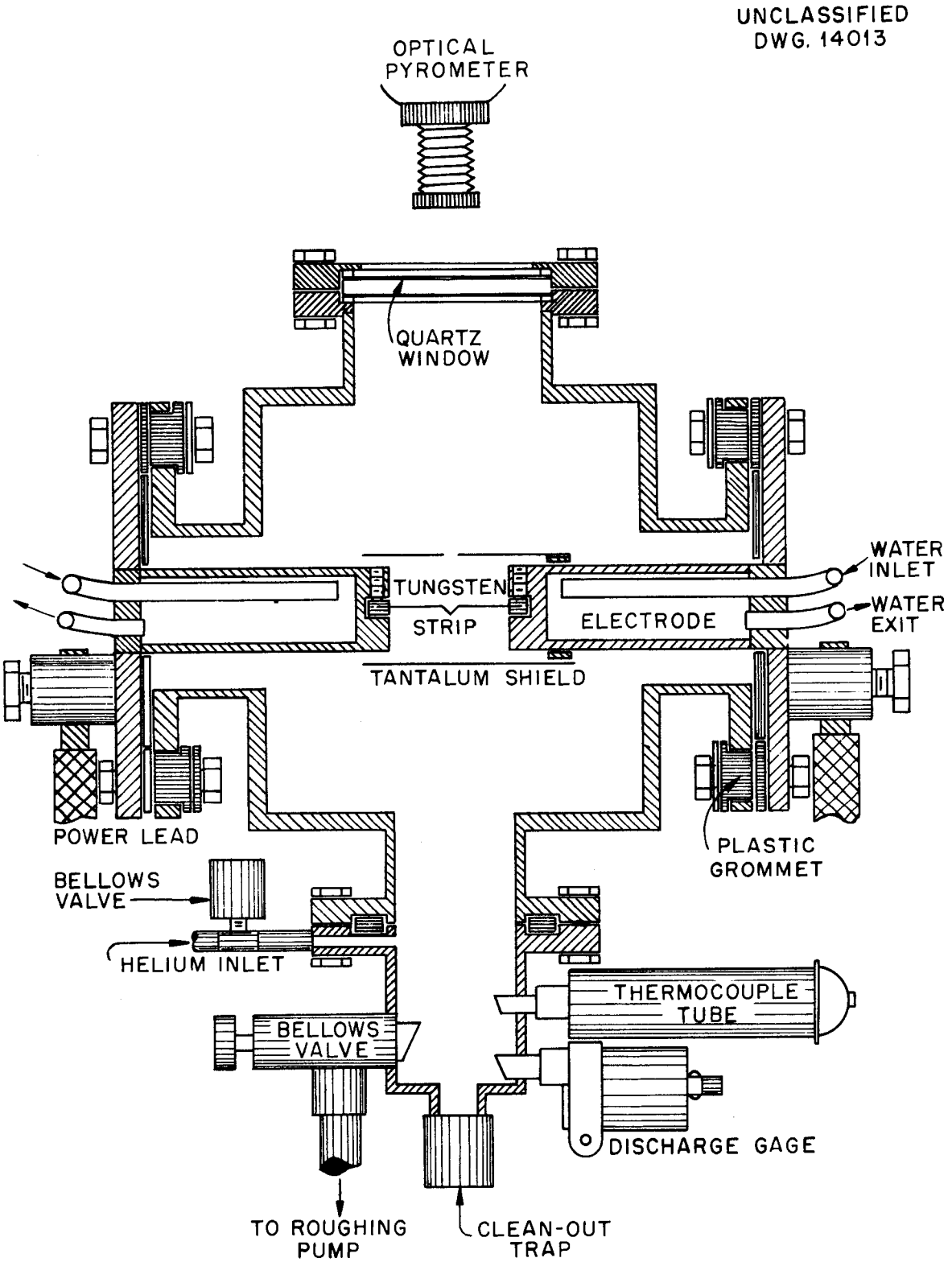


Fig. 12. Microvacuum Furnace.

pump-down of the furnace chamber permit a rapid turnover of samples. A general freedom from metal vapor condensation on the optical window and considerable heat conservation are obtained by the use of a tantalum heat shield with a minimum aperture.

Furnace Heater Strip. A metallic strip of tungsten, tantalum, or molybdenum is usually used as the heater; carbon may be used, but it is not desirable because it is volatile at high temperatures and darkens the optical windows. It was found that a light tungsten strip (5 mils) was usually satisfactory, and a width of ¼ in. could be heated with the transformer available. The heater strip was difficult to form at first, but it was found that free application of heat with a small hand torch until the tungsten was a bright red color simplified the cutting and bending operations.

The determination of the shape of the tungsten strip was a problem requiring much experimentation until, at the suggestion of the Pyrometry Division of the Bureau of Standards,[4] a simple, shallow V arrangement was adopted to minimize the temperature difference between the strip and the sample. The tungsten strip, already cut to width and length, was deformed into a V and cleaned by brightening in a hot, strong potassium hydroxide solution. Slotted copper lugs, carefully fitted to the slots in the water-cooled copper electrodes, were slipped over each end of the strip.

Calibration of the Optical Pyrometer and the Heater Strip. A standard Leeds & Northrup, Morse-type, disappearing-filament optical pyrometer (Model 8622) was used. It was calibrated by comparison with an identical "reference" pyrometer and with a tungsten-ribbon-filament lamp (located in the ORNL Instrument Division) that was calibrated by the Bureau of Standards.[5] Although it was not possible to use the lamp for calibration above 1900°C, the pyrometers agreed with each other and with the lamp to its stated calibration accuracy of ±6°C. Since an unknown difference in temperature exists between components of any other than an ideal black-body system, the heater strip was calibrated against the melting points of well-characterized substances (Fig. 13). The materials used were the platinum metals, the only metals for which the melting points are known accurately, and sapphire (Al_2O_3), which has a median melting temperature and does not alloy with tungsten.

Melting Point Determinations. The samples of powdered, hydrogen-reduced, technetium metal used for the melting point determinations were prepared by this group, C. M. Nelson, and J. W. Cobble. Each sample was prepared from previously sublimed Tc_2O_7 and was analyzed as "spectrochemically pure." A separate activation type of rhenium analysis showed a range of 0.1 to 0.02% in rhenium content.

For each determination, a small weighed sample of powdered technetium metal held by a trace of water was placed in the center of the V strip, and the temperature at which the particles coalesced was read on the optical pyrometer. Since the apex region exhibited a fairly uniform temperature, it was felt that an approach to black-body conditions

[4] R. J. Corruccini, Division of Pyrometry of National Bureau of Standards, private communication.

[5] R. J. Corruccini, Division of Pyrometry of National Bureau of Standards, Calibration No. 120877, June 7, 1949.

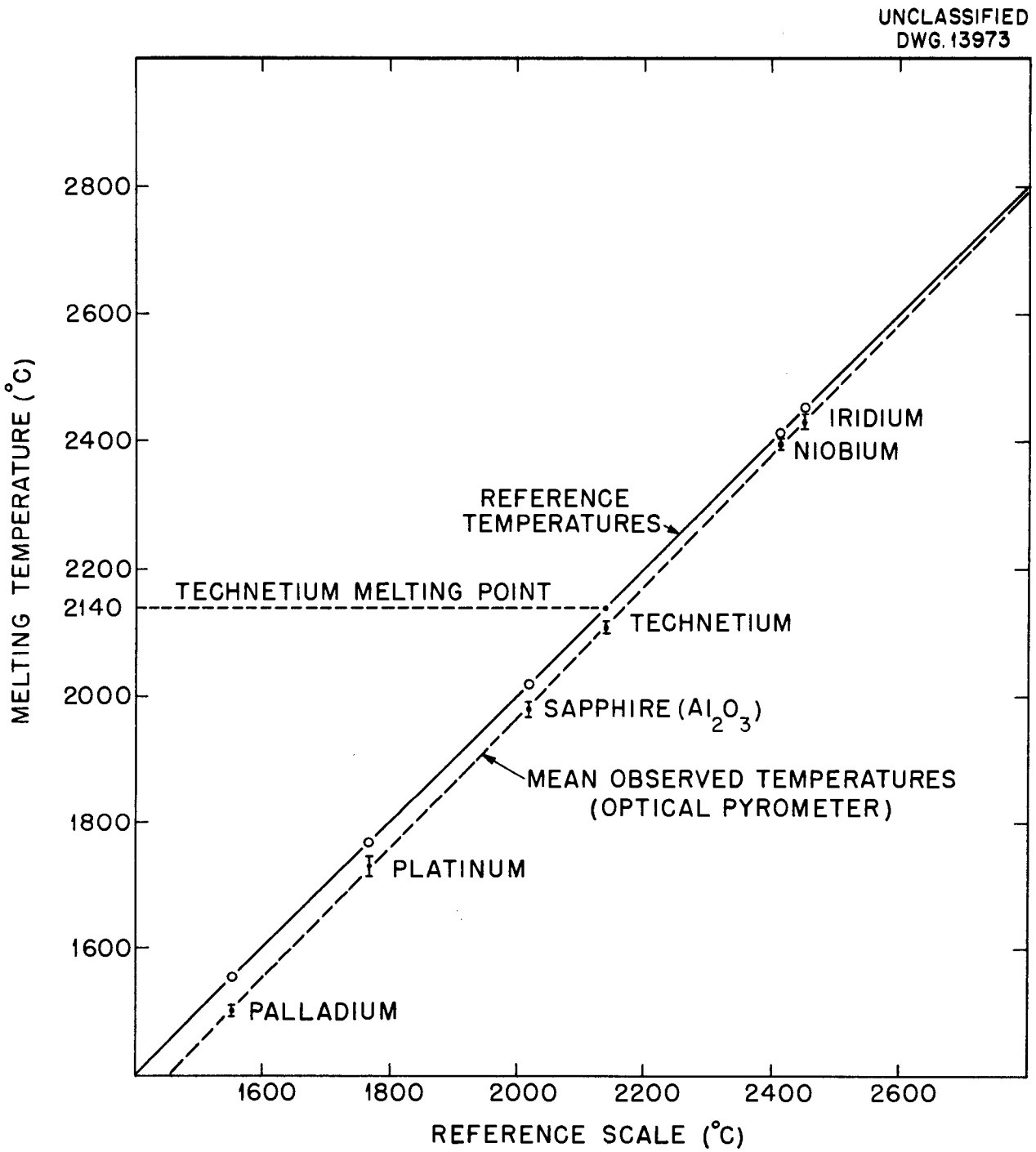


Fig. 13. Calibration Curve for Microvacuum Apparatus for Melting Point Determinations.

TABLE 15

Observed Melting Points

	MELTING POINTS (°C)				
	PLATINUM (chemically pure)	SAPPHIRE (clean Al_2O_3, Linde)	TECHNETIUM (spectrochemically pure)	NIOBIUM (99.9% pure)	IRIDIUM (99.5% pure)
Reference	1773 ± 1	2020 ± 10	Unknown	2415 ± 15	2454 ± 3
Sample No.					
1	1735	1968	2113	2393	2421
2	1707	1993	2099	2399	2410
3	1724	1993	2121		2441
4	1727	1977	2107		2449
5	1732	1971	2118		2447
6	1749		2110		
7	1746		2110		
Mean	1731	1980	2111 (uncorrected)	2396	2433

prevailed[6] and that reproducibility might be expected. Several determinations were made on each sample, and the results showed that the determinations were essentially identical and well within the reproducibility of the method (±20°C).

Table 15 is a summary of the observed melting points of samples of technetium and of the standards of various sizes (0.5 to 2 mg). It was observed that the melting temperatures are proportional to sample size and are affected by such factors as particle size, contact with the strip, distribution, etc., but no attempt has yet been made to treat these variables quantitatively. By providing uniform conditions, for example, only powdered samples of a given range in weight, it is felt that these factors have been calibrated out.

Figure 14 is a plot of the melting points of the transition heavy metals, which shows the estimated melting point of technetium at 2235°C (an average of the divergence from normal of manganese and rhenium) and the observed melting point at 2140°C.

[6] T. J. Rhodes, *Industrial Instruments for Measurement and Control*, p. 177, McGraw-Hill, New York, 1941.

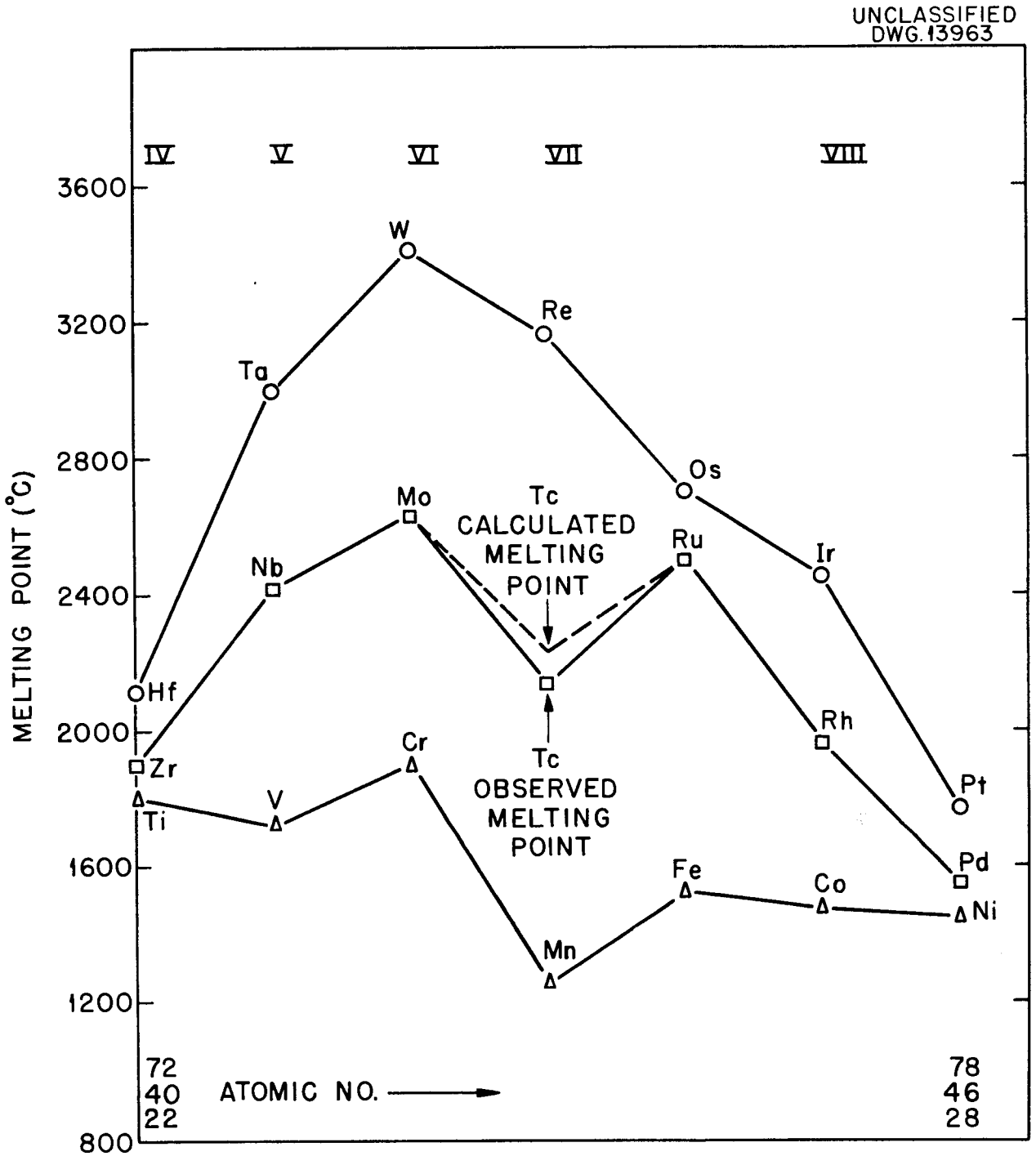


Fig. 14. Melting Points of the Transition Heavy Metals.

RADIO-ORGANIC CHEMISTRY

RADIATION CHEMISTRY

E. J. Dowling A. R. Jones
W. J. Skraba

Radiation Experiments. Experimental investigation of the nature of the gamma-radiation-induced reactions of aqueous solutions of carboxylic acids has continued. The principal reactions occurring when a dilute aqueous solution of acetic acid was irradiated with 10^6r of gamma radiation from Co^{60} were decarboxylation and coupling at the alpha-carbon atom.

The carboxyl carbon was thus converted to carbon dioxide or became the carboxyl carbon of succinic acid. A trace of noncondensable gas indicated a minor conversion to carbon monoxide.

A part of the alpha carbon (the methyl position of acetic acid) became the alpha carbon of succinic acid. A small fraction was converted to carbon dioxide and noncondensable gas (probably methane). The remainder of the methyl carbon atom of acetic acid – specifically, that released by the decarboxylation reaction – was shown to be present in the form of a nonvolatile acidic material for which the chemical constituents have not been determined. None of the methyl group of the acetic acid was converted to the following likely products: methanol, ethanol, formaldehyde, acetaldehyde, formic acid, propionic acid, or oxalic acid.

The possible causative agents for reactions of dilute solutions of organic materials in water under gamma irradiation have been considered to be H°, OH°, HO°_2, H_2O_2, and activated water molecules. The chemical effects due to these reagents and the effects of the concentration, pH, dissolved gas, and additives upon the decarboxylation and coupling reactions were investigated for the aqueous acetic acid system. The experimental data are tabulated in Table 16. Some significant results follow:

1. No succinic acid was obtained by the action of hydrogen peroxide on dilute aqueous acetic acid, alone, or in the presence of a trace of ferrous sulfate; the latter reaction mixture, known as Fenton's reagent, is a source of hydroxyl radicals. These experiments tentatively eliminated H_2O_2 and OH° as reagents for the coupling reaction.

2. Irradiation of dilute aqueous acetic acid in the presence of excess ferrous sulfate (which removes hydroxyl radicals) led to the elimination of the coupling reaction. This indicates that hydrogen atoms are not the active reagents.

3. Only a trace of succinic acid was formed when an oxygen-swept, dilute aqueous acetic acid solution containing hydrogen peroxide was irradiated. Such a solution should have contained HO°_2 radicals.

4. If energy were transferred by some physical process from the gamma-activated water molecules to the acetic acid molecules, it might be expected to be in amounts similar to that produced by direct absorption of ultraviolet quanta by acetic acid molecules. A dilute solution of acetic acid in water was irradiated with the light from an ultraviolet lamp of such a type and in such a way that very little energy was present in wavelengths shorter than 2400 Å. After several hours the solution had become opaque, although both acetic acid and water are practically transparent to radiation of wavelengths longer than 2100 Å. It was evaporated

to dryness and triturated with ether. The eluate was paper chromatographed; no nonvolatile acidic material was found.

5. When an aqueous solution of acetic acid and hydrogen peroxide was irradiated for several hours with ultraviolet light of wavelengths shorter than 2100 Å and then evaporated to dryness, a solid product was isolated, which was proved by its melting point to be succinic acid. Since the ultraviolet irradiation of aqueous hydrogen peroxide apparently leads to the formation of hydroxyl radicals, a tentative assumption can be made that the coupling reaction is initiated by hydroxyl radicals.

It must be assumed that in the Fenton's reagent experiment described above, hydroxyl radicals were not produced under suitable circumstances to promote the coupling reaction. It seems possible that the hydroxyl radicals produced reacted faster with ferrous ion than with the organic compound.

It had previously been noted[1] that the products of the radiolysis of aqueous acetic acid by gamma radition were carbon dioxide, carbon monoxide, succinic acid, glycolic acid, and a third unidentified nonvolatile acidic material. It has since been impossible to duplicate this result; the only nonvolatile acidic product found in all the radiations of acetic acid conducted since that time (even in those with the same stock solution that had given the anomalous result) has been succinic acid. No explanation for this phenomenon has been found.

The fate of the methyl carbon atom of acetic acid when the decarboxylation reaction occurs remains unknown. It has been shown that only a very small part is converted to gaseous products, carbon dioxide and methane, and volatile neutral materials. Since specific analyses for formic and propionic acids were negative, it is unlikely that the methyl carbon atom will be found in the form of steam-volatile acidic substances. Paper chromatography of the nonvolatile acidic material proved the absence of oxalic acid as a radiolysis product and revealed the presence of only one substance, succinic acid.

The fact that the acidity of an aqueous acetic acid solution decreased by 30% at the same time that gamma radiolysis caused 30% decarboxylation shows that the methyl group residue left by the decarboxylation reaction is not converted to formic acid, for then the acidity of the solution would have remained unchanged.

It has definitely been established by paper chromatographic comparisons, by using three different chromatographing solvents, that the only nonvolatile acidic product formed by gamma radiolysis of aqueous butyric acid is 2,3-diethylsuccinic acid. As with acetic acid, the principal reactions are those of decarboxylation and coupling in the alpha position. Similar results are indicated for valeric acid.

An interesting exploratory experiment was performed in which a homogeneous mixture of benzene, water, and acetic acid in volume ratio 10:12:40 was irradiated and evaporated to dryness. A small amount of viscous oil was obtained with the strong characteristic odor of phenylacetic acid. Since the decomposition of benzoyl peroxide (which yields phenyl radicals) in acetic acid does not lead to the formation of phenylacetic

(1) *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951*, ORNL-1116.

TABLE 16

Summary of Experimental Data on Irradiated Aqueous Aliphatic Acid Solutions

SUBSTANCE IRRADIATED	MOLAR CONCENTRATION	LABELED POSITION	MILLIMOLES OF STARTING MATERIAL	MICROCURIES OF STARTING MATERIAL	DISSOLVED GAS	DOSE (r)	ELECTRON VOLTS ($\times 10^{20}$)	MICROCURIES $C^{14}O_2$ FORMED	MILLIMOLES OF $C^{14}O_2$ FORMED	G VALUES FOR CO_2 FORMATION	MICROCURIES OF $C^{14}O$ FORMED	MILLIMOLES OF $C^{14}O$ FORMED	G VALUES FOR CO FORMATION	MILLIGRAMS OF SUCCINIC ACID FORMED	MILLIMOLES OF SUCCINIC ACID FORMED	G VALUES FOR SUCCINIC ACID FORMATION	ADDITIVES
CH_3COOH	0.00082	1	0.02	5.8	H_2	0.92×10^6	0.48	1.75	0.00603	7.62	trace						
	0.0041	1	0.07	10.5	H_2	4.6	2.41	2.52	0.0168	4.22	no analysis						Trace of $KMnO_4$
	0.0041	1	0.08	11.1	H_2	4.8	2.52	3.53									
	0.0079	1	0.16	22.0	H_2	4.5	2.36	3.97	0.0254	6.11	no analysis						
	0.0079	1	0.15	20.8	H_2	5.5	2.88	3.31	0.0289	7.42	no analysis						
	0.0098	2	0.213	16.6	H_2	5.3	2.78	0.44	0.0239	5.03	trace						
	0.01	1	0.19	25.1	H_2	0.46	0.24	0.60	0.00565	12.3	0.089	0.00114	0.248				
	0.01	1	0.19	24.8	H_2	2.7	1.42	2.99	0.00454	11.5	no analysis						
C_4H_9COOH	0.01	1	0.22	14.6	H_2	5.5	2.88	0.23	0.0229	9.78	no analysis						
CH_3COOH	0.235	1	9.62	26.2	H_2	13.7	7.18	0.42	0.00346	0.728	no analysis						
	0.24	2	9.10	20.5	He			0.013	0.154	13.0	no analysis						
	0.26	1	4.67	17.8	H_2	4.6	2.41	0.089			0.034						
	0.26	1	4.89	18.6	O_2	5.2	2.73	0.108	0.0234	5.88	trace						H_2SO_4
	0.26	1	4.89	18.0	O_2	4.0	2.10	trace	0.0284	6.31	no analysis						H_2SO_4
C_3H_7COOH	0.26	1	4.84	13.3	H_2	6.4	3.35	0.047			no analysis			29	0.246	71.0	H_2SO_4
CH_3COOH	0.28	1	4.75	16.8	H_2	49	25.7	1.22	0.0171	3.09	no analysis						
	0.28	1	4.35	14.8	O_2	4.4	2.31	0.43	0.0345	0.813	trace						H_2O_2
	0.28	1	6.05	21.3	H_2	4.0	2.10	0	0.127	33.3	0.04	0.00118	0.309	0.2	0.0017	0.446	
	0.28	1	4.48	14.5	O_2	4.4	2.31	0.43	0	0	0			0		0	$FeSO_4$
	0.28	1	10.9	24.2	H_2	5.5	2.88	0	0.133	34.9	0.04	0.00124	0.324	0.2	0.0017	0.446	H_2O_2
	0.29	1	5.8	20.1	H_2	4.5	2.36	0.05	0	0	trace			0		0	C_6H_6
	0.29	1	5.75	6.3	O_2	4.0	2.10	0.15	0.0144	3.70	trace			2	0.017	4.37	NaOH
	0.29	1	5.86	6.47	H_2	4.5	2.36	no analysis	0.137	39.5	no analysis			4	0.034	9.82	
	0.29	1	4.35	14.8	O_2	4.3	2.26	0.068			no analysis			17.6	0.149	38.3	
	0.29	1	4.35	17.9	H_2	5.8	3.04	0.033	0.0200	5.36	no analysis			0.3	0.0025	0.672	H_2O_2
	0.29	1	4.35	4.8	He	4.0	2.10	no analysis	0.00803	1.60	no analysis			0			$FeSO_4$
	97%	1	330		H_2	9.3	4.88				no analysis			1.2	0.0102	2.95	H_2O_2
	0.248	2	6.2	25.8	H_2	46.5	24.4	0.056	0.0135	0.336	0.23	0.0553	1.38				HOAC

[redacted]

[redacted]

[redacted]

acid,[2] this product presumably was formed by the attack of $-CH_2COOH$ radicals on benzene.

Exploratory experiments on aqueous solutions of other types of compounds have revealed that: (1) dilute aqueous methanol upon irradiation was converted largely to carbon dioxide, and (2) dilute aqueous methylamine hydrochloride was converted largely to carbon dioxide and formaldehyde.

EXPERIMENTAL

Irradiation of Aqueous Acetic-2-C^{14} Acid to Determine the Fate of the Methyl Carbon. A hydrogen-purged 0.0098 *M* solution of acetic-2-C^{14} acid, 0.213 mmoles, 16.6 microcuries (0.766 microcuries/g) of solution weighing 21.75 g was irradiated in a sealed ampoule with 5.32×10^6 r of gamma rays from Co^{60}. The cell was opened and the solution was purged with oxygen. The exit gas was passed through a dry-ice trap and washed with dilute sodium hydroxide solution to remove the carbon dioxide. It was then passed over copper oxide at 750°C, and the carbon dioxide formed by the combustion of the carbon monoxide or hydrocarbon gases was removed by a second scrubbing with dilute sodium hydroxide solution.

Acidification of the scrubber solution and radioassay of the gas evolved (and swept into ion chambers with inert carbon dioxide) showed that 2.6%, 0.44 microcuries, of the methyl group of the acetic acid had been converted to carbon dioxide, and that 0.53%, 0.089 microcuries, had been converted to carbon monoxide or hydrocarbon gas (probably methane) by the radiolysis. Several 100-μl aliquots of the degassed solution were burned and the remaining activity was determined as 15.9 microcuries.

The remainder of the degassed solution was titrated with standard sodium hydroxide solution. The solution contained 0.149 mmoles of acid, indicating that 30.1%, 0.64 mmoles, of decarboxylation had occurred. This is in very good agreement with the results obtained by gamma radiolysis of acetic-1-C^{14} acid. The titrated solution was made slightly basic with sodium hydroxide and was then almost completely distilled. The residue was diluted to 25 ml and aliquots were removed and burned for radioassay. The total activity was 15.6 microcuries. The test for formaldehyde in the distillate was negative.

The basic solution was acidified with sulfuric acid and steam-distilled. The distillate and residual solutions were made basic and concentrated. They were then each diluted to 25 ml and aliquots were burned for radioassay. In this way it was shown that 41.3%, 6.86 microcuries, of the acetic acid was converted to acidic material that was not steam-volatile and that 50.6%, 8.40 microcuries, of the acetic acid was unchanged by the radiation.

The organic acidic material that was not steam-volatile was paper chromatographed with ether–acetic acid–water solution in the volume ratio 14:1:1. Only one spot was obtained that was acidic to an indicator and radioactive; it compared exactly with succinic acid.

Action of Fenton's Reagent on Aqueous Acetic Acid. To 20 ml of a solution of 0.20 mmoles of acetic acid and 0.40 mmoles of hydrogen peroxide, 2 ml of 0.07 *M* ferrous sulfate solution was slowly added. The mixture became brown and gas was evolved. After several hours the mixture was steam-distilled. The distillate was titrated with standard sodium hydroxide; it contained 0.136 moles of acidic material, presumably unreacted acetic acid. The solution of non-distillable material was thoroughly extracted with ethyl acetate, but the extract on evaporation left only a trace of residual oil with a caramel-like odor.

Irradiation of Aqueous Butyric-1-C^{14} Acid. Irradiation of a 0.25 *M* solution of butyric-1-C^{14} acid with 5.5×10^6 r of Co^{60}

[2] H. Gelissen and P. H. Hermans, "Über neue Synthesen mittels organischer Peroxyde, VI.," *Ber.* **58** Band I, 770 (1925).

gamma rays and examination of the products in the manner described for acetic acid revealed the presence of 0.017 mmoles (0.36%) of carbon dioxide from decarboxylation. α,α'-Diethylsuccinic acid was the sole nonvolatile product, as determined by paper chromotography.

Analytical Developments. In agreement with unpublished work of the Biology Division, it has been found that several hundredths millimoles each of acetic and propionic acids may be conveniently and rapidly separated by partition chromatography using celite and chloroform 0.5% *n*-butanol-dilute sulfuric acid.

The paper chromatographic isolation and identification of 2,3-diethylsuccinic acid were accomplished with the following solvents: (1) 90% ethanol, 5% concentrated ammonium hydroxide, 5% water (volume per cent); (2) 14 volumes of ether, 1 volume of glacial acetic acid, 1 volume of water: (3) the organic layer from 2 volumes of benzene shaken with 1 volume of 50% (by volume) acetic acid in water.

Preparative Methods. Since in all aliphatic acids studied to date the chief reaction occurring in radiolysis is coupling in the alpha position, it seems of interest to determine the course of reaction in aliphatic acids containing no alpha hydrogens. The labeled pivalic acids (2,2-dimethylpropionic acid) are therefore being prepared. Methods for the preparation of 2,2-dimethylpropionic-3-C^{14} acid have been examined. A suitable set of reactions seems to be the following:[3,4]

$$C^{14}H_3OH + HI \longrightarrow C^{14}H_3I \xrightarrow[(2)\ CO(OC_2H_5)_2]{(1)\ Mg}$$

$$(C^{14}H_3)_3COH \xrightarrow{HCl}$$

$$(C^{14}H_3)_3CCl \xrightarrow[(3)\ NH_4Cl\ (soln.)]{(1)\ Mg,\ (2)\ CO_2}$$

$$(C^{14}H_3)_3C\text{—}COOH.$$

The small-scale conversion of methanol to methyl iodide is easily accomplished in almost quantitative yield by Ronzio's[3] procedure. The Grignard reaction in ether solution occurs more smoothly with diethylcarbonate than with acetone or carbon dioxide. The yield of *t*-butyl alcohol was poor, however, in all cases. Gaseous hydrogen chloride bubbled through a water solution of the alcohol produced good yields of *t*-butyl chloride. The Grignard reagent of the latter was difficult to prepare on a small scale and the yield of pivalic acid was poor. Further dead runs will be necessary before 2,2-dimethylpropionic-3-C^{14} acid can be made.

2,2-Dimethylpropionic-1-C^{14} acid was, however, prepared with low yield by reaction of C^{14}-dioxide with *t*-butyl magnesium chloride in low yield.

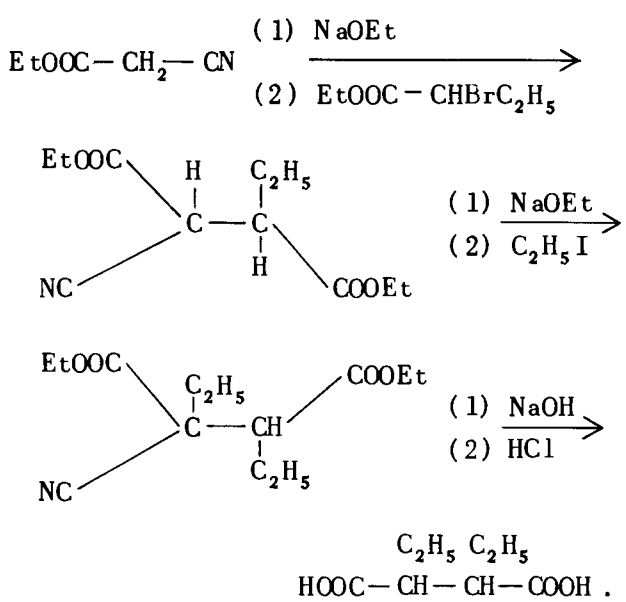
2,3-Diethylsuccinic acid has been prepared[5] for comparison with the nonvolatile acidic product of the gamma radiolysis of aqueous butyric

(3) A. R. Ronzio, *Micro Syntheses with Tracer Elements; XXVII. The Synthesis of C^{14} Methyl Iodide*, AECU-1435.

(4) W. W. Moyer and C. S. Marvel, "Triethyl Carbinol," *Organic Syntheses* (A. H. Blatt, ed.) Coll. Vol. **II**, 602, Wiley, New York (1943).

(5) H. Wren and J. W. E. Haller, "Optically Active Alkylsuccinic Acids. II. The Stereochemical Configuration of the Symmetrical Diethylsuccinic Acids," *J. Chem. Soc.*, p. 230 (1937).

acid solutions. The scheme followed may be represented as:



ISOTOPE EFFECT STUDIES

Measurement of the Carbon^{13} Isotope Effect in the Dehydration of Formic Acid (A. J. Weinberger, G. A. Ropp, O. K. Neville). Formic acid of normal C^{13} content and containing approximately 1 microcurie of C^{14} per millimole was dehydrated in concentrated sulfuric acid at two temperatures, 0 and 24.04°C, and mass spectroscopic determinations were made of the C^{13}/C^{12} ratio of the successive fractions of the CO evolved. The value of the C^{13} isotope effect, expressed as

$$\frac{k_{12} - k_{13}}{k_{12}},$$

was calculated to be approximately 5.8% at 0°C and 5.7% at 24.04°C. The C^{14} isotope effect was found to be approximately the same at 0°C as that reported previously.[6]

The apparatus used in making these determinations is described in the following and shown in Fig. 15. The portion of the apparatus at the left of section A-A is the same as that described previously.[1] Item 1 is a mercury-sealed, glass-frit valve[7] for maintaining constant pressure in the apparatus to the left of section A-A, whereas the pressure in the bulb system shown between sections A-A and B-B varies. The bulbs in the bulb system each have a volume of about 50 ml and are connected by 2-mm capillary tubing. Item 2 is a 2-mm capillary manometer.

Before a run was made the entire apparatus was evacuated through stopcock 7. Stopcock 3 and all the bulb stopcocks except one were closed off. The reaction was then started in the apparatus to the left of section A-A and the carbon monoxide produced entered the bulb system through valve 1. When the pressure in the first bulb became approximately one atmosphere as indicated by manometer 2, the open bulb stopcock was closed and the next stopcock was opened. These operations were repeated until all the formic acid was decomposed.

After the reaction was complete, the gas was transferred to the analytical system shown at the right of stopcock 3, one bulbful at a time. Each sample was first transferred by means of the automatic Toepler pump 4 to the known volume, which was bounded by *a*. From pressure and temperature readings of the gas in the known volume, the number of millimoles of gas was calculated. The gas was then burned by cycling it through the copper oxide packed quartz tube in the furnace 5 with the Toepler pump. The carbon dioxide produced was frozen

(6) G. A. Ropp, A. J. Weinberger, and O. K. Neville, "The Determination of the Isotope Effect and its Variation with Temperature in the Dehydration of Formic-C^{14} Acid," *J. Am. Chem. Soc.* **73**, 5573 (1951).

(7) O. K. Neville, "C^{14} Tracer Studies in the Rearrangements of Unsymmetrical α-Diketones: Phenylglyoxal to Mandelic Acid," *J. Am. Chem. Soc.* **70**, 3501 (1948).

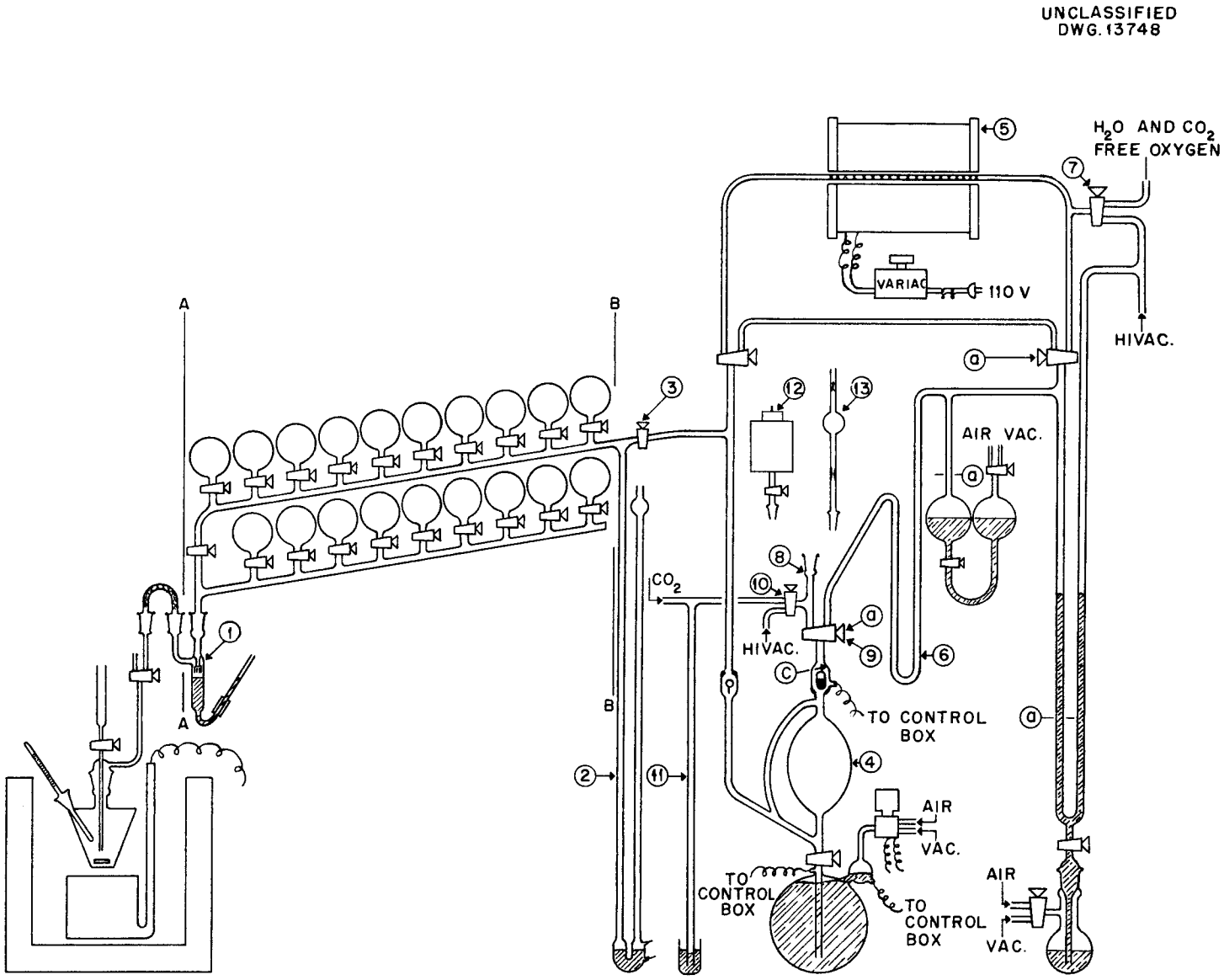


Fig. 15. Apparatus for Determination of the Carbon[13] Isotope Effect in the Formic Acid Dehydration.

out in trap 6. Noncombustible gas was pumped away through stopcock 7. The carbon dioxide was allowed to vaporize in the known volume, and the quantity produced and the unburned gas were measured.

An aliquot of the carbon dioxide was introduced into ionization chamber 12, which is attached to the apparatus at joint 8. This was done by momentarily connecting the known volume to the free space *c* through stopcock 9 into the joint 8 section with the mercury pump. Tank carbon dioxide let in at stopcock 10 swept the gas aliquot into the ionization chamber. When the pressure of CO_2 in the ionization chamber reached atmospheric, as indicated by manometer 11, the ionization chamber was closed off and the C^{14} activity in it was measured with a vibrating-reed electrometer 2. The amount of $C^{14}O_2$ introduced into the chamber as a sample was given by the difference of the original and residual quantities of $C^{14}O_2$ as measured in the known volume. From these values, the specific activity of the $C^{14}O_2$ was calculated.

In a similar way, a sample for the mass spectroscopic measurement of the C^{13} content was introduced into tube 13, which contains a break-off seal. No tank gas was used to sweep this sample in and no measurement of the amount of sample was needed. Tube 13 was sealed off with a torch.

Mass spectroscopic measurements were made by the analytical group under R. F. Hibbs. The results of these experiments have been submitted to A. W. Kimball of the Mathematics Panel for statistical treatment prior to a final report of the isotope effect values.

Measurement of the Isotope Effect in the Decarboxylation of Malonic-2-C^{14} Acid at 154°C (G. A. Ropp and V. F. Raaen). In an attempt to obtain a clearer understanding of C^{14} isotope effects an effort is being made to evaluate and compare the isotope effects in the following pair of bond-breaking reactions:

1. decarboxylation of malonic-2-C^{14} acid,
2. decarboxylation of malonic-1-C^{14} acid.

The reactions are identical except for the location of the tagged carbon atom, which is first at one end of the bond that breaks during the reaction and then at the other end of the same bond. The study of the isotope fractionation in reaction 1 has been completed and the corresponding study of reaction 2 has begun. For reaction 1, the value of $100(k_{12} - k_{14})/k_{12}$, which represents one hundred times the difference between the first-order rate constants for decarboxylation of the two isotopic species of malonic acid divided by the kinetically determined rate constant, has been shown to be 6.8. The method used is described in the following.

The reactions of the two species and their rate constants are:

$$H_2C^{12}\begin{matrix} C^{12}OOH \\ C^{12}OOH \end{matrix} \xrightarrow{k_{12}} H_3C^{12}-C^{12}OOH + C^{12}O_2\,, \qquad (1)$$

and

$$H_2C^{14}\begin{matrix} C^{12}OOH \\ C^{12}OOH \end{matrix} \xrightarrow{k_{14}} H_3C^{14}-C^{12}OOH + C^{12}O_2\,. \qquad (2)$$

In this particular reaction the isotope fractionation is most readily followed as the variation of the specific activity of the unreacted malonic acid with time. From the integrated rate expression for a first-order reaction, it is seen that for reaction 1

$$n_{12} = n_{12}^{0}\ e^{-k_{12}t},$$

and for reaction 2

$$n_{14} = n_{14}^{0}\ e^{-k_{14}t},$$

where

n_{12} and n_{14} are the number of moles of unlabeled and labeled malonic acids, respectively, at time, t, and,

n_{12}^{0} and n_{14}^{0} are the number of moles of the respective malonic acids at $t = 0$.

Therefore,

$$\frac{n_{14}}{n_{12}} = \frac{n_{14}^{0}\ e^{-k_{14}t}}{n_{12}^{0}\ e^{-k_{12}t}} = \frac{n_{14}^{0}}{n_{12}^{0}}\ e^{(k_{12} - k_{14})t}$$

and

$$2.303 \log n_{14}/n_{12} = 2.303 \log n_{14}^{0}/n_{12}^{0} - (k_{12} - k_{14})t.$$

Since at tracer level the ratio n_{14}/n_{12} represents the specific activity of the malonic acid remaining at time t, $k_{12} - k_{14}$ may be evaluated from the slope of the plot of the log of the specific activity of the malonic acid vs. time. This difference between the reaction rate constants so obtained is multiplied by 100 and divided by the kinetic rate constant measured independently to give the value of the isotope effect, $100(k_{12} - k_{14})/k_{12}$.

EXPERIMENTAL

Synthesis of Malonic-2-C^{14} Acid. The malonic acid used, m.p. 135°C, was prepared by chlorination of acetic-2-C^{14} acid, reaction with sodium cyanide, hydrolysis of the resulting cyanoacetic acid, and extraction of the product with ether. The acid was prepared by a high specific activity synthesis, and 1 millicurie of recovered product was diluted about 5000-fold with Eastman's c.p. malonic acid in acetone solution. The solution was filtered and evaporated and the solid was recrystallized from c.p. acetone.

Determination of the First-Order Rate Constant. Four grams of the acid was decomposed in a small glass vessel heated by the vapors above boiling anisole. The rate of evolution of carbon dioxide was determined by collecting the gas over 85% phosphoric acid. The measured rate constant was 0.0672, which is in fair agreement with the value of 0.0643 obtained by Hinshelwood[8] at 153.2°C.

Evaluation of $k_{12} - k_{14}$. Two grams of malonic-2-C^{14} acid was decomposed under the same conditions as in the above-mentioned experiment. The first carbon dioxide evolved was allowed to escape. Beginning with the eighth minute after the reaction started, samples were taken from the pot at 4-min intervals and quickly quenched in cold ligroin. The ligroin was allowed to evaporate from the acid samples. Each malonic acid sample was sublimed at 90 to 100°C at a pressure of less than 1 mm Hg to remove acetic acid and any impurities present. The samples were assayed by wet combustion with Van Slyke solution and ion-current determination with the vibrating-reed electrometer. The data obtained for the calculation of the isotope effect are shown in Table 17.

(8) C. N. Hinshelwood, "The Rate of Decomposition of Malonic Acid," *J. Chem. Soc.* **117**, 156 (1920).

TABLE 17

Data Obtained in Evaluating (k_{12} - k_{14}) for Calculation of the Isotope Effect in the Decarboxylation of Malonic-2-C^{14} Acid

TIME (min)	SPECIFIC ACTIVITY (μc/mmole)	LOG OF SPECIFIC ACTIVITY
8	1.995	0.2999
12	2.021	0.3056
16	2.085	0.3191
20	2.097	0.3216
24	2.165	0.3355
28	2.178	0.3381
32	2.207	0.3438

The point at 32 min and the points above 32 min were below the line of the slope obtained by plotting the first six points, because the reaction rate was no longer first order after this time. The slope did not pass through the origin (t = 0), because several minutes elapsed before all the acid melted and began to react. The calculated value of k_{12} - k_{14} was 0.00455.

Evaluation of the Isotope Effect in the Saponification of Ethyl *p*-Anisate-7-C^{14} at 25°C (V. F. Raaen and G. A. Ropp). As part of a broad study of the effect of *para*-substituents on the isotope effects in the saponification of ethyl benzoates,[9] ethyl *p*-anisate (ethyl *p*-methoxybenzoate) labeled with C^{14} in the carboxyl group has been shown to hydrolyze at 25°C in alkaline solution with isotope fractionation amounting to a value of 0.915 for the ratio, k_{14}/k_{12}, of the hydrolysis rate constants of the two isotopic species. For the evaluation of this isotope effect a method was worked out and shown to be applicable to all the isotope effects to be studied in this series of esters. The method involves the isolation and assay of the first small portion of product formed and comparison of its specific activity with that of the product from the complete reaction. The ratio of the hydrolysis rate constants of the two isotopic species may then be calculated from the equation

$$\frac{k_{14}}{k_{12}} = \frac{S_0}{S_{100}} ,$$

where S_0 is the specific activity of the first acid produced by hydrolysis of a given sample of ester, and S_{100} is the average specific activity of all the acid produced by total hydrolysis of a given sample of ester. Within the limits of error of assaying the acid samples,

$$\frac{k_{14}}{k_{12}} = \frac{S_0}{S_{100}} = \frac{S_3}{S_{100}} \cong \frac{S_6}{S_{100}} ,$$

where S_3 and S_6 represent the specific activities of the acid samples produced by 3 and 6% hydrolysis. In practice S_3 and S_6 are measured by adding to an aqueous alcoholic solution of ethyl *p*-anisate exactly enough sodium hydroxide to saponify 3 or 6% of the ester. The acid produced by saponification is in each case recovered by extraction and then purified and assayed. The value of S_3 is then divided by the value of S_{100} to give k_{14}/k_{12}.

This method must be applied with caution; in particular, pure esters must be used. If any free acid is present in the ester the values obtained for S_3 and S_6 will differ appreciably from the true specific

[9] G. A. Ropp and V. F. Raaen, "Comparison of the Isotope Effects in the Alkaline Hydrolysis of Four *para*-Substituted Ethyl Benzoates Labeled in the Carbonyl Group," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1951*, ORNL-1153.

activity of the first ester hydrolyzed. However, agreement between S_3 and S_6 is a good indication that both values are free of such errors. In addition, the value of S_0 is best checked on two samples of acid, one of which has been carried through one more stage of purification than the other. This method should be generally applicable to the evaluation of isotope effects in cases where the reactions involved are first order in the compounds bearing the label. It must be borne in mind, however, that complicating factors sometimes appear during the first few per cent of reaction.

Table 18 presents the results of the study of hydrolysis of ethyl *p*-anisate.

EXPERIMENTAL

Purification of Carboxyl-labeled Ethyl p-Anisate. The distilled ester was washed in ether solution with cold, dilute sodium bicarbonate solution. The ester solution was dried over magnesium sulfate and the ester was recovered by distillation. Its freedom from uncombined anisic acid was shown by the fact that only a trace of *N*/10 sodium hydroxide solution gave color to phenolphthalein in the presence of 1 g of the ester.

Determination of the Average Specific Activity, S_{100}, of the Ester. A small sample of the ester was hydrolyzed completely with normal sodium hydroxide. The alkaline solution was acidified and the free acid was extracted with ether, crystallized once from water, dried, and sublimed *in vacuo*. Its specific activity was determined by combustion of a number of samples with Van Slyke mixture and assay of the resulting carbon dioxide with the vibrating-reed electrometer.

Preparation of S_3 and S_6 Samples. Two 30-mmole ester samples, each dissolved in 100 ml of absolute ethanol, were cooled in closed vessels in a thermostat at 25°C. Each sample contained a drop of phenolphthalein indicator. Sufficient standard alkali (0.15

TABLE 18

Assay Values (μc/mg) in the Measurement of the Isotope Effect in the Saponification of Ethyl *p*-Anisate at 25°C

S_{100}	S_{100}*	S_3	S_6	S_3/S_{100}
0.01404	0.01414	0.01280	0.01297	
0.01410	0.01414	0.01276	0.01303	
	0.01414	0.01295	0.01300	
	0.01415	0.01295	0.01300	
	0.01410	0.01305	0.01297	
	0.01406	0.01293	0.01307	
	0.01412	0.01295	0.01300	
	0.01417	0.01302	0.01303	
			0.01302	
Average 0.01407	0.01413	0.01293	0.01301	0.915

*S_{100} values in column 2 are the specific activities determined after resublimation of the samples whose specific activities are recorded in column 1.

TABLE 19

Data Obtained for the Evaluation of the Isotope Effect in the Saponification of Ethyl Benzoate-7-C^{14} at Three Temperatures (activities in $\mu c/mg \times 10^4$)

TEMPERATURE (°C)	S_{100}	S_3	S_4	S_6	$S_3/S_{100} = k_{14}/k_{12}$
0	770	711			0.924
25	770	716	721	723	0.929
60	770	717		715	0.931

to 0.30 *N*) was added to hydrolyze one sample to the extent of 3% and the other to 6%. The solutions were kept in the thermostat until the phenolphthalein indicator color had disappeared. From the alkaline solutions the excess ester was removed by ether extraction. The aqueous solutions were acidified and the free-acid samples were recovered, purified, and assayed as indicated above. For convenience in obtaining assay samples, 81.5 mg of each acid sample was weighed out, taken up in sodium hydroxide, and aliquoted into 8.15-mg samples, which were then evaporated to dryness in the pots to be used for wet combustion. The combustions were performed with Van Slyke solution. The ion-current determinations were made with a vibrating-reed electrometer.

Evaluation of the Isotope Effect in the Saponification of Ethyl Benzoate-7-C^{14} at Three Temperatures (G. A. Ropp and V. F. Raaen). In connection with the study of the effect of *para*-substituents on the isotope effects in the saponification of ethyl benzoates labeled with C^{14} in the carboxyl groups (see previous section for the study of ethyl *p*-anisate-7-C^{14}), the isotope fractionation in the case of ethyl benzoate has been investigated by two methods:

1. The original procedure used by Stevens and Attree[10] has been repeated by using wet combustion of the benzoic acid samples instead of solid counting. By this procedure the ratio of the hydrolysis rate constants, k_{14}/k_{12}, was found to be 0.91 as compared with the value of 0.86 reported by Stevens and Attree.

2. The method applied to ethyl *p*-anisate has been applied to ethyl benzoate at three temperatures, and the preliminary results tabulated in Table 18 were obtained. This method is particularly well suited to measuring the relative isotope effects in the same reaction under different experimental conditions, since the value of S_{100} and the attendant errors cancel out.

$$\frac{\left[\dfrac{k_{14}}{k_{12}}\right]_{T_1}}{\left[\dfrac{k_{14}}{k_{12}}\right]_{T_2}} = \frac{\dfrac{(S_3)_{T_1}}{S_\infty\ 100}}{\dfrac{(S_3)_{T_2}}{S_\infty\ 100}} = \frac{(S_3)_{T_1}}{(S_3)_{T_2}}.$$

Although the values of k_{14}/k_{12} reported in Table 19 are preliminary

(10) W. H. Stevens and R. W. Attree, "Effect on Reaction Rates Caused by the Substitution of C^{14} for C^{12}. I. Alkaline Hydrolysis of Carboxyl-labeled Ethyl Benzoate," *Can. J. Res.* **27B**, 807 (1949).

figures and subject to further checking, they indicate that there is little or no variation of this ratio with changes in temperature.

EXPERIMENTAL

Method 1. Nine millimoles of labeled ethyl benzoate was hydrolyzed 3 1/2 min at 25°C in 50 ml of absolute ethanol to which 50 ml of *N*/2 sodium hydroxide was added. A mixture of 500 ml of ice and water was added to stop the reaction, and the mixture was quickly extracted five times with 70-ml portions of chloroform. The chloroform layers were combined and washed with water, which was added to the alkaline solution. The alkaline solution was evaporated to dryness on the steam bath, and the benzoic acid (1.95 mmole or 18.5% reaction) was isolated by acidification and ether extraction. The amount of benzoic acid was determined by titration. The titrated acid was again isolated, purified by sublimation, and burned with Van Slyke mixture. The evolved carbon dioxide was collected in an ion chamber and assayed with the vibrating-reed electrometer. The data obtained and the Stevens and Attree calculations were:

$$f = 0.185,$$

$$r = 83.4/91,$$

$$rf = 0.170,$$

$$k_{14}/k_{12} = \log(1 - 0.170)/\log(1 - 0.185) = 0.91,$$

where

f is the per cent reaction

r is the ratio of the specific activities of samples from incomplete and complete reaction

rf is the product of r and f.

Method 2. The second method was the same as that applied to the study of ethyl *p*-anisate saponification (see previous section).

STUDIES ON THE MECHANISM OF ORGANIC REACTIONS

Migratory Aptitudes from the Rearrangement of Diaryl Ethanols (J. G. Burr, Jr. and L. S. Ciereszko[11]). With the aim of obtaining less ambiguous data on the intrinsic migratory aptitudes[12] of substituted aryl groups, the acid-catalyzed rearrangement of C^{14}-labeled diaryl ethanols (such as VI) has been investigated by using an idea suggested by the work of Collins, Burr, and Hess.[13] Four cases have been studied in which *R* is *p*-methyl, *m*-methyl, *p*-phenyl, and *p*-methoxy. Studies using other substituents are in progress.

The general method of synthesis of the diaryl ethanols is outlined in the following scheme:

$$\underset{\text{I}}{x\text{-}C_6H_4COC_6H_5} \xrightarrow[\text{NaOH}]{\text{Zn}} \underset{\text{II}}{x\text{-}C_6H_4CHOHC_6H_5} \longrightarrow$$

$$\underset{\text{III}}{x\text{-}C_6H_4CHClC_6H_5} \xrightarrow[65\text{-}85\%]{CuC^{14}N}$$

$$\underset{\text{IV}}{x\text{-}C_6H_4\overset{C^{14}N}{\overset{|}{C}}HC_6H_5} \xrightarrow[90\%]{H_2SO_4} \underset{\text{V}}{x\text{-}C_6H_4\overset{C^{14}OOH}{\overset{|}{C}}HC_6H_5}$$

$$\xrightarrow[90\%]{LiAlH_4} \underset{\text{VI}}{x\text{-}C_6H_4\overset{C^{14}H_2OH}{\overset{|}{C}}H\text{—}C_6H_5} .$$

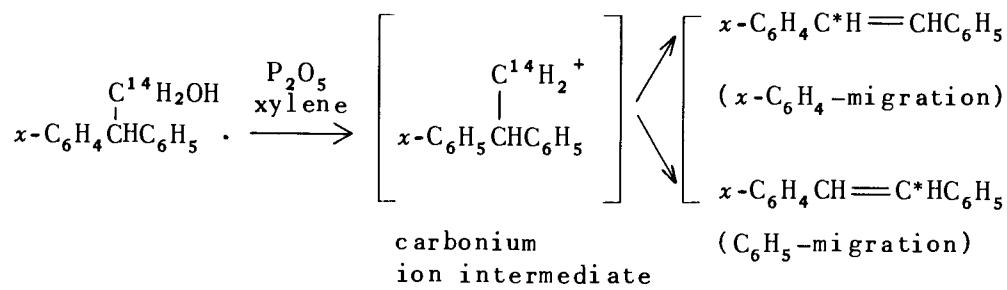
(11) Member of the Research Participation Program sponsored jointly by the Oak Ridge National Laboratory and the Oak Ridge Institute of Nuclear Studies; permanent address, University of Oklahoma, Norman, Oklahoma.

(12) G. W. Wheland, *Advanced Organic Chemistry*, 2d ed., Wiley, New York (1949), p. 513 *et. seq.*

(13) C. J. Collins, J. G. Burr, Jr., and D. N. Hess, " Studies in the Wagner Rearrangement. II. The Synthesis and Structure Determination of Benz[a]anthracene-5,6-C^{14}," *J. Am. Chem. Soc.* **73**, 5176 (1951).

The data obtained by these processes for the four series of compounds mentioned above are summarized in Table 20.

The rearrangement of the carbinols (VI) was carried out by refluxing them briefly (15 min) with a suspension of phosphorus pentoxide in xylene.



It seemed probable from the color changes observed that the rearrangement was largely accomplished long before the xylene reached the boiling point, so the temperature at which the rearrangement occurred is uncertain. However, since all four substances were treated as nearly alike as possible, the results obtained should be comparable. The stilbenes obtained by this process were crystallized and then oxidized to an easily isolable acid. These procedures are summarized in Table 21.

The values for the migration ratios obtained by these studies are summarized in Table 22. The data for the similarly constituted amine hydrochlorides are included, since they formed part of the base level of C^{14} activity used for the calculation of migration ratios. These amines, obtained by reduction of the above nitriles, are being used for a study of migration aptitudes in the amine-nitrous acid reaction. This work is reported in a subsequent section.

The order of the migratory preference observed in this rearrangement differs somewhat from that observed by Bachmann and Ferguson[14] in the rearrangement of symmetrical pinacols (a series of reactions attended by stereochemical uncertainty) in that the order observed by Bachmann was *p*-anisyl > *p*-tolyl > *m*-tolyl > *p*-xenyl. The relative positions of the migrations as observed in the present reaction, while differing from Bachmann's observation, are in agreement with those suggested by the relative values of the respective Hammett sigma coefficients.[15] In addition, the numerical values of the relative migration ratios observed here are much more in line with those suggested by the sigma coefficients than with the ratios observed by Bachmann. If the logarithms of the migration ratios observed here are plotted against the sigma functions, all the values except that for *p*-methoxy fall on a straight line. However, there is no good *a priori* reason to expect the values for migration ratios to form a straight line on a Hammett plot, since this rearrangement is probably more analogous to aromatic substitution than it is to the types of displacement reactions that form the basis for Hammett's calculations.

(14) W. E. Bachmann and J. W. Ferguson, "The Pinacol-Pinacolone Rearrangement. VI. The Rearrangement of Symmetrical Aromatic Pinacols," *J. Am. Chem. Soc.* **56**, 2081 (1934).

(15) L. P. Hammett, *Physical Organic Chemistry; Reaction Rates, Equilibrium, and Mechanisms*, McGraw-Hill, New York (1940), p. 188.

TABLE 20

Compounds and Derivatives Prepared

SERIES	CHLORIDE		CYANIDE		ACID		CARBINOL	
	m.p. (°C)	YIELD (%)	m.p. (°C)	YIELD (%)	m.p. (°C)	YIELD (%)	m.p. (°C)	YIELD (%)
m-$CH_3C_2H_4CHC_2H_5$	b.p. 136[a]		26[b]	75 to 85	122[c]	93	oil[d]	92
p-$CH_3C_6H_4CH-C_6H_5$	oil	84	60 to 61[e]	64	110 to 112[f]	89	43 to 44[g]	93
p-$C_6H_5C_6H_4CHC_6H_5$	62[h]	72	131 to 132[i]	70	142 to 143[j]	88	100 to 101[k]	88
p-$CH_3OC_6H_4CH-C_6H_5$	61[l]	55	130[m]	71	96[n]	68	oil	93

[a] n_D^{25} d_4^{25}, 1.09; MR_D calcd.: 65.14. Found: 65.48.

[b] n_D^{25}, 1.5760.

[c] Calcd. for $C_{15}H_{14}O_2$: C, 79.6; H, 6.24. Found: C, 79.9; H, 6.36. Amide, m.p. 113.5°C, calcd. for $C_{15}H_{15}OH$: N, 6.21. Found: 6.35. Anilide, m.p. 153 to 154°C, calcd. for $C_{21}H_{20}NO$: Found: N, 4.66.

[d] α-Naphthyl urethane, m.p. 118°C, calcd. for $C_{26}H_{23}O_2N$: N, 3.67. Found: N, 3.80.

[e] Cf. 61°C, Michael and Jean Petre, *Ber.* **25**, 1676 (1892).

[f] Cf. 115°C, McKenzie and Widdows, *J. Chem. Soc.* **107**, 713 (1915).

[g] Cf. 45 to 60°C, Remart and Amagat, *Comptes Rend.* **179**, 901 (1924).

[h] Cf. 62.5°C, Wittig and Petri, *Ann.* **513**, 26 (1934).

[i] Cf. 130 to 131°C, *ibid.*

[j] Cf. 141 to 142°C, Blicke and Grier, *J. Am. Chem. Soc.* **65**, 1725 (1943).

[k] Calcd. for $C_{20}H_{18}O$: C, 87.5; H, 6.57. Found: C, 87.4, H, 6.60.

[l] Calcd. for $C_{14}H_{13}OCL$: Cl, 15.2. Found: Cl, 15.3.

[m] Calcd. for $C_{15}H_{13}ON$: N, 6.27. Found: N, 6.30.

[n] Cf. 100°C, Poincet, *Comptes Rend.* **148**, 419 (1909).

TABLE 21

Stilbene Degradations

x IN STRUCTURE $x-C_6H_4CH{=}CHC_6H_5$	OXIDATION CONDITIONS	OXIDATION PRODUCT ISOLATED	MELTING POINT OF OXIDATION PRODUCT (°C)
p-CH_3	Aqueous alkaline permanganate, boiling	Terephthalic acid	over 300
m-CH_3	Aqueous alkaline permanganate, boiling	Isophthalic acid	over 300
p-C_6H_5	Permanganate in dry acetone, boiling	p-Phenylbenzoic acid	225
p-OCH_3	Permanganate in boiling aqueous acetone	p-Hydroxybenzoic acid*	213 to 214

*The oxidation products were benzoic and anisic acid. The anisic acid was cleaved as described in the experimental section.

TABLE 22

Experimentally Determined Radioactivities of Organic Compounds (microcuries per millimole)

DERIVATIVE	p-TOLYL	m-TOLYL	p-PHENYL	p-METHOXY
Diaryl acetic acid	4.40	4.08	4.32	4.04
Diaryl ethylaminehydrochloride	4.45	4.06	4.23	(4.00)*
Stilbene	4.31	4.10		4.10
Average of above three	4.39	4.08	4.25	4.05
Oxidation product (see Table 20)	2.84	2.50	2.43	3.87
Migration of substituted phenyl group (%)	64.7	61.3	57.2	95.5

*This value is for the p-anisyl(phenyl)acetonitrile.

EXPERIMENTAL[16]

Since each one of these series of compounds was carried through a similar set of reactions under closely similar conditions, and since the pertinent experimental data is summarized in Table 21, only the experiments upon the phenyl (*p*-anisyl series) are reported below. This series is chosen, not because it is typical, but because it presented difficulties not found in the other series.

p-*Methoxybenzohydryl Chloride.* The reduction of 106 g of *p*-methoxybenzophenone with zinc dust and alkali in alcohol solution gave a noncrystalline benzohydrol. This syrup was dried and then refluxed in benzene solution with 40 ml of thionyl chloride. The volatile solvents and excess thionyl chloride were removed by distillation and the dark, residual syrup distilled under high vacuum. The light-green distillate was redistilled to give, in several fractions, 58 g (55%) of a colorless liquid that immediately solidified and was recrystallized to give white needles (m.p. 61°C); Norris and Banta[17] report this as red oil.

2-Phenyl-2-(p-anisyl)acetonitrile-1-C^{14}. An intimate mixture of 8.3 g of the above chloride and 3.2 g of cuprous cyanide-C^{14} (prepared[18] by the interaction of cupric sulfate, sodium bisulfite, and sodium cyanide-C^{14} and dried in an oven at 110°C) was prepared and the flask containing it immersed in an oil bath preheated to 180°C. After 1 hr (during which time the bath temperature rose to 190°C), the flask was removed and partly cooled. The fluid product was extracted with chloroform. The filtered chloroform solution was concentrated and then diluted with hexane. The first crop of nitrile (2.8 g, m.p. 130°C) crystallized on cooling, and from the filtrate, an additional 2.0 g was obtained, giving a total yield of 4.8 g (71%). Repeated recrystallizations did not raise the melting point above 130°C.

Assay: 4.00 μc of C^{14} per millimole.

2-Phenyl-2-(p-anisyl)acetic-1-C^{14} *Acid.* Hydrolysis of the nitrile in boiling 70% sulfuric acid for from 1 to 6 hr produced only neutral gums. However, when 2.85 g of the nitrile was refluxed with a solution of 15 g of potassium hydroxide in a mixture of 15 ml of water and 50 ml of ethanol for two days, the acidic product was 3.08 g of a light-brown oil. Repeated extraction of this with boiling hexane and recovery of the acid from the hexane gave a white, crystalline acid (m.p. 96°C, 2.37 g, 68%).

Assay: 4.04 μc of C^{14} per millimole.

2-Phenyl-2-(p-anisyl)ethanol-1-C^{14}. The acid (2.00 g) was refluxed for 1 hr with 2.0 g of lithium aluminum hydride in about 75 ml of ether. After the excess hydride was destroyed by cautious addition of ethyl acetate, the hydrolysis was completed with 10% sodium hydroxide. Filtration and evaporation of the dried filtrate gave 1.75 g (93%) of a colorless oil.

p-*Methoxystilbene-*α,β*-*C^{14}. The noncrystalline carbinol obtained above was added to a suspension of phosphorus pentoxide in 25 ml of xylene, and this mixture was heated to boiling. After 15 min, the solution was cooled; the xylene was decanted; and the flask was rinsed with ether. The filtered solution was evaporated and the pale-yellow, crystalline residue crystallized from hexane to give 0.65 g of the stilbene as colorless prisms (m.p. 135°C).

Assay: 4.09, 4.11 μc of C^{14} per millimole.

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(16) Melting points were taken either upon a calibrated Fisher-Johns Block or upon a Kofler Heizbank. C^{14} assays were accomplished by a wet combustion of the compounds and ionization-chamber counting of the evolved carbon dioxide on a vibrating-reed electrometer. Microanalyses for carbon, hydrogen, nitrogen, and halogen were done by H. W. Galbraith, Knoxville, Tennessee.

(17) J. F. Norris and C. Banta, "The Reactivity of Atoms and Groups in Organic Compounds. IV. Second Contribution on the Carbon-Chlorine Bonds: The Rates of the Reactions of Certain Derivatives of Diphenylchloromethane with Ethyl Alcohol and with Isopropyl Alcohol," *J. Am. Chem. Soc.* **50**, 1604 (1928).

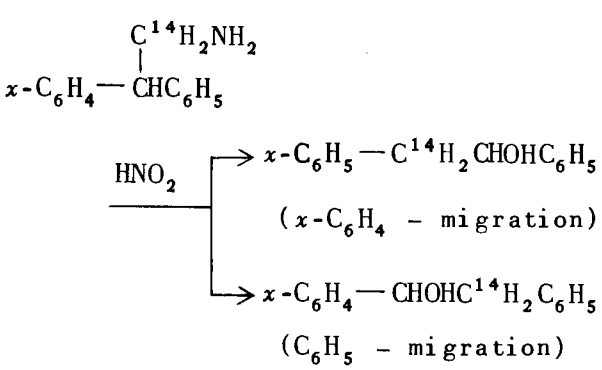
(18) H. J. Barber, "Cuprous Cyanide - Its Preparation and Use," *J. Chem. Soc.*, p. 79 (1943).

Oxidation of p-Methoxystilbene-α,β-C^{14}. A sample of the stilbene was refluxed for 15 min with a solution of 3 g of potassium permanganate in a mixture of 45 ml of acetone and 30 ml of water. The precipitated manganese dioxide was filtered off, and the colorless filtrate was concentrated in an air blast. After acidification, ether extraction, and evaporation of the solvent, 0.60 g of a mixture of benzoic and anisic acids was obtained. This mixture was dissolved in 30 ml of benzene, and the solution was refluxed 1.5 hr with 2 g of aluminum bromide. Evaporation of the dried ether extract gave 0.50 g of demethylated acid mixture. Extraction of this with carbon disulfide gave a residue of crude *p*-hydroxybenzoic acid (0.15 g), which after crystallization from dilute alcohol formed a white, crystalline powder (m.p. 213 to 214°C).

Assay: 3.90, 3.92, 3.80 μc of C^{14} per millimole.

A second recrystallization did not change the the C^{14} value.

Migratory Aptitudes in the Nitrous Acid Rearrangement of Diarylethylamines (L. S. Ciereszko[11] and J. G. Burr, Jr.). In connection with a recent study of migratory aptitude exhibited in the acid catalyzed rearrangement of C^{14}-labeled diarylethanols it was of interest to compare the data thus obtained with the migratory aptitudes observable in the nitrous acid-induced rearrangement of C^{14}-labeled diarylethylamine. The amine was produced by reduction of the appropriate nitrile with an alkaline Raney nickel catalyst. The nitrile was the reaction product of the corresponding benzhydryl chlorides with cuprous cyanide-C^{14} as described in the previous section.



The amines studied are those in which *x* is *p*-methyl, *m*-methyl, *p*-phenyl, and *p*-methoxy. These were obtained in 70 to 85% yield and isolated as the hydrochlorides. The reduction of 2-phenyl-2-(*p*-anisyl)acetonitrile-1-C^{14} was exceptional in that a poor yield of the amine hydrochloride was obtained.

The rearrangements were carried out by mixing a water solution of the amine hydrochloride with an excess of sodium nitrite dissolved in a small amount of water. A clear, stable solution resulted. In several cases a crystalline salt precipitated, which dissolved when more water was added or when the solution was warmed. The salt, 2,2-diphenylethylamine, when filtered, washed with water, and dried melted at 115 to 118°C with gas evolution. The analysis corresponded to that of the amine nitrite. It contained no ionic halogen and thus could not be the diazonium chloride that has the same elementary analysis for carbon, hydrogen, and nitrogen.

When these clear water solutions of the amine hydrochloride and sodium nitrite were warmed, gas evolution began at 70 to 80°C, and an oil deposited, which in some cases solidified. In the case of 2,2-diphenylethylamine, the product has been shown to consist only of desoxybenzoin.[19] In partial confirmation of this, it has been observed here that 1.70 g of this amine hydrochloride gave a rearranged crude carbinol from which a

[19] L. Hellerman, M. L. Cohn, and R. E. Hoen, "The Thermal Decomposition of Nitrites. The Nitrites of Triphenylethylomine and Diphenylethylamine," *J. Am. Chem. Soc.* **50**, 1724 (1928).

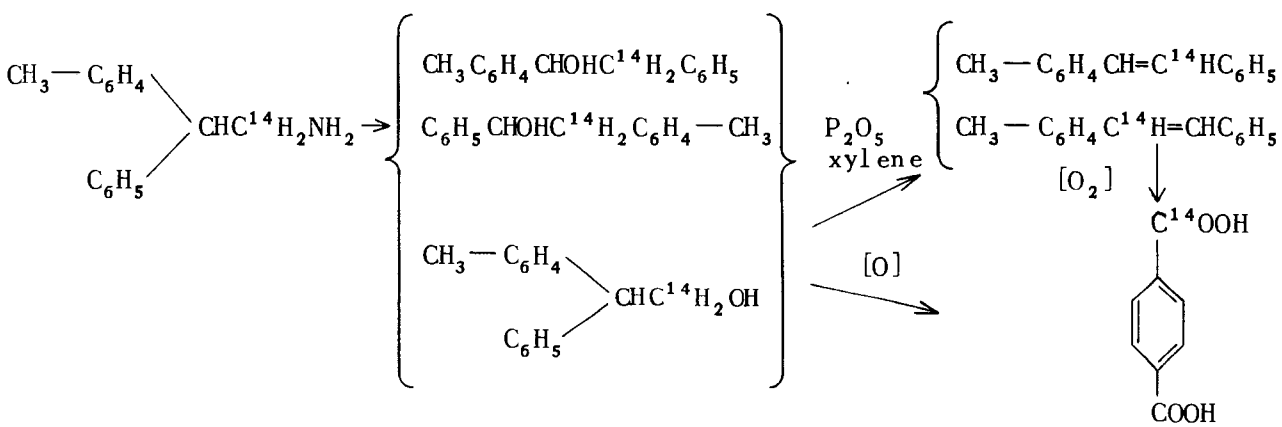
66% yield of recrystallized desoxybenzoin was isolated.

In order to determine whether appreciable amounts of unrearranged primary carbinol were present in the crude carbinol mixture so obtained, a portion of it was oxidized (as shown in the scheme below for the *p*-tolyl series), and another portion was dehydrated with phosphorus pentoxide in boiling xylene, the stilbene isolated, recrystallized, and oxidized. In the case of the *p*-tolyl series, the *m*-tolyl series, and the *p*-phenyl series, assay of each of the oxidation products so obtained gave values so nearly the same that calculations (making certain simplifying assumptions) showed that insufficient primary carbinol was present to affect appreciably the migration ratios observed.

The conditions of oxidation of the carbinol mixtures and stilbenes and the isolated oxidation product are shown in Table 25.

The comparison in Table 26 of these data with the results of the diaryl ethanol rearrangements (see Table 21) shows some striking contrasts.

The different values observed in these two rearrangements seem to be caused by the different conditions for the two types of reactions. The important differences are probably those of solvent and reagent, rather than temperature, since the temperatures of the two rearrangements are not very different. These factors are being studied in greater detail.



The data thus obtained by these processes is shown in Table 23. The C^{14} values are shown for the acids, since they were generally more easily handled than the nitriles and in addition were needed for the study of the carbinol rearrangement.

The yields, derivatives, and physical constants of the amines,

$$-C_6H_4\overset{\displaystyle C^{14}H_2NH_2}{\overset{|}{C}}H-C_6H_5\ ,$$

are shown in Table 24.

EXPERIMENTAL[20]

Each of these series of compounds was carried through the same series of reactions under essentially the same conditions, and the pertinent experimental data are summarized in Tables 23 and 24. Thus only

[20] Melting points were taken either upon a calibrated Fisher-Johns Block or upon a Kofler Heizbank. C^{14} assays were accomplished by a wet combustion of the compounds and ionization-chamber counting of the evolved carbon dioxide on a vibrating-reed electrometer. Microanalyses for carbon, hydrogen, nitrogen, and halogen were done by H. W. Galbraith, Knoxville, Tennessee.

TABLE 23

Experimentally Determined Radioactivities (microcuries per millimole)

COMPOUND	SERIES			
	p-TOLYL	*m*-TOLYL	*p*-PHENYL	*p*-METHOXY
Nitrile				4.16
Acid	4.42	4.08	4.32	
Amine hydrochloride	4.45	4.06	4.23	
Average	4.43	4.07	4.28	4.16
Oxidation product				
O_1	1.96	1.97	2.04	
O_2	2.14	1.96	2.14	2.44
Migration of substituted phenyl (%)	47	48	50	59

TABLE 24

Diarylethylamines and Derivatives

SERIES	AMINE		HYDROCHLORIDE	PICRATE
	YIELD (%)	m.p. (°C)	m.p. (°C)	m.p. (°C)
p-Methyl	68	oil	236[a]	203[b]
m-Methyl	86	oil	245[c]	196[d]
p-Phenyl	70	90[e]	252[f]	220[g]
p-Methoxy	23	oil	195[h]	

[a] Calcd. for $C_{15}H_{18}ClN$: Cl, 14.3; N, 5.66. Found: Cl, 14.2; N, 5.64.

[b] Calcd. for $C_{21}H_{20}N_4O_7$: N, 12.7. Found: N, 12.7.

[c] Calcd. for $C_{15}H_{18}ClN$: Cl, 14.3; N, 5.66. Found: Cl, 14.5; N, 5.66.

[d] Calcd. for $C_{21}H_{20}N_4O_7$: N, 12.6. Found: 12.6.

[e] Calcd. for $C_{20}H_{19}N$: N, 5.12. Found: N.

[f] Calcd. for $C_{20}H_{20}NCl$: Cl, 11.3; N, 4.47. Found: C, N.

[g] Calcd. for $C_{26}H_{22}N_4O_7$: N, 11.2. Found: N, 11.0.

[h] Calcd. for $C_{15}H_{18}ONCl$: Cl, 13.4; N, 5.31. Found: Cl, 13.6; N, 5.34.

TABLE 25

Stilbene Degradations

SERIES	STILBENE m.p. (°C)	OXIDATION CONDITIONS	OXIDATION PRODUCT ISOLATED AND MELTING POINT
p-Tolyl	120[a]	Boiling aqueous alkaline permanganate	Terephthalic acid; over 300°C
m-Tolyl	oil[b]	Boiling aqueous alkaline permanganate	Isophthalic acid; over 300°C
p-Phenyl	222[c]	Permanganate in anhydrous acetone, boiling	*p*-Phenylbenzoic acid; 225°C
p-Anisyl	135[d]	Permanganate in boiling aqueous acetone	*p*-Hydroxybenzoic acid[e]; 204°C

[a] Cf. 120°C, Anschultz, *Ber.* **18**, 1946 (1895).

[b] Cf. 49 to 50°C, Bergmann and Shapiro, *J. Org. Chem.* **12**, 57 (1947).

[c] Cf. 221°C, Bergmann and Weymann, *J. Org. Chem.* **9**, 415 (1944).

[d] Cf. 135 to 136°C, Van Duin, *Receiux De Trav. Chim.* **45**, 347 (1926).

[e] The oxidation products were benzoic and *p*-anisic acids. The anisic acid was cleaved by refluxing the mixture with aluminum bromide in benzene and the *p*-hydroxybenzoic acid isolated from the cleavage mixture by extraction with carbon disulfide in which it is insoluble.

TABLE 26

Experimental Migration Percentages

SERIES	SUBSTITUTED PHENYL GROUP MIGRATION (%)	
	CARBINOL (II) REARRANGEMENT	AMINE (I) REARRANGEMENT
p-Methyl	65	47
m-Methyl	61	48
p-Phenyl	57	50
p-Methoxy	96	59

the experimental details for the 2-phenyl-2(*p*-xenyl)ethylamine-1-C^{14} series are given here. This series is typical of all except the series containing *p*-methoxy in which conditions were similar but yields were lower.

2-Phenyl-2-(p-phenyl)ethylamine-1-C^{14}. Reduction of the nitrile (3.0 g, 11.5 mmoles) in alcohol solution with an alkaline W-7 Raney nickel catalyst was complete in 18 hr. The hydrogen uptake was 15 mmoles (65%). The nitrile was difficult to dissolve in alcohol; some nitrile remained at the end. The catalyst was filtered off and the filtrate evaporated. The residue partly crystallized. It was stirred with 50 ml of 20% hydrochloric acid. The resulting solid was filtered, dissolved in alcohol, and precipitated by addition of ether to give 1.90 g of white, crystalline solid (m.p. 252°C). An additional 0.50 g was isolated from the solvents, and thus a total of 2.40 g (70%) was obtained. The hydrochloride was difficult to dissolve in water, and recrystallization from water

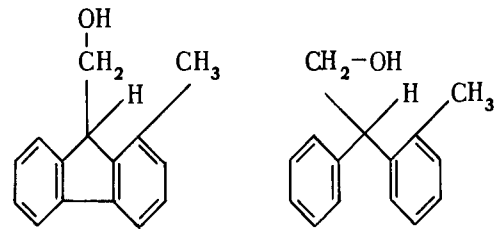
did not change the melting point. The picrate formed yellow needles melting at 220°C.

Rearrangement of 2-Phenyl-2-(p-biphenylyl)-1-C^{14}. A warm solution of 1.60 g of the hydrochloride in 176 ml of water was prepared, and a solution of 2.0 g of sodium nitrite in 5 ml of water was added. A thick mush of colorless crystals resulted that evolved a gas at 70 to 80°C. After about ½ hr the formation of a yellow oil was complete. The oil crystallized upon cooling.

Oxidation - O_1. A portion (0.65 g) of this crude carbinol mixture was refluxed 3 hr with a solution of 3 g of potassium permanganate in 50 ml of acetone. The acetone was filtered, and the manganese dioxide cake was washed thoroughly with dilute sodium hydroxide and water. Acidification of the aqueous filtrate gave a white precipitate. The crude *p*-phenylbenzoic acid was filtered, washed repeatedly with hot water, and recrystallized from benzene. It formed white needles (70 to 80 mg) that melted at 225°C.

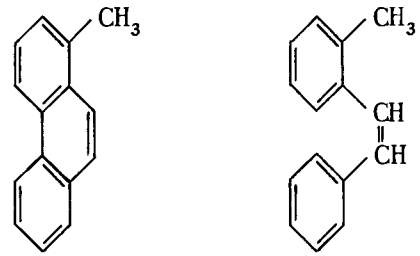
Oxidation - O_2. The remaining crude carbinol mixture (0.61 g) was refluxed for 30 min with phosphorous pentoxide in benzene (30 ml). The solvent was then decanted, chased with benzene, and evaporated. The residual, pale-yellow, crystalline solid (m.p. 217°C) was recrystallized from benzene-hexane to give 0.35 g of white, lustrous plates (m.p. 222°C). This crystalline product was oxidized as previously described. The yield of recrystallized *p*-phenylbenzoic acid (m.p. 225°C) was 70 to 80 milligrams.

Wagner Rearrangement of 2-Phenyl-2-(*o*-tolyl)-ethanol (B. M. Benjamin[21] and C. J. Collins). In conjunction with the work on 1-methylphenanthrene[22] it was of interest to compare results of the Wagner rearrangements of the two compounds, 1-methyl-9-fluorenmethanol (I) and 2-phenyl-2-(*o*-tolyl)-ethanol (II).



I II

These two compounds are quite similar, the essential structural difference being the bond between the two phenyl rings. Since the fluorene derivative (I) is a rigid planar molecule, the the rings must remain in approximately the same plane during the transition to 1-methylphenanthrene (III).



III IV

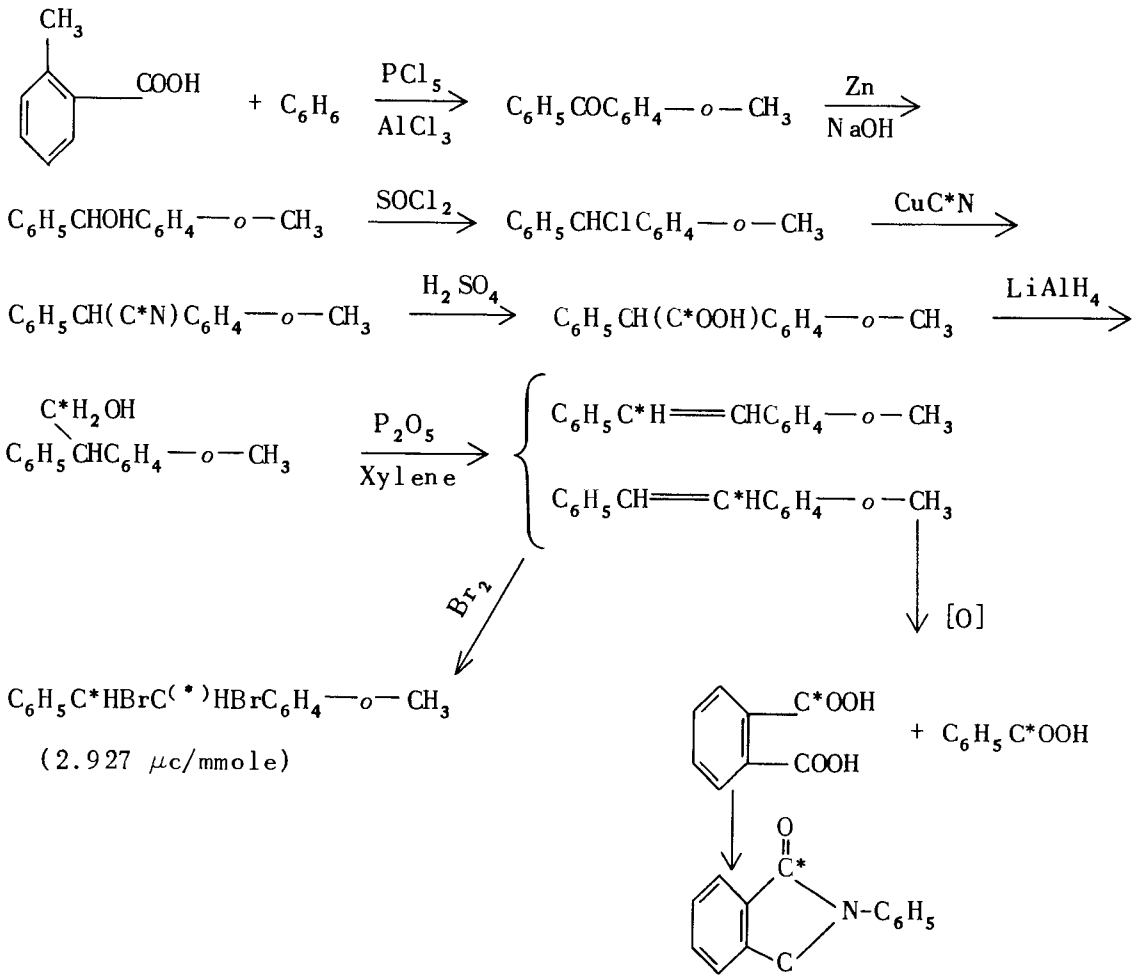
On the other hand, the rings of a molecule of the ethanol derivative (II) are not bound rigidly and are free to orient themselves in the most desirable position in the transition state insofar as steric factors will permit. The ethanol derivative (II) rearranges to form the stilbene (IV) whose structure is similar to that of phenanthrene (III) except for the bond between the two phenyl groups.

In the fluorene compound the *o*-tolyl and phenyl groups showed an equal tendency to migrate. In the ethanol compound the *o*-tolyl group migrated to an extent of 45% and the phenyl, 55%.

(21) Oak Ridge Institute of Nuclear Studies, Graduate Fellow from the University of Florida, Gainesville, Florida.

(22) B. M. Benjamin and C. J. Collins, *Chemistry Division Quarterly Progress Reports*, ORNL-1053, p. 75; ORNL-1116, p. 49; and ORNL-1153, p. 44.

The following flow sheet shows the reactions performed and data obtained in the preparation, rearrangement, and degradation of 2-phenyl-2-(*o*-tolyl)-ethanol. The experiments performed on 1-methylphenanthrene are described in a subsequent section.



EXPERIMENTAL

2-Methylbenzophenone. A Friedel-Crafts reaction was employed, following the procedure of Reddelien,[23] to condense *o*-tolyl chloride with benzene.

2-Methylbenzohydrol. The organic synthesis procedure[24] was employed to reduce 2-methylbenzophenone, except that heating was required after ½ hr of reaction. The 2-methylbenzohydrol melted at 95°C.[25]

2-Methylbenzohydryl Chloride.[26] The 2-methylbenzohydryl chloride was obtained

(23) G. Reddelien, "Ein Beitrag zur Frage nach der sterischen Hinderung," *Ber.* **48** Band II, 1468 (1915).

(24) F. Y. Wiselogle and H. Sonneberg, III., "Benyohydrol," *Organic Syntheses*, Coll. Vol. I, 2d ed. (H. Gilman and A. H. Blatt, eds.) p. 90-91.

(25) A. E. Tschitschibabin, "Phenyl-*o*-tolylcarbinol," *Journ. Russ. Phys.-Chem. Ges.* **41**, 1116 (1909). *Chem. Centr.* 32, Part I (1910).

(26) J. F. Norris and J. T. Blake, "The Reactivity of Atoms and Groups in Organic Compounds. V. Third Contribution on the Carbon-Chloride Bond: The Rates of the Reactions of Certain Derivatives of Diphenylchloromethane with Ethyl Alcohol," *J. Am. Chem. Soc.* **50**, 1808-12 (1928).

in 90% yield from the benzohydrol and a 5% excess of thionyl chloride. The reactants were mixed in benzene, and when the spontaneous reaction subsided, heat was applied gently on the steam bath for 15 minutes. All volatile material was removed with a water aspirator, and the material was distilled under vacuum. The distillate crystallized slowly (m.p. 40°C).

Phenyl-o-tolylacetonitrile. 1-Methylbenzohydryl chloride (25.76 g) was heated with freshly prepared cuprous cyanide[18] (7.19 g), whose radioactivity was 3 μc/mmole. Heating was continued in an oil bath at 250°C for 1 hour. The soluble organic material was taken up with ether and acetone. All solvents were evaporated and the nitrile was distilled at a pressure of 0.06 mm Hg; b.p. 109 to 111°C, yield 13.62 g; 83.4% based on CuCN.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.0; H, 6.32. Found: C, 85.9; H, 6.06.

Phenyl-o-tolylacetic Acid. Phenyl-(*o*-tolyl)-acetonitrile (4.56 g) was hydrolyzed with 70% sulfuric acid (50 ml) by boiling and stirring rapidly for 2 hours. The acid was extracted with ether, and the unhydrolyzed material was removed by taking up the acid in sodium bicarbonate solution. Acidification and extraction with ether gave 4.62 g (97.3%) of nearly pure acid. After three recrystallizations from cyclohexane, the melting point was constant at 96 to 97.6°C.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.24; H, 6.02.

2-Phenyl-2-(o-tolyl)-ethanol. Phenyl-(*o*-tolyl)-acetic acid (2 g) was added in small portions as an ether solution to an excess of lithium aluminum hydride in ether. When additions were complete, refluxing was continued for 1 hour, the complex was hydrolyzed, and the solution was made acid and extracted with ether. The ether solution was treated with dilute base to remove unreacted acid. The yield was 1.5 g (80%) of alcohol, which solidified upon standing. The melting point was constant at 58.5 to 59°C after five recrystallizations from cyclohexane.

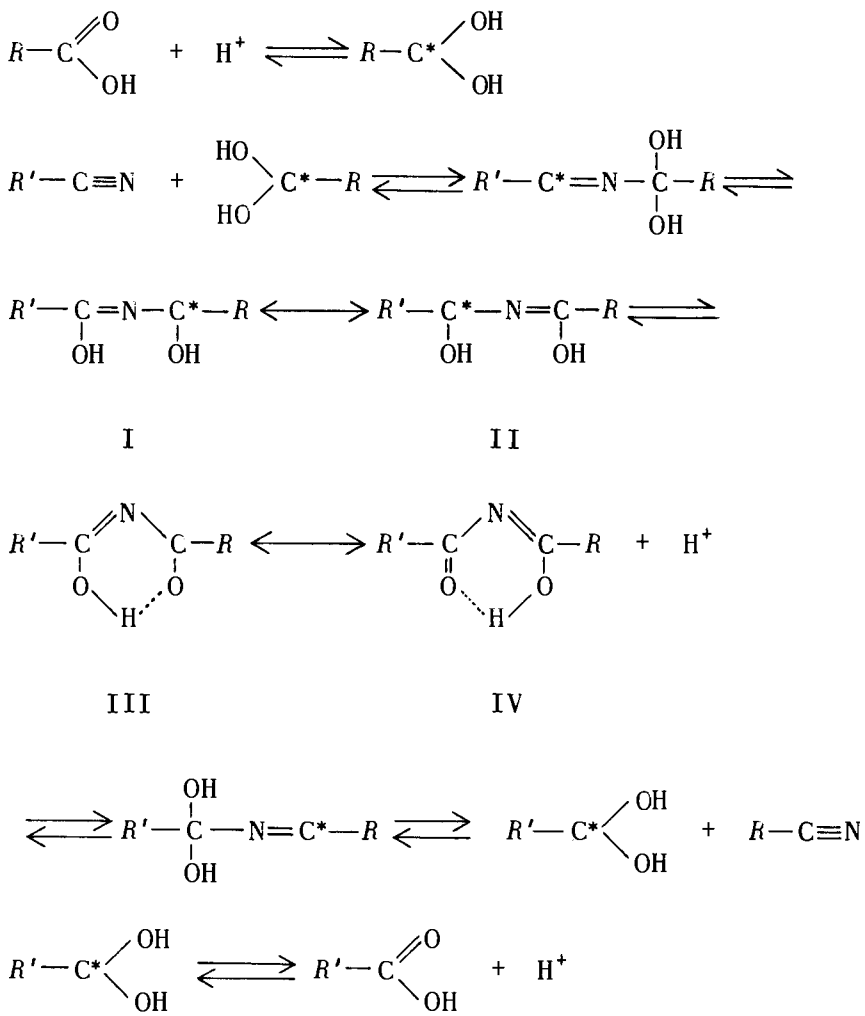
Anal. Calcd. for $C_{15}H_{16}O$: C, 84.8; H, 7.60. Found: C, 84.0; H, 7.59.

2-Methylstilbene. The phenyl-(*o*-tolyl)-ethanol (1.49 g) was dissolved in 15 ml of xylene, and about 4 g of phosphorus pentoxide was added. The mixture was refluxed for ½ hour. Water was added continuously and the xylene was blown off. Ether extraction gave 1.7 g of viscous oil. A portion of the oil was refluxed with bromine in carbon tetrachloride to give 2-methyldibromostilbene[27] (m.p. 160°C).

The second portion was placed in a vacuum desiccator for 24 hr to remove the last traces of xylene. It was then dissolved in 15 ml of acetic acid and refluxed with 4 ml of 40% peracetic acid for 1 hour. The acetic acid was evaporated and the residue oxidized with 4 g of potassium permanganate in 50 ml of water by refluxing 2 hours. The excess permanganate was reduced with ethanol and the manganese dioxide filtered off and washed with dilute base. The basic solution was extracted with ether, acidified, and reextracted continuously for 6 hours. The ether was evaporated and the solid residue washed with chloroform to remove benzoic acid. The impure phthalic acid was heated with aniline to make phthalanil, which could be conveniently purified and assayed. The phthalanil was recrystallized from ethanol to a constant melting point of 206 to 207°C.

Reaction of Acetonitrile with Benzoic Acid (A. R. Jones). The reaction of acetonitrile at 280°C

[27] F. Bergmann and D. Schapiro, "Application of the Meerwein Reaction. IV. The Synthesis of New Mono- and Disubstituted Stilbenes," *J. Org. Chem.* **12**, 57-66 (1947).



(1)

(2)

(3)

with benzoic acid to produce benzonitrile[28] and with adipic acid to produce adiponitrile[29] has been investigated. This reaction may be indicated formally by the equation:

$$R\text{—}COOH + R'\text{—}CN \longrightarrow R\text{—}CN + R'COOH$$

Clearly, either the cyanide and carboxyl groups or the —N and —OOH groups have exchanged places. It was of interest to utilize isotopic carbon to determine whether the carbon atoms of the two functional groups interchanged positions.

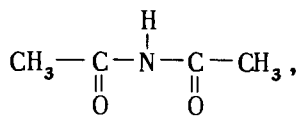
Benzoic acid, labeled with C^{14} in the carboxyl group, was heated to 280°C with acetonitrile and a trace of phosphoric acid. The acetic acid, isolated and identified as sodium acetate and benzyl thiuronium acetate, was nonradioactive. This result demonstrated that no exchange of the two functional groups had occurred. That the reaction was reversible was shown by heating acetic acid with benzonitrile in the presence of phosphoric acid; a good yield of benzoic acid was obtained.

A plausible reaction scheme is proposed involving acid catalyzed equilibria and an intermediate whose important contributing resonance forms are depicted as I and II or possibly as III and IV.

(28) C. E. Colby and F. D. Dodge, "The Action of Nitriles on Organic Acids," *Am. Chem. J.* **13**, 2 (1891).

(29) D. J. Loder (to duPont), U. S. Patent 2,377,795, June 5, 1945.

This formulation receives support from the experimental work of Gautier,[30] which showed that at 200°C acetonitrile and acetic acid yielded biacetamide (V)



V

which is the "keto" form of (III) or of the conjugate base of (I); and of Hentschel,[31] which showed that the pyrolysis of biacetamide at 250°C yielded acetonitrile and acetic acid.

EXPERIMENTAL

Benzoic-C^{14} acid (6.10 g, 18.73 microcuries) was placed in a stainless steel, high-pressure bomb with 8.20 g (200 mmoles) of acetonitrile and one drop of 85% phosphoric acid. The bomb was closed and heated in a rocking cradle to 280°C. After 5 min at that temperature, the bomb was allowed to cool overnight. There was no internal pressure evident when the bomb was opened. A strong odor of benzonitrile was present. The contents of the bomb were poured into a round-bottomed flask, which was then cooled in an ice bath. The volatile material was vacuum-distilled from an ice bath through an ice-cooled trap into one cooled with dry ice. The distillate was washed with water into an Erlenmeyer flask. Titration with standard sodium hydroxide, using phenolphthalein as an indicator, showed the presence of 13.8 mmoles of acidic material.[32] The solution was thoroughly extracted with ether and then boiled momentarily to remove all traces of the ether. One-half of the solution was evaporated to dryness and partial dehydration occurred (m.p. 320 to 325°C after loss of water; sodium acetate, m.p. 324°C). The remaining one-half of the solution was evaporated to 5 ml and cooled. Several drops of concentrated hydrochloric acid were added. The mixture was added to a solution of 2 g of benzyl thiuronium chloride in 10 ml of water and the resulting solution was placed in a refrigerator overnight. The crystalline salt was filtered, washed with water, and dried at 50°C. The crude solid (1.12 g, m.p. 133 to 136°C) was recrystallized from aqueous alcohol, and material of melting point 134.5 to 136°C was obtained. A mixture melting point with benzyl thiuronium acetate prepared from pure acetic acid was not depressed.

The sodium acetate and benzyl thiuronium acetate were tested for radioactivity. The solids were assayed with a Geiger-Mueller tube counter; the carbon dioxide obtained by combustion was placed in an ionization chamber and assayed with a vibrating-reed electrometer. Neither compound showed activity above background.

Benzonitrile (10.0 g) was heated to 280°C with 10.5 g (175 mmoles) of glacial acetic acid and one drop of 85% phosphoric acid in a stainless steel bomb. After 5 min at that temperature, the bomb was allowed to cool overnight. There was a slight internal pressure evident when the bomb was opened. The product, a semisolid mass, was dissolved in ether. The ether solution was extracted with 1.5 *N* sodium hydroxide solution. The basic extract was washed thoroughly with ether. It was then boiled for several minutes to remove all traces of ether, cooled, and acidified with concentrated hydrochloric acid. The precipitate was filtered, washed thoroughly with water, and dried in air. The tan solid weighed 8.24 g and the melting point (120.8 to 122°C) was not depressed by admixture with pure benzoic acid (m.p. 122.0 to 120.6°C).

(30) M. A. Gautier, "Action des acides organiques sur des les nitriles da la serie des acides gras," *Compt. Rend.* 67, 1256 (1868).

(31) W. Hentschel, "Ueber Dincetamid," *Ber.* 23 Band II, 2395 (1890).

(32) An experiment performed in the same manner, except that the benzoic acid was omitted, yielded 0.2 mmoles of acidic material, presumably due to hydrolysis of acetonitrile by water in the 85% phosphoric acid.

Isotope-Exchange Reactions Involving the Carbon-Carbon Bond (C. D. Douglass[33] and O. K. Neville). The study of the exchange of the benzal moiety in compounds formed by the "aldol" type of condensation reactions[34] has been extended to the Perkin reaction.

$$C_6H_5CHO + (CH_3CO)_2O + NaOAC \longrightarrow C_6H_5CH{=}CHCOOH$$

The exchange of the benzal group in cinnamic acid with benzaldehyde-7-C^{14} has been attempted under several reaction conditions and found not to occur; thus, the irreversibility of the Perkin reaction was demonstrated.

In a previously reported experiment,[34] 2,4-dinitrostilbene was found to exchange with benzaldehyde-7-C^{14} in the presence of a catalytic amount of piperidine. Since no water or equivalent substance was added, these results were unexpected in that they indicated a path of exchange not involving addition of water to the double bond. Therefore the result was checked after carefully purifying all materials by carrying out the experiment under anhydrous conditions. In the presence of pure piperidine or pure piperidine acetate, 2,4-dinitrostilbene was found not to exchange with benzaldehyde-7-C^{14}. In the presence of piperidine plus a molar proportion of water, exchange was complete at 110°C in 2 hours. Thus water was proved to be necessary for exchange to occur. Table 27 shows the results of several of these experiments.

EXPERIMENTAL

The preparation of benzaldehyde-7-C^{14} has been described previously.[34] In a typical experiment, 0.63 g of 2,4-dinitrostilbene and 0.25 ml of benzaldehyde-7-C^{14} were mixed and heated under reflux in an oil bath at 140°C. One drop of water and one drop of piperidine were added. The heating was continued for 2 hours. After cooling, the resulting solid was washed with cold benzene and cold methanol several times and finally crystallized from benzene twice. The Geiger-Mueller counter showed the compound to be nonradioactive.

STRUCTURE DETERMINATION STUDIES

Structure Determination of Carbon-14 Labeled 1-Methylphenanthrene (B. M. Benjamin[21] and C. J. Collins). Additional proof of the structure of the methylfluorenonecarboxylic acid[35] from the degradation of 1-methylphenanthrene has been obtained. The acid has been decarboxylated with quinoline and copper chromite catalyst. The oxidation of the methylfluorenone gave, in addition to fluorenone-3-carboxylic acid, an acid that was identified as trimelletic acid. 3-Methylfluorenone was prepared independently by the method of Ullmann.[36] The oxime of 3-methylfluorenone was prepared (m.p. 185°C) and compared by mixed melting point with the oxime of the methylfluorenone from the decarboxylation experiment. No depression in melting point was found.

The degradation was repeated with tracer level 1-methylphenanthrene. The C^{14} was found to be equally

(33) Oak Ridge Institute of Nuclear Studies, Graduate Fellow from the University of Oklahoma, Norman, Oklahoma.

(34) C. D. Douglass and O. K. Neville, "Isotope-Exchange Reactions Involving the Carbon-Carbon Bond," *op. cit.*, ORNL-1153.

(35) Benjamin and Collins, "Structure Determination Studies," *op. cit.*, ORNL-1153, p. 44.

(36) F. Ullmann and E. Mallet, "Ueber einige Fluorenonderivate," *Ber.* 31 Band II, 1694-6 (1898); F. Ullmann and H. Bleier, "Zur Darstelluag von o-Aminobenzophenonderivaten," *Ber.* 35 Band IV, 4273-80 (1902).

distributed between positions nine and ten. Table 28 shows the reactions and compounds involved and data obtained. Apparently the 1-methyl group has no influence upon the direction of rearrangement of 1-methyl-9-fluorenmethanol in the Wagner rearrangement.

EXPERIMENTAL

3-Methylfluorenone oxime was prepared from 3-methylfluorenone, hydroxyl-aminehydrochloride, and sodium hydroxide by heating to near reflux in aqueous alcohol for 2 hours. After the solution was allowed to stand, light-yellow crystals formed. Recrystallization four times from cyclohexane gave a white powder (m.p. 185°C).

The oil obtained by decarboxylation of 3-methyl-4-fluorenonecarboxylic acid was treated with hydroxylamine as above. Seven recrystallizations gave a white product (m.p. 175 to 180°C). A mixed melting point of the two oximes showed no depression.

The carbon dioxide from the decarboxylation of 3-methyl-4-fluorenonecarboxylic acid was caught in a barium hydroxide trap. The barium carbonate was purified by centrifugation and washing with water free of carbon dioxide until no alkaline reaction to phenolphthalein appeared in the supernatent liquid. After a final washing with acetone, the barium carbonate was dried in vacuum at 76°C for 5 hr before assay.

Structure Determination of Chrysene-5,6-C_1^{14} (D. N. Hess and C. J. Collins). Chrysene-5,6-C_1^{14} has been degraded according to the scheme outlined

TABLE 27

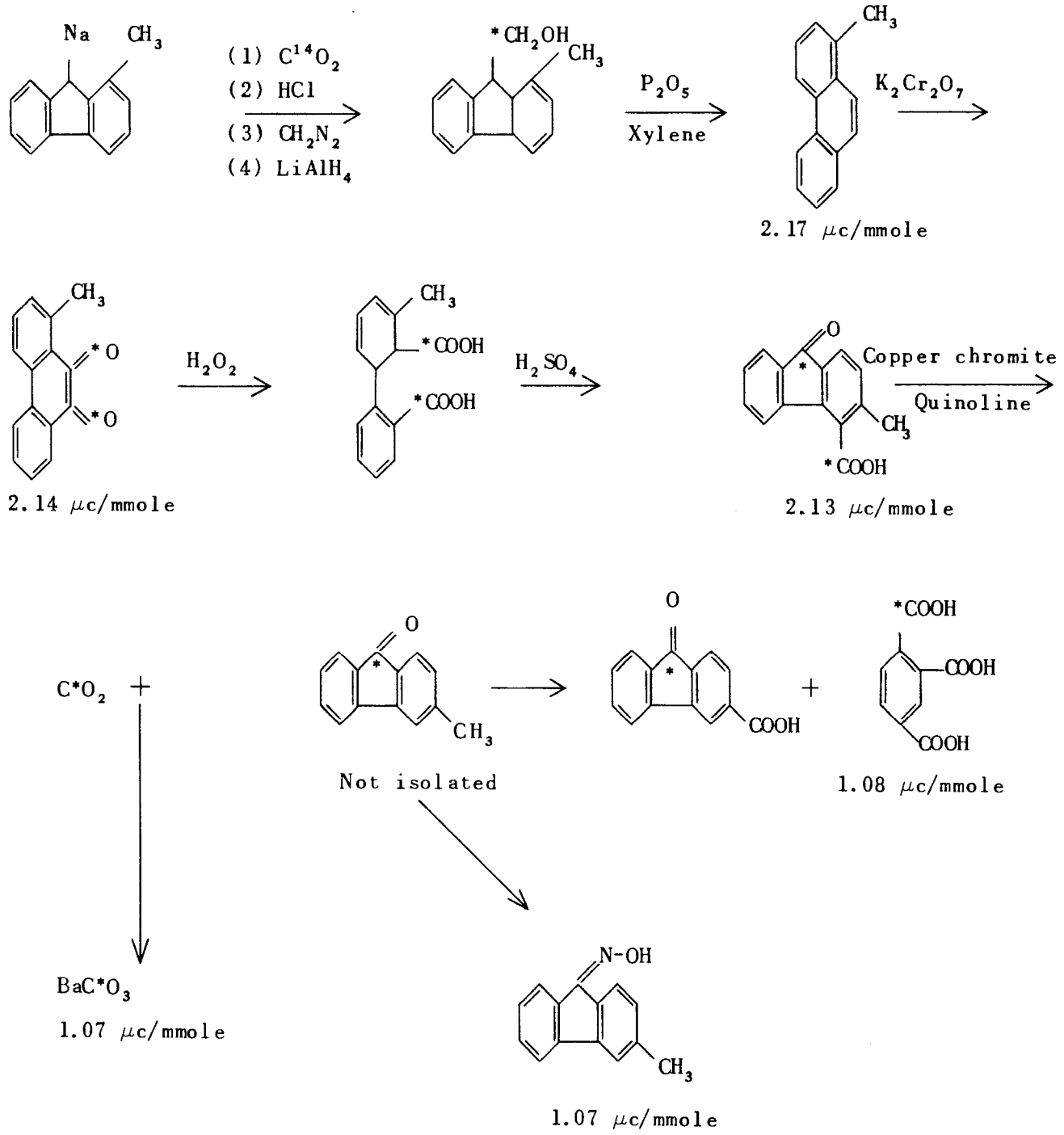
Results of Exchange Studies on Condensation Reactions

REACTANTS	CATALYST	TEMPERATURE (°C)	TIME (hr)	SOLVENT	EXCHANGE*	REMARKS
$2,4-(NO_2)_2C_6H_3CH=CHC_6H_5{}^{14}HO$	Piperdine	Room	20	None	-	Precautions taken to exclude water from reaction
	Piperdine acetate	140	2	None	-	Precautions taken to exclude water from reaction
	Piperdine	140	2	None	+	Small amount of water present
	Piperdine	110	2	None	-	Water was excluded
$C_6H_5CH=CHCOOH-C_6H_5C^{14}HO$	Potassium acetate	170	6	Biphenyl	-	
$C_6H_5CH=CHCOOH + CH_3COOCOC^{14}H_3$	Sodium acetate	170 to 175	4	None	-	

* + = exchange.
- = no exchange.

TABLE 28

Flowsheet of Preparation and Degradation of 1-Methylphenanthrene



previously.[37] It has been shown that the C^{14} is distributed between positions 5 and 6 in the ratio 76:24.

EXPERIMENTAL

Chrysene-5,6-C_1^{14} of high level activity was added to chrysene obtained from the Reilly Tar and Chemical Company. It was purified by dissolving it in benzene and extracting six times with concentrated sulfuric acid and finally with water.

The chrysene (I) was oxidized to chrysoquinone (II) in 71% yield (m.p. 137 to 138°C) by the method of Graebe and Honigsberger.[38] Oxidation of the quinone with hydrogen peroxide in acetic acid solution resulted in a 49% yield of 2-phenylnapththylene-1,2′-dicarboxylic acid (III) (m.p. 205 to 208°C).

Treatment of the dicarboxylic acid with concentrated sulfuric acid at room temperature yielded a mixture of two keto acids: H-benzo[a]fluoren-11-one-7-carboxylic acid and H-benzo[b]fluoren-11-one-6-carboxylic acid. The yield of crude product was 48%. In order to separate the two isomeric keto acids, the angular keto acid was selectively esterified with methyl alcohol and acetyl chloride catalyst to give the methyl ester(IV) (m.p. 174 to 175°C). Based on the yield of ester, the amount of angular keto acid present in the mixture was 45%.

The linear keto acid was not pure at this point; the presence of an impurity was definitely shown. In spite of successive recrystallizations from different solvents, chromatography, sublimation, and the repeated preparation of the sodium salt of the keto acid and subsequent acidification, no removal of the impurity was effected. Consequently, the ester of the linear keto acid (V) was prepared by conversion to the acid chloride, which was refluxed with methanol. The ester had a melting point of 155 to 156°C.

Each of the esters was saponified by using 4% sodium hydroxide in a 4:1 alcohol-water solution. The angular keto acid (VI) had a melting point of 283 to 288°C and the linear keto acid (VII) had a melting point of 258 to 259°C.

The keto acids were decarboxylated in quinoline to their respective ketones with 85% yield by using copper chromite as catalyst. The H-benzo[a]fluor-11-one (VIII) had a melting point of 135 to 136°C and the H-benzo[b]fluor-11-one (IX) had a melting point of 156 to 157°C.

Radioanalyses. Table 29 illustrates the degradative procedure and the distribution of the C^{14}.

The average of 18 analyses for the specific activity of II, IV, V, VI, and VII was 2.04 ± 0.03 μc/mmole. The specific activity of the angular ketone (VIII) was 1.80 μc/mmole and for the linear ketone (IV) 1.27 μc/mmole, based on two analyses for each ketone.

The following relations of radioactivities of the positions are apparent:

$$\text{molar radioactivity of I} = x + y;$$

$$\text{molar radioactivity of IX} = y + \frac{x}{2};$$

$$\text{molar radioactivity of VIII} = x + \frac{y}{2},$$

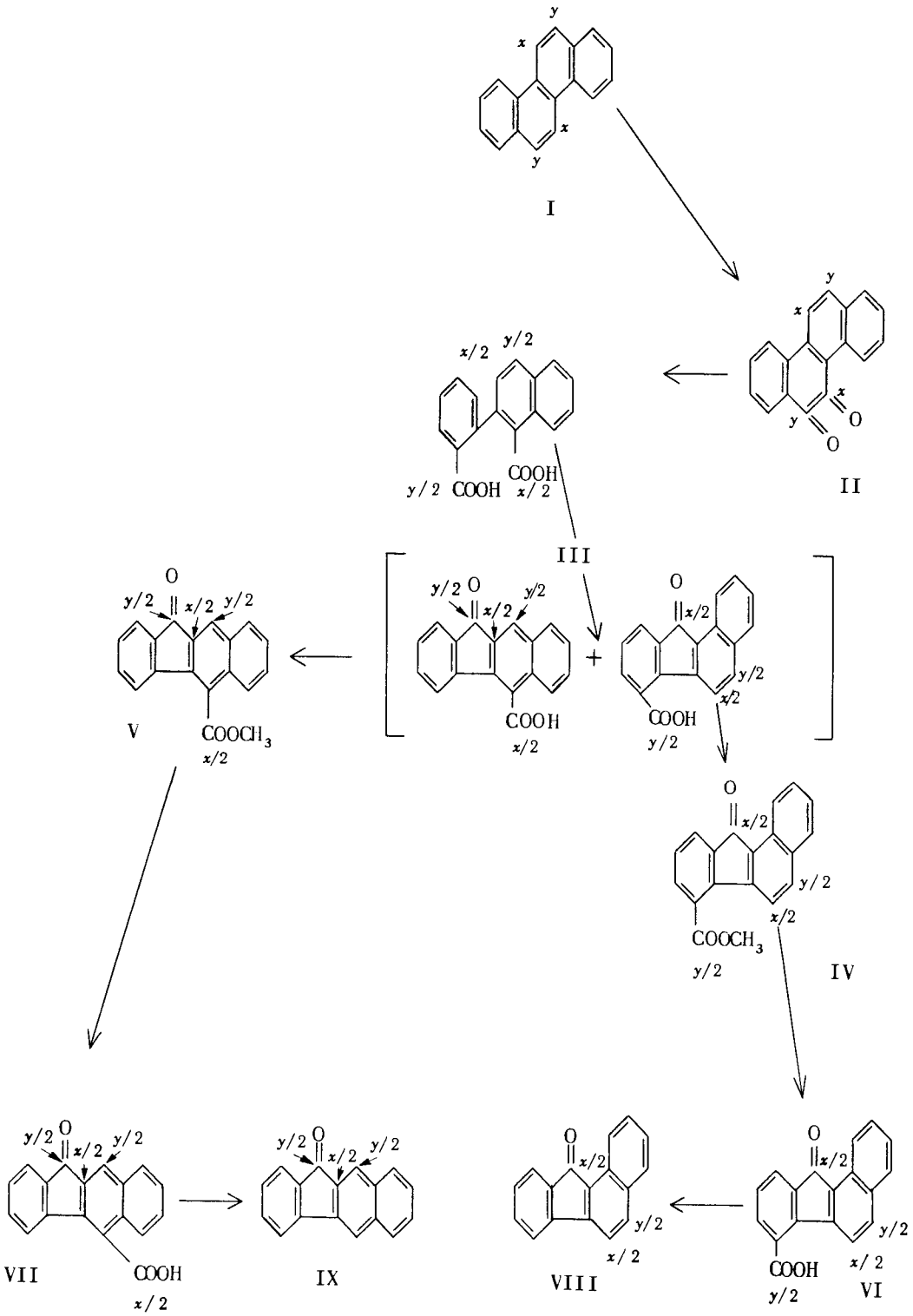
where x is the molar radioactivity of the five position of chrysene-5,6-C_1^{14} (I), and y is the molar radioactivity of the six position. From these data x = 1.55 μc/mmole and y = 0.49 μc/mmole, and the C^{14} was distributed between positions five and six of the chrysene structure (I) in the ratio of 76:24.

(37) D. N. Hess and C. J. Collins, "Structure Determination Studies," *op. cit.*, ORNL-1153, p. 45.

(38) C. Graebe and F. Honigsberger, "Ueber die Oxydationsproducte des Chrysens," *Ann.* **311**, 262 (1900).

TABLE 29

Degradation of Chrysene-5,6-C_1^{14} and Distribution of C^{14}



CHEMISTRY OF SEPARATIONS PROCESSES

PROTIUM-DEUTERIUM EXCHANGE IN ION-EXCHANGE RESINS

P. Agron J. Halperin

Several sieved portions of Dowex-50 resin have been washed and conditioned for the proposed exchange studies. Density-gradient tubes have been set up in a temperature-controlled bath for analysis of D_2O-H_2O mixtures by density determination, and calibration of the gradients is now in progress. The construction of four cells for irradiation studies in the Van de Graaff electron beam is nearing completion.

ORGANIC CHEMISTRY OF SOLVENTS

W. H. Baldwin C. E. Higgins

***n*-Butyl Phosphorus Compounds.** Phosphonic acid esters have been successfully employed in the extraction of uranium from aqueous nitric acid solutions.[1,2] It was in an effort to extend the range of compounds with carbon to phosphorus bonds that the series of compounds (1) tri-*n*-butyl phosphate, (2) di-*n*-butyl *n*-butylphosphonate, (3) *n*-butyl di-*n*-butylphosphinate, and (4) tri-*n*-butyl phosphine oxide were obtained and compared on the basis of extraction of uranium. It has been found that as the number of direct carbon-to-phosphorus linkages was increased, the extraction of uranium increased so that the phosphinate and phosphine oxide removed nearly all the uranium from aqueous uranyl nitrate solution that contained no additional salting agent. Furthermore, the phosphine oxide removed nearly all the uranium from aqueous solutions of uranyl sulfate, uranyl chloride, and uranyl fluoride (see Tables 30 and 31).

Tri-n-butyl Phosphate (TBP). The commercial product, $(BuO)_3PO$, obtained from the Chemical Technology Division pilot plant was further purified by distillation under reduced pressure just before use.

Di-n-butyl n-Butylphosphonate. Sodium di-*n*-butyl phosphite was reacted with *n*-butyl bromide to form $(BuO)_2BuPO$ according to Kosolapoff's[3] procedure.

n-Butyl Di-n-butylphosphinate. The previously unreported compound, $(BuO)Bu_2PO$, was prepared by the reaction between *n*-butyl magnesium bromide and di-*n*-butyl chlorophosphate.

Tri-n-butyl Phosphine Oxide. The phosphine oxide, Bu_3PO, was prepared by the reaction between *n*-butyl magnesium bromide and phosphorus oxychloride as described by Davies and Jones.[4] Tributyl phosphine oxide is a crystalline solid at room temperature, whereas all the others are liquid. The identity of each of the compounds was established through the determination of phosphorus.

Distribution of Uranyl Nitrate. Equilibration tests were made at 25°C with 0.1 *M* uranyl nitrate aqueous solutions containing (1) no additional acid, (2) 0.6 *M* nitric acid, and (3) 3 *M* nitric acid. Equal volumes of aqueous phase and the 0.75 *M* compound in CCl_4 were tumbled end-over-end for

(1) W. H. Baldwin and C. E. Higgins, "Organic Chemistry of Solvents," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1951*, ORNL-1053, p. 83-88.

(2) C. M. Slansky, "Solvent Extraction Research," *Quarterly Report, July Through September, 1951 - Chemical Research*, HW-22138.

(3) G. M. Kosolapoff, "Isomerization of Alkylphosphites. III. The Synthesis of *n*-Alkylphosphonic Acids," *J. Am. Chem. Soc.* **67**, 1180 (1945).

(4) W. O. Davies and W. J. Jones, "Tertiary Phosphines Containing the Butyl Radical," *J. Chem. Soc.* p. 33 (1929).

TABLE 30

Extraction of Uranium with Butyl Phosphorus Compounds

Conditions: Equal volumes of aqueous feed (0.1 *M* in uranium and HNO_3 molarity as indicated) and organic feed (0.75 *M* compound in CCl_4) tumbled end-over-end at 25°C for 1 hr, centrifuged, and separated.

SOLVENT	URANIUM EXTRACTED (%)		
	FOR 0.1 *M* HNO_3	FOR 0.6 *M* HNO_3	FOR 3.0 *M* HNO_3
Tri-*n*-butyl phosphate, $(BuO)_3PO$	15.6	56.0	96.5
Di-*n*-butyl *n*-butyl-phosphonate $(BuO)_2BuPO$	60.0	98.0	99.4
n-Butyl di-*n*-butyl-phosphinate $(BuO)Bu_2PO$	98.5	99.9	99.9
Tri-*n*-butyl phosphine oxide, Bu_3PO	99.7	99.9	99.9

1 hr, centrifuged, and separated (see Table 30).

Tributyl phosphine oxide extracted nearly all the uranium under all the conditions studied and the phosphinate extracted nearly as much. The phosphonate, although not extracting so much uranium as the phosphinate and the phosphine oxide, did extract more than TBP at the three acidities. The extraction of nitric acid followed the same pattern as the extraction of uranyl nitrate.

Distribution in the Presence of Other Anions. Qualitative tests were made with other uranyl salts (see Table 31), and again the phosphine oxide extracted nearly all the uranium from aqueous solutions of the sulfate, chloride, and fluoride. The extraction by the esters was not so complete as with the phosphine oxide but was increased by the addition of acids.

Discussion. The carbon-to-phosphorus bond in the phosphonate, phosphinate, and phosphine oxide has much greater stability toward hydrolytic cleavage than does the ester linkage (carbon-to-oxygen-to-phosphorus). The phosphine oxide has no ester linkages and should be much more stable in acid solutions than the three esters TBP, phosphonate, and phosphinate.

Pickard and Kenyon[5] isolated compounds that had been formed by the addition of acids or salts to the phosphine oxides. The compounds have the general formulas $2R_3PO \cdot HX$ and $2R_3PO \cdot MX_2$, where M is a divalent metal. There is qualitative evidence of compound formation between uranyl nitrate and tributyl phosphine oxide, and it is expected that an analytically pure compound can be isolated. Compound formation of this type may be involved in the extraction mechanism.

[5] R. H. Pickard and J. Kenyon, "Contributions to the Chemistry of Oxygen Compounds. I.," *J. Chem. Soc.* **89T**, 262 (1906).

TABLE 31

Qualitative Observations on the Effect of Other Anions on Uranium Extraction*

Organic feed: 0.75 *M* phosphorus compound in CCl_4

Aqueous feed: 0.1 *M* uranyl salt plus additions as indicated

SOLVENT	URANYL SULFATE EXTRACTED	URANYL CHLORIDE EXTRACTED	URANYL FLUORIDE EXTRACTED
TBP	Negligible amount from aqueous solution Negligible amount from 0.25 *M* HNO_3	Negligible amount from aqueous solution	Negligible amount from aqueous solution All from 3 *M* HNO_3
Di-*n*-butyl *n*-butyl-phosphonate		Negligible amount from aqueous solution 90% from 3 *M* HCl	Negligible amount from aqueous solution All from 1.5 *M* HNO_3
n-Butyl di-*n*-butyl-phosphinate	Negligible amount from aqueous solution All from 0.25 *M* HNO_3 60 to 70% from 0.2 *M* NH_4NO_3 80% from 4 *M* H_2SO_4	30 to 40% from aqueous solution All from 0.5 *M* HCl	50% from aqueous solution All from 0.5 *M* HNO_3
Tri-*n*-butyl phosphine oxide	All from aqueous solution	90% from aqueous solution 100% from 0.5 *M* HCl	All from aqueous solution

*These estimates are based upon visual observation of the color in the two phases after equilibration.

Status of the Problem. The observations reported here show that compounds of these types are potentially useful. Their utility will be more exactly defined when quantitative data are available to demonstrate their physical and chemical properties. Quantitative data needed include:

1. stability toward hydrolysis, as hydrolysis of the C-O-P linkage might be affected by the presence of C-P bonds,
2. solubility in water,
3. radiation stability,
4. behavior of fission products and plutonium during extraction,
5. behavior of other cations (Th, Pa, Al, Fe, etc.), and
6. viscosity.

The fact that phosphonates do extract uranium so readily leads inevitably to the consideration of diphosphonate esters of the general formula $(RO)_2P(O)(CH_2)_xP(O)(OR)_2$. Compounds of this type should combine the desired properties of low miscibility with water and low equivalent weight per phosphorus atom. Such

compounds will be tested as they become available.

Tribenzyl Phosphate. The mechanism of extraction is believed to involve the oxygen on the phosphorus atom rather than the ester oxygens of the phosphates (note the extraction by phosphine oxide). The phenyl esters extract less uranium than the alkyl esters,[1] and this can be explained by the inductive effect of the phenyl group on the P-O bond. It was expected that the effect of the phenyl group would be lessened if it were further away from the phosphorus atom as in tribenzyl phosphate. It was found (Table 32) that tribenzyl phosphate did extract more uranium (17.6%) than triphenyl phosphate (0.004%) but less than tributyl phosphate (56.5%).

TABLE 32

Extraction by Phosphates

Conditions: Equal volumes of aqueous (0.1 *M* UNH, 0.6 *M* HNO_3) and organic (0.75 *M* phosphate in CCl_4) solutions were tumbled end-over-end at 25°C for 1 hour.

	URANIUM EXTRACTED (%)
Tribenzyl phosphate	17.6
Triphenyl phosphate	0.004
Tributyl phosphate	56.5

ZIRCONIUM SPECIES IN HCl-$HClO_4$ SOLUTIONS

J. P. McBride

The investigation of the extraction of zirconium from chloride solutions using thenoyltrifluoroacetone in benzene has been completed and a report is being issued.[6]

[6] J. P. McBride, *Zirconium Species in HCl-$HClO_4$ Solutions*, ORNL-1201.

FUNDAMENTAL ION-EXCHANGE STUDIES

Rate Studies with Ion Exchangers (B. A. Soldano and G. E. Boyd). Heavy oxygen (O^{18}) containing water has been used in fundamental studies on the nature of the gel water in ion exchangers. In one series of experiments chromium(III) ion was placed in a cation exchanger (nominal 16% DVB) and equilibrated with 1.4% H_2O^{18}. This preparation was then placed in pure ordinary water, and the rate at which O^{18} left the exchanger was determined. It was hoped that two processes might be distinguished by (1) a rapid diffusion of the "free" or solvent water out of the exchanger and (2) a slow exchange of the water of hydration on the chromium(III) in the exchanger. Earlier studies[7,8] had shown that H_2O^{18} contained on chromium(III) slowly exchanged in homogeneous aqueous solutions. Actually two rates were observed; one reaction was extremely fast with a half-time of less than 30 sec, and the other was a slow reaction with a half-time approximately the same as found in homogeneous solutions. An estimate of the quantity of water associated with the slow process yielded 6 H_2O per chromium(III) ion and confirmed the view that the chromic hydration water was involved.

Further heavy-water self-diffusion experiments were performed with hydrogen resin of nominal 4, 8, and 16% DVB cross linking, and the results are summarized in Table 33.

When the values at 25°C (Table 33) are compared with the value of

[7] J. P. Hunt and H. Taube, "The Exchange of Water Between Hydrated Cations and Solvent," *J. Chem. Phys.* **19**, 602 (1951).

[8] R. A. Plane and H. Taube, "Observations of the Kinetics of the Exchange of Water Between $Cr(H_2O)_6^{+++}$ and Solvent," *J. Phys. Chem.* **56**, 33 (1952). We would like to thank R. A. Plane for his helpful advice in the interpretation of the experiments with Cr(III) in cation exchangers.

TABLE 33

Self-Diffusion of H_2O^{18} in Dowex-50 Type Cation Exchangers

NOMINAL % DVB	$D_{3.4°}$ (cm^2/sec)	$D_{25°}$	E_{act} (cal/mole)
4	4.51×10^{-6}	9.14×10^{-6}	4600
8	$(1.23 \text{ to } 1.5) \times 10^{-6}$	3.25×10^{-6}	~5000
16	1.1×10^{-6}	2.2×10^{-6}	~5000

TABLE 34

Self-Diffusion in the Na^+-Rb^+ Exchange System

Ionic strength of external electrolyte constant at μ = 0.22 molar

COMPOSITION OF EXCHANGER	ION	$D_{0.3°}$ (cm^2/sec)	$D_{25°}$	E_{act} (cal/mole)
100 NaR	Na^+	3.42×10^{-7}	9.44×10^{-7}	6500
41 RbR + 59 NaR	Na^+	4.71×10^{-7}	1.12×10^{-6}	5760
	Rb^+	5.76×10^{-7}	1.32×10^{-6}	4810
100 RbR	Rb^+	6.06×10^{-7}	1.38×10^{-6}	5140

30.0×10^{-6} cm^2/sec for the self-diffusion of H_2O^{18} in water[9] at the same temperature, it is seen that the resin acts to hinder the diffusion of its water of gelation. Interestingly, however, the activation energies are almost the same, namely 4410 for pure water and 4600 to 5000 cal/mole for the exchanger. This suggests that the relative slowness of self-diffusion in the exchanger is to be attributed to steric effects. It does not seem that H_2O^{18} molecules are transported by the self-diffusing hydrated ions in the exchanger, since the rates for even the fastest ions are three or more times smaller than the values listed in Table 33.

Ionic self-diffusion studies have also been conducted on exchangers containing two ions. Data typical of such "mixed diffusions" are given in Table 34. A comparison of the self-diffusions of Na^+ and Rb^+ ions in the mixed exchanger with their respective values in pure Na or Rb exchanger shows in the mixed exchanger that the faster Rb^+ ion is slowed down, whereas the slower Na^+ ion is speeded up. This change is accompanied by a lowering of the activation energy for both ions. An increase in the rate of Na^+ ion and a lowering of its activation energy for self-diffusion were also found in the Na^+-H^+ and Na^+-Cs^+ exchange systems.

[9] J. H. Wang, "Self-diffusion and Structure of Liquid Water. II. Measurement of Self-diffusion of Liquid Water with O^{18} as Tracer," *J. Am. Chem. Soc.* **73**, 4181 (1951).

Since the self-diffusion coefficients for the alkali metal cations are all nearly the same, further experiments were done with binary exchange systems in which the charges on the two ions differed. Results on the Na^+-Zn^{++} system with nominal 16% DVB Dowex-50 are given in Table 35. It was seen that the faster moving Na^+ ion was slowed and its activation energy for self-diffusion increased in the presence of Zn^{++} ion, whereas the latter, slower moving ion was speeded and its activation energy decreased by the presence of Na^+ ion. Analogous results were observed in the Na^+-La^{+++} system when using the same cation exchanger.

TABLE 35

Self-Diffusion in the Na^+-Zn^{++} Exchange System

Normality of external electrolyte constant at 0.22 *N*

COMPOSITION OF EXCHANGER	ION	$D_{0.3°}$	$D_{25°}$	E_{act} (cal/mole)
100 NaR	Na^+	6.58×10^{-8}	2.4×10^{-7}	8400
50 NaR + 50 ZnR	Na^+		1.22×10^{-7}	
50 NaR + 50 ZnR	Zn^{++}	6.02×10^{-9}	1.82×10^{-8}	7200
2 NaR + 98 ZnR	Na^+	1.99×10^{-8}	8.14×10^{-8}	9200
100 ZnR	Zn^{++}	3.12×10^{-9}	1.16×10^{-8}	8500

Donnan Equilibria (G. E. Boyd and Q. V. Larson). In an earlier progress report[10] data were presented showing that the uptake of diffusible anions in solution by cation exchangers (or of diffusible cations by anion exchangers) was dependent on (1) the nature of the anion (or cation), (2) the salt form of the cation (or anion) exchanger, (3) the cross linkings of the exchanger, and (4) the concentration of the diffusible ion in the external aqueous solution. Data were also given showing that the moisture contents of various Dowex-50 type cation exchangers depended on their cross linking, salt forms, and on the ionic strength of the external solution. Figure 16 presents additional swelling water–ionic strength measurements for a strong-base type of anion exchanger in two differently cross-linked preparations. A comparison of Fig. 20 in the earlier report[10] with Fig. 16 shows that the hydrogen form of nominal 8% DVB preparation of Dowex-50 contains approximately 42% moisture compared with about 36% for an 8% DVB preparation of Dowex-1 in the chloride form. Part of this difference arises from differing hydrations of the exchange groups plus counter ions. However, in the main, the lower water content for the anion exchanger is probably a consequence of the appreciably smaller capacity of the exchanger.

[10] G. E. Boyd and Q. V. Larson, "Ion Exchange Equilibria: Distribution of Indifferent Electrolyte Between Aqueous Solutions and Organic Ion-Exchange Polymers," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, ORNL-795, p. 109.

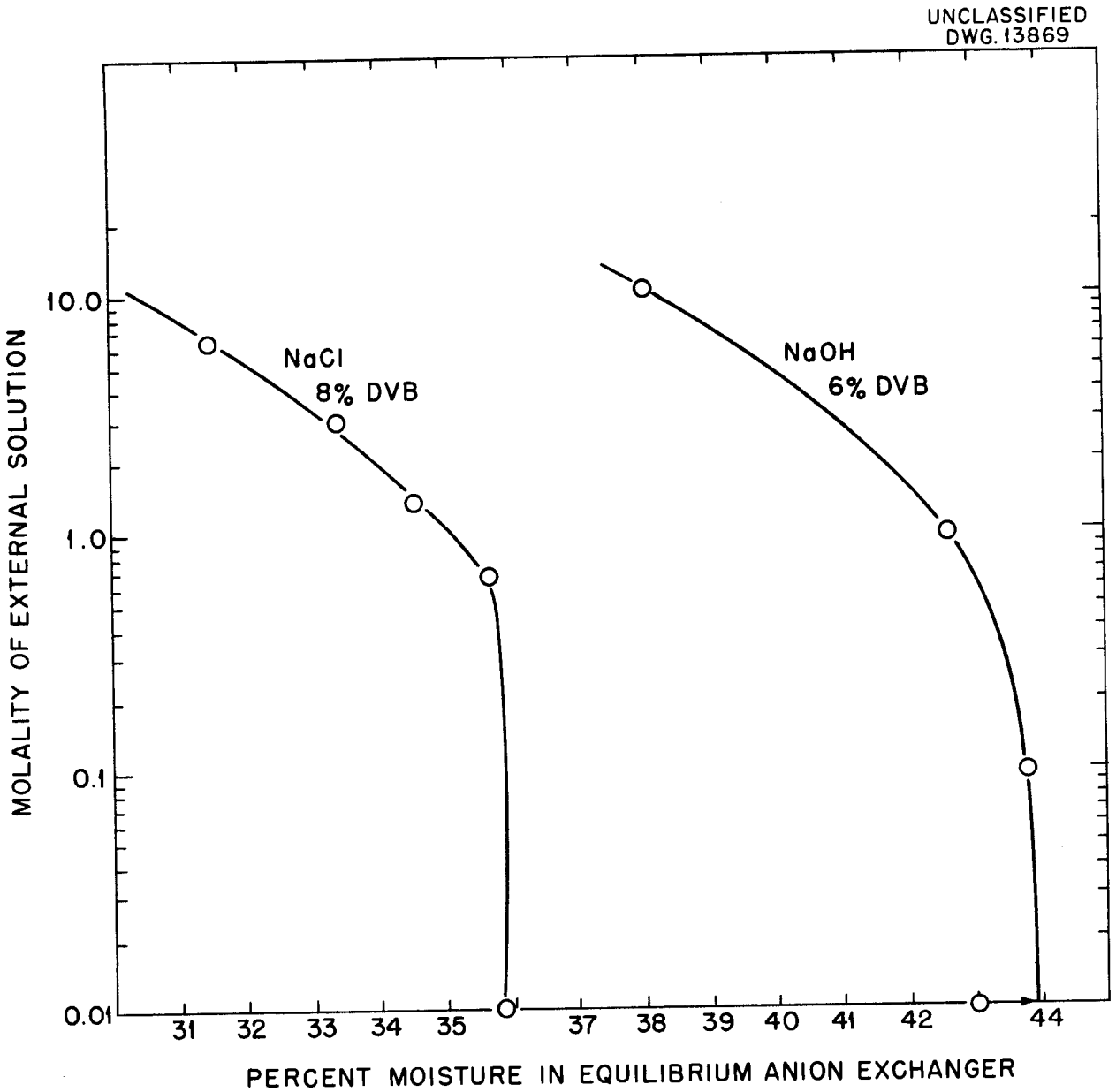


Fig. 16. Moisture Distribution with Dowex-1.

Data presented in Fig. 22 of the earlier report[10] are plotted in Fig. 17 in a manner better designed to show (1) the Donnan exclusion of diffusible chloride ion; and, in particular, to show (2) the apparent constant ratio of HCl in the exchanger (α) to HCl in the external aqueous solution (β) obtaining as the latter became more dilute. Work during the past quarter has shown (2) to be the consequence of an imperfect separation of the exchanger from its equilibrium solution. A liquid film of only 3.7 μ thickness

held to the surface of a 230-μ-dia. spherical particle (60/70 mesh) will, when the Donnan exclusion ratio

$$m^{\alpha}_{HCl} : m^{\beta}_{HCl}$$

falls below 0.1, cause 100% error in the estimation of m^{α}_{HCl}. Figure 18 shows a comparison between the predicted variation of the exclusion ratio with external concentration and that observed when a phase-separation procedure consisting of suction drying followed by blotting and vapor-phase equilibration with the equilibrium solution was employed. Evidently special techniques are required when the ratio falls below about 0.1. Figure 19 shows a replot of the earlier Fig. 24.[10] It is seen that Br^- penetrates the exchanger (HR) better than Cl^- ion, and that Cl^- ion can enter the lithium form (LiR) to a slightly greater extent than the acid form (HR) when the exclusion ratios are compared at the same external electrolyte activities.

In an attempt to understand the swelling properties (see Fig. 20 in ref. 10 and Fig. 16 in this report) and ionic "permi-selectivity" of ion exchangers revealed by the distributions shown in Figs. 17 and 19, it will be assumed that a membrane equilibrium is involved. The exchanger acts as its own semipermeable membrane. Further, the gel-solution phase of the exchanger will be considered as a typical strong electrolyte. Hence, a chloride ion (accompanied by an H^+ ion to maintain electric neutrality) upon moving from a dilute aqueous HCl solution into the acid form of a strong acid cation exchanger will encounter a region both of high hydrogen-ion concentration and of high ionic strength. According to the Gibbs-Donnan equation (assuming the swelling free-energy change to be negligible) the activity products for HCl in both phases must be equal,

$$a^{\alpha}_{H^+} \cdot a^{\alpha}_{Cl^-} = a^{\beta}_{H^+} \cdot a^{\beta}_{Cl^-} \quad . \qquad (1)$$

Expressing activities in terms of molalities and activity coefficients,

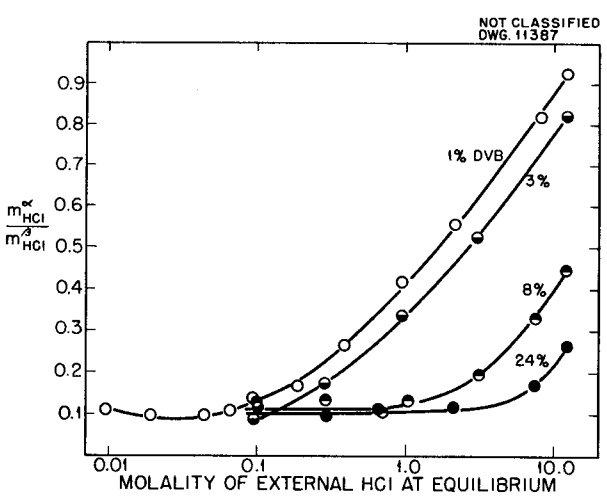


Fig. 17. Variation of Distribution of Diffusible Chloride Ion with External Concentration and Cross Linking.

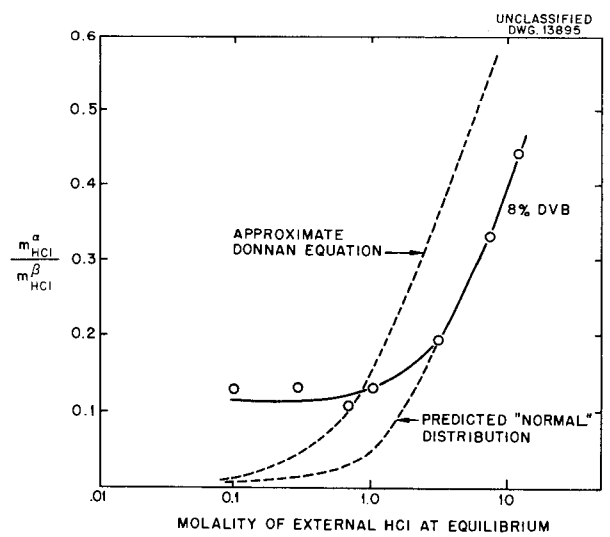


Fig. 18. Comparison of Observed Uptake of Diffusible Chloride Ion with Theory.

and remembering in the exchanger that $m_{H^+} = m_{HR} + m_{HCl}$, Eq. 1 becomes

$$\left[m^{\alpha}_{HR} + m^{\alpha}_{HCl}\right] m_{Cl^-} \left[\gamma^{\alpha}_{HCl}\right]^2 = \left[m^{\beta}_{HCl}\ \gamma^{\beta}_{HCl}\right]^2 . \quad (2)$$

Equation 2 suggests that two effects may operate to prevent the concentration of chloride ion in the exchanger from attaining a value as large as in the external aqueous solution: (1) a "common-ion" effect arising from the high H^+-ion concentration in the exchanger, and (2) activity-coefficient effects. Considering aqueous solutions more dilute than 1.5 m, $\gamma^{\beta}_{HCl} < 1.0$ and $\left[\gamma^{\beta}_{HCl}\right]^2$ may become as small as 0.57 for $m = 0.4$. In general, $\gamma^{\alpha}_{HCl} > 1$, since when small amounts of HCl enter the exchanger the

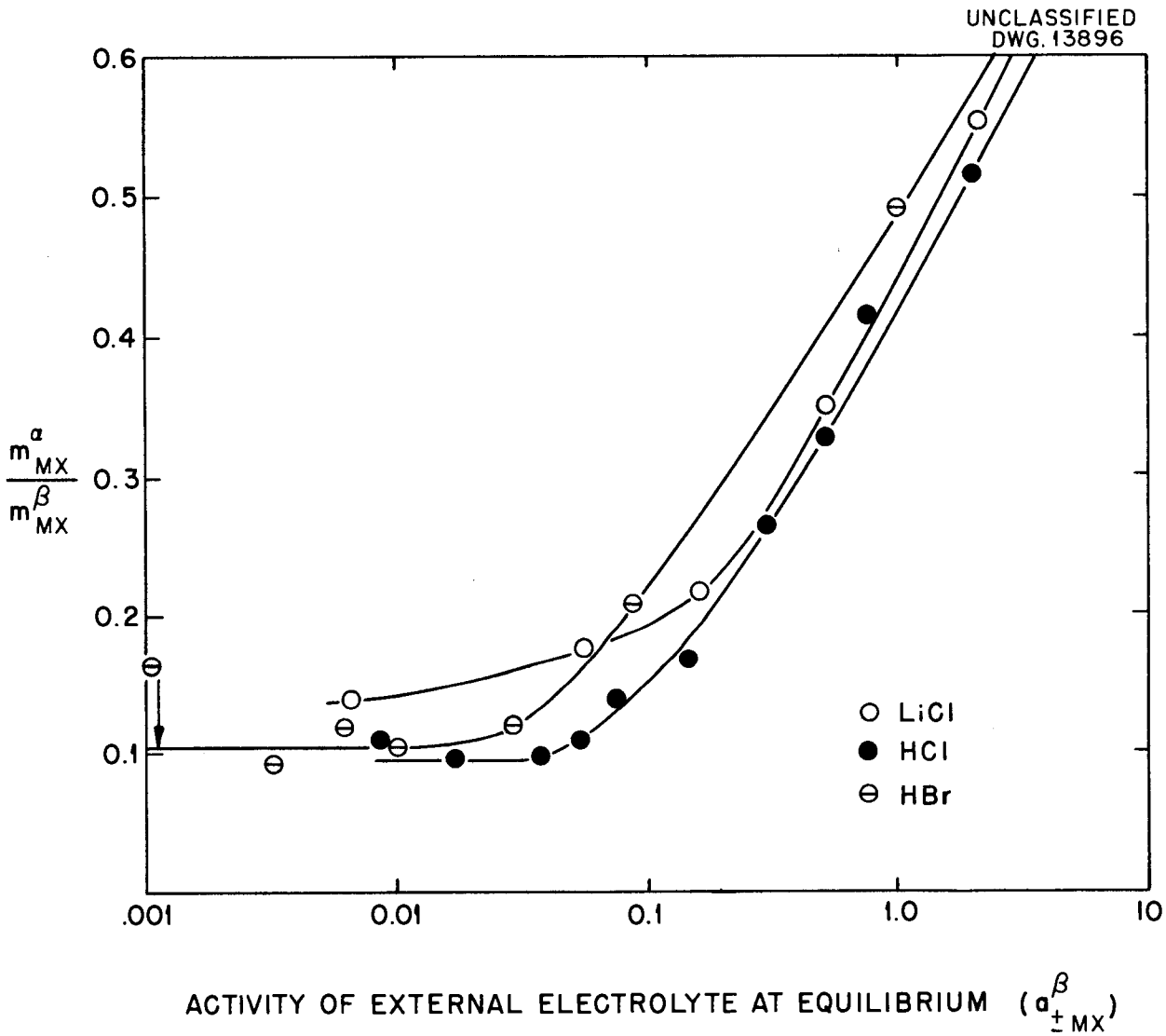


Fig. 19. Distribution of Diffusible Chloride and Bromide Ions with 1% DVB Cation Exchanger.

activity coefficient tends to approach that for the major component, the strong electrolyte, namely HR, if it is assumed as before that the latter behaves as a typical 1-1 strong electrolyte.

By solving Eq. 2 for the exclusion ratio, R,

$$R = \frac{m^{\alpha}_{Cl^-}}{m^{\beta}_{Cl^-}} = \frac{m^{\beta}_{Cl^-}\left[\gamma^{\beta}_{HCl}\right]^2}{\left[m^{\alpha}_{R^-} + m^{\alpha}_{Cl^-}\right]\left[\gamma^{\alpha}_{HCl}\right]^2}, \quad (3)$$

it is seen that as m^{α}_{HCl} becomes negligibly small relative to m^{α}_{HR} and γ^{α}_{HCl} approaches constancy, R will vary as the activity of the HCl in the aqueous phase (Fig. 18). Also, it is seen that even with concentrated external HCl solutions R will be less than unity, since

$$\left[m^{\alpha}_{R^-} + m^{\alpha}_{Cl^-}\right] > m^{\beta}_{Cl^-}$$

and

$$\gamma^{\alpha}_{HCl} > \gamma^{\beta}_{HCl}$$

Equation 3 shows, also, that for not too concentrated solutions the exclusion of bromide will be less than chloride, at equal molalities, since

$$\gamma^{\beta}_{HBr} > \gamma^{\beta}_{HCl},$$

whereas

$$\gamma^{\alpha}_{HBr} \approx \gamma^{\alpha}_{HCl},$$

owing to the "averaging" effect of the resin acid HR (Cf. Fig. 19).

A further quantitative discussion may be based upon an application of the Harned rule for electrolyte mixtures. This, however, will be reserved for a subsequent report, for at present it is not clear whether the assumption that the resin acid (HR) or the salt (MR) may be regarded as truly a 1-1 electrolyte.

ION-EXCHANGE SEPARATIONS

R. W. Atteberry Q. V. Larson
G. E. Boyd

Continued attention has been devoted to developing rapid, convenient ion-exchange column separations of the fission-product elements. As mentioned in an earlier quarterly report[11] separations of Cd, In, Sn, Sb, and Te have been of interest, particularly in connection with studies on symmetric fission that were initiated by investigations of the nuclear chemistry of tin.[12] To study the cadmium-indium separation, neutron-irradiated indium metal was added to a 3 *M* HCl solution containing $Cd^{115}Cl_2$. This solution was passed through a 1 by 30-cm bed of Dowex-2 that had been converted to the chloride form with 3 *M* HCl. The liquid chromatogram obtained by using 3 *M* HCl followed by 0.05 *M* NH_4Cl as eluting agents is given in Fig. 20. Further, a precision half life of 54.0 ± 0.1 min for In^{116} was determined by measuring the decay of the activity contained in the middle fraction of the first peak shown. This value, which is of importance owing to the widespread use of the indium-foil technique for thermal neutron intensity measurements, agrees rather well with two previous values of 54.05 min[13] and 53.93 min,[14] but not with an earlier

(11) R. W. Atteberry and G. E. Boyd, "Ion-exchange Separations," *op. cit.*, ORNL-1053, p. 89.

(12) C. M. Nelson, B. H. Ketelle, and G. E. Boyd, *Studies on the Nuclear Chemistry of Tin*, ORNL-828, Nov. 10, 1950.

(13) A. C. Graves and R. L. Walker, "A Method for Measuring Half Lives," *Phys. Rev.* **71**, 1 (1947).

(14) L. M. Silver, "Precision Measurement of Half-Lives," *Phys. Rev.* **76**, 589(A) (1949).

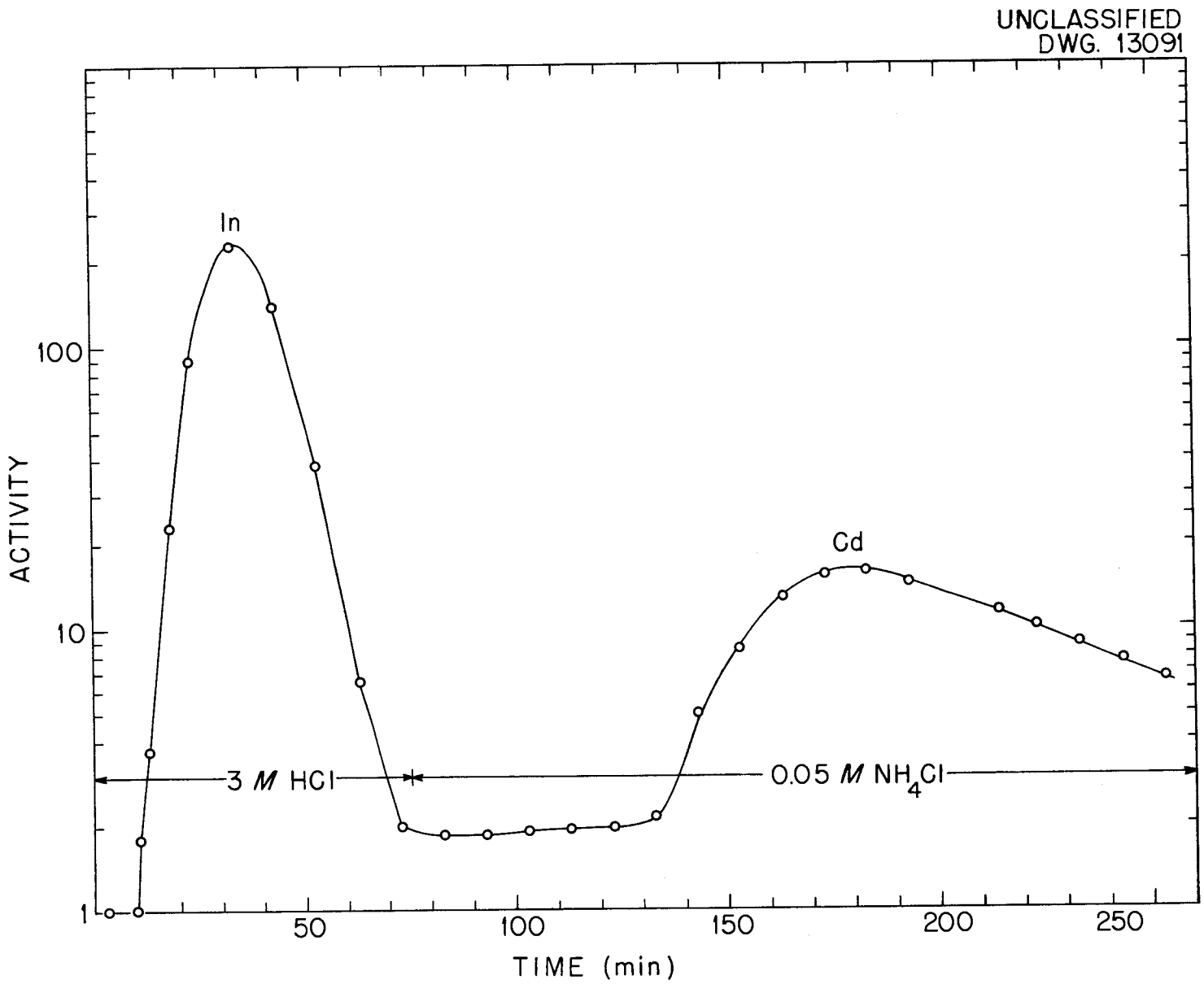


Fig. 20. Separation of Fission-Product Mixture of Cadmium and Indium.

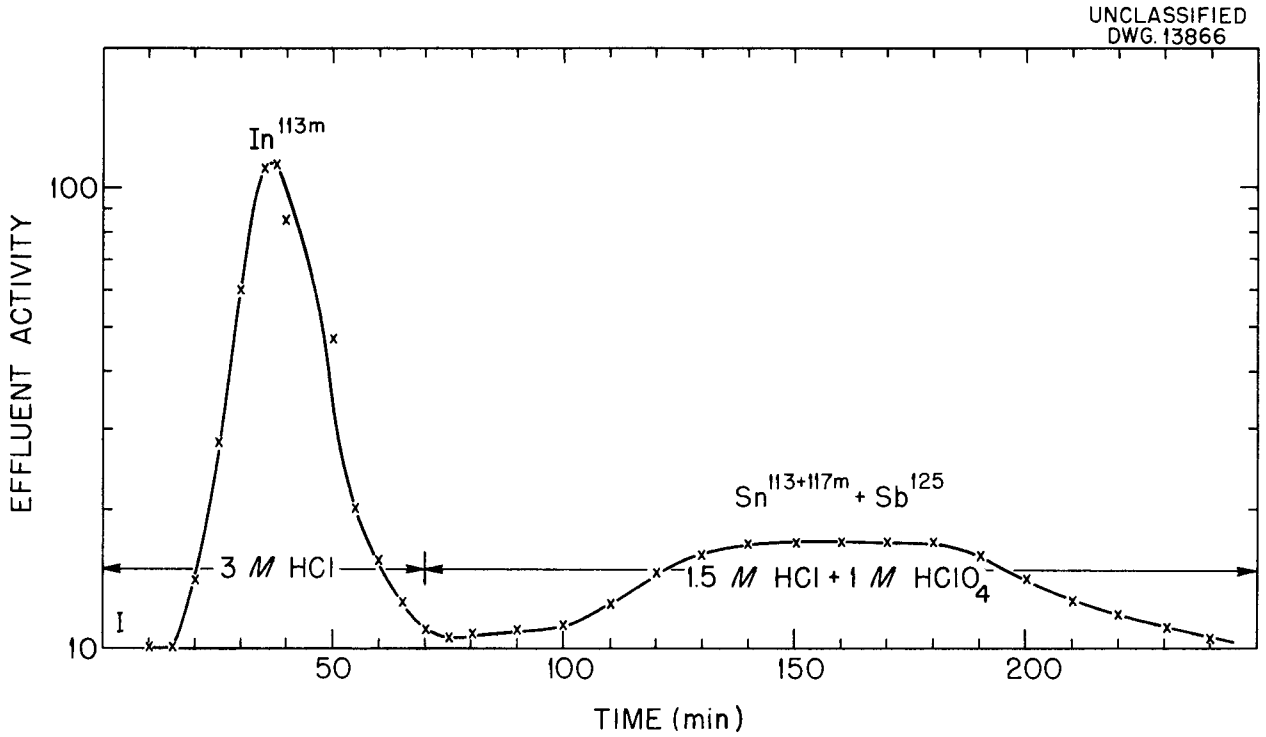


Fig. 21. Separation of Indium from Neutron-Irradiated, Enriched Tin^{116} Preparation.

value of 54.31 min.[15] Next, a small quantity of pure cadmium metal was irradiated with neutrons, allowed to decay for 48 hr, dissolved in HCl, and subjected to an ion-exchange column separation. The pure In^{115m} activity in the peak, which came at the same position as in Fig. 20, showed only a 340-kev gamma ray on a sodium iodide scintillation counter spectrometer and decayed with a half life of 4.50 ± 0.005 hr, which is in good agreement with an earlier value of 4.50 hours.[16]

In another experiment, about 100 mg of pure tin metal was irradiated with neutrons for two weeks, allowed to cool, dissolved in HCl, and then chromatographed. The liquid chromatogram (Fig. 21) showed that a good separation of the 105-min In^{113m} formed by the decay of 112-day Sn^{113} had been effected. Subsequent examination of the second peak showed it to be a mixture of several long-lived tin activities together with 2.7-year Sb^{125} formed by the decay of Sn^{125}. A further investigation of conditions for the separation of antimony(III) and tin(II) will be undertaken.

A rapid, convenient separation of molybdenum from technetium and rhenium was devised using $NaClO_4$ solutions (Fig. 22). Further, equilibrium distribution studies (Fig. 23) show that a chromatographic separation of rhenium(VII) and technetium(VII) may be based upon $NaClO_4$ as an eluting agent. Perchlorate ion appears to possess an exchange affinity for Dowex-2

(15) B. Russell and A. Wattenberg, *The Half-life of Indium*, CP-3305, Oct. 19, 1945.

(16) J. V. Dunworth and B. Pontecorvo, "Excitation of In^{113} by X-rays," *Proc. Cambridge Phil. Soc.* **43**, 123 (1947).

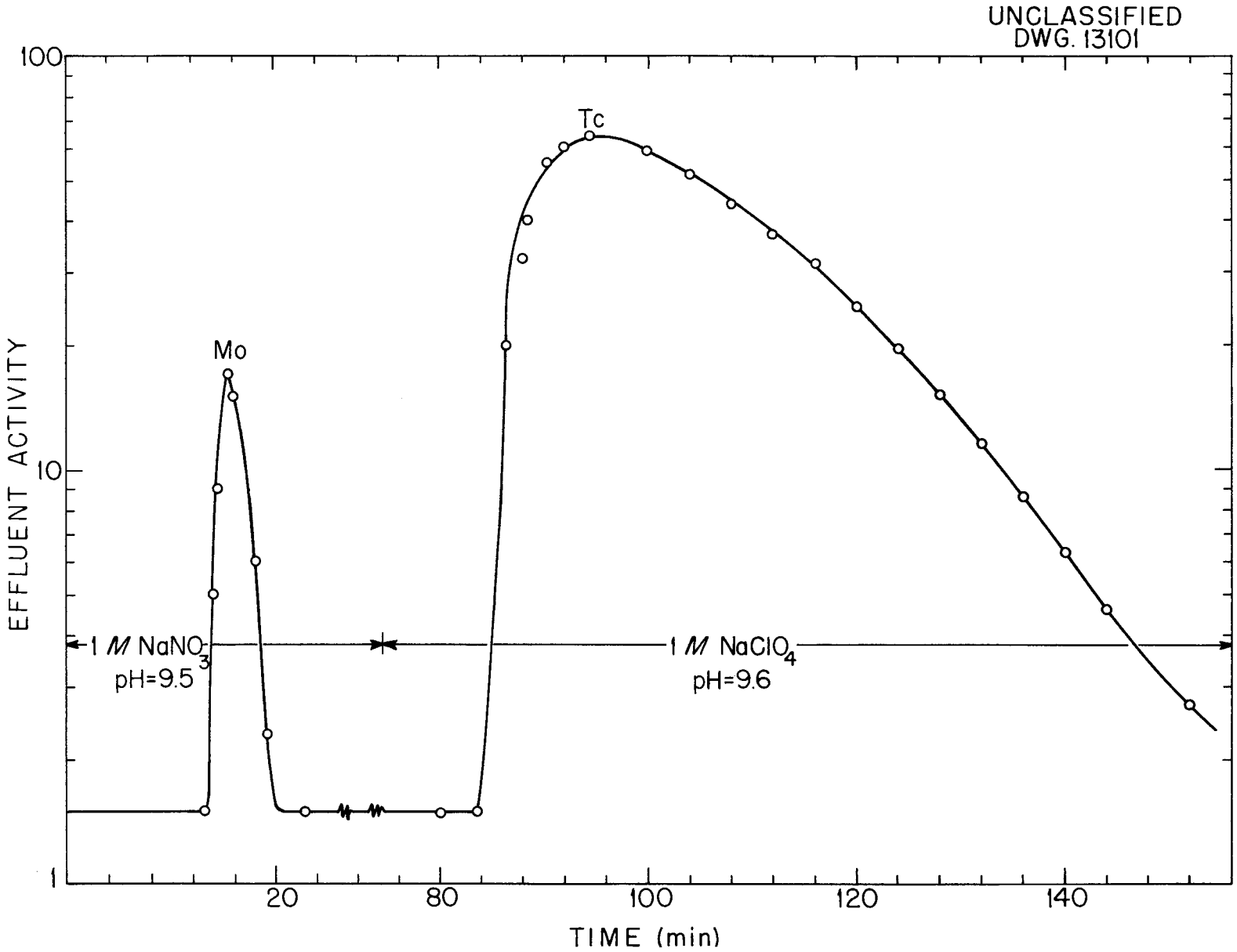


Fig. 22. Separation of Molybdenum and Technetium Mixture.

exceeding that for any other singly charged anion. The foregoing observations have been put to good use in current searches for technetium in nature.

A rapid separation of fission-product selenium from tellurium was devised by using 3 *M* HCl followed by 1 *M* NH_4SCN + 1 *M* HCl as eluting agents (Fig. 24). Also, a good separation of fission-product arsenic from antimony was achieved (Fig. 25), although the recovery of the latter still leaves much to be desired. Finally, a very rapid and convenient separation of fission-product zinc from cadmium has been realized (Fig. 26).

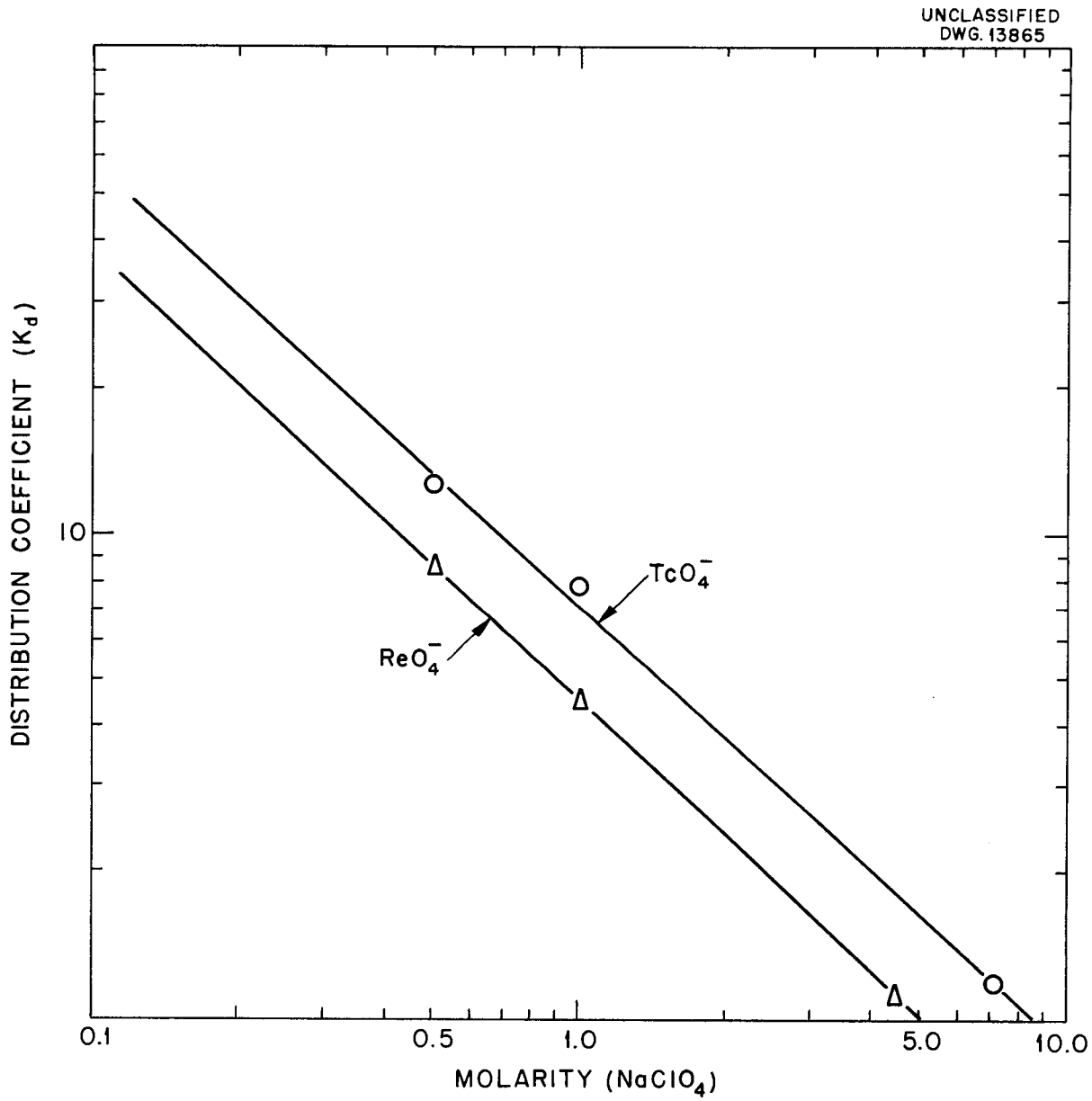


Fig. 23. Equilibrium Distribution of Pertechnetate and Perrhenate Between Aqueous $NaClO_4$ Solution (pH ~ 9) and Dowex-2 (ClO_4^- Form).

Separations experiences with anion exchanges thus far may be summarized in terms of several generalizations or separations principles:

1. Chromatographic separation may be achieved by changes in complex-ion concentration. Thus, changes in HCl concentration may alter both the amount (and nature) of the complex-ion eluted. This principle has found ample demonstration in the work of K. A. Kraus and his group.

2. Chromatographic separation may be achieved by changing the nature of the complex ion. Thus, HBr, HSCN, HCN, or HF, or mixtures thereof may be employed instead of HCl, as in the Group IV-A and V-A separations of Kraus and of E. H. Huffman and his group, or in our own work with Sn and Sb using HBr, or with Se and Te using HSCN, etc.

3. Chromatographic separation may be achieved by changing the oxidation state of the central element of a complex anion, as for example: (a) in the elution of $FeCl_4^-$ from an anion exchanger using H_2SO_3 to produce Fe(II), which forms only a very weak chloride complex; or (b) in the elution of Sb(III) ($SbCl_4^-$?) using an oxidant to form the weakly complexed Sb(V).

4. Chromatographic separation may be achieved by charge reversal, as in the rapid elution of $ZnCl_4^=$ from an anion exchanger by using ammonia to form and stabilize $Zn(NH_3)_4^{++}$.

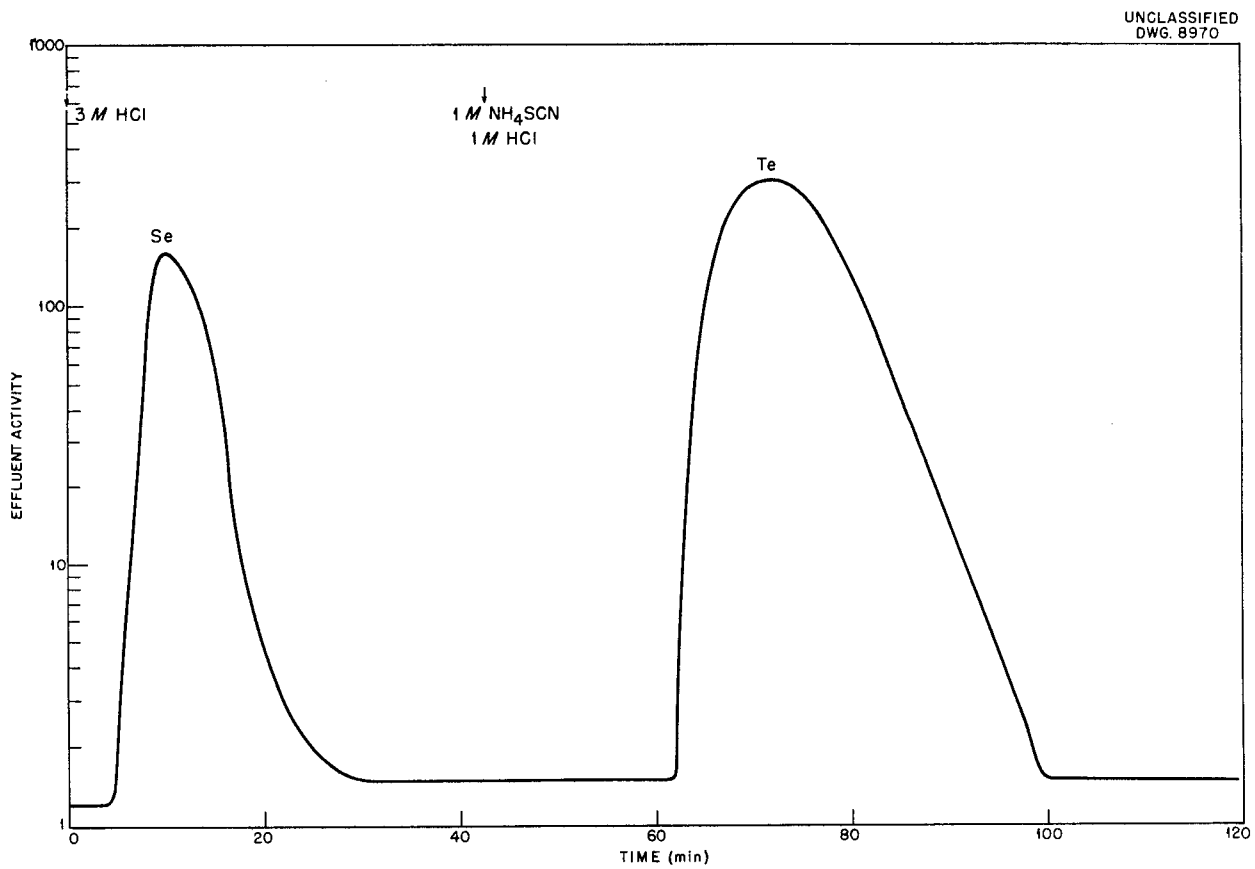
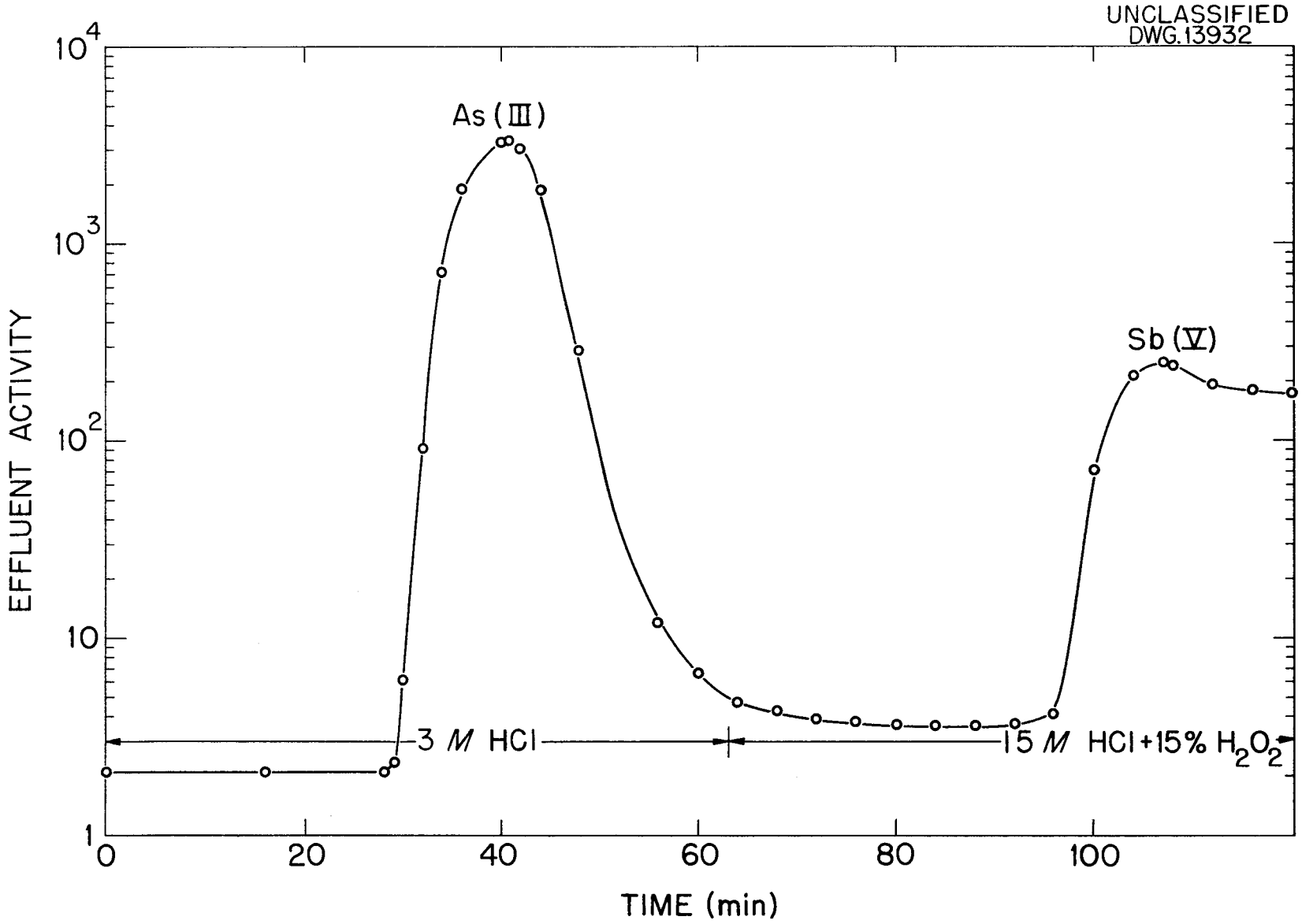


Fig. 24. Selenium-Tellurium Separation on Dowex-2.


UNCLASSIFIED
DWG.13932
As (III)
Sb (V)
3 M HCl
15 M HCl+15% H2O2
EFFLUENT ACTIVITY
TIME (min)
10^4
10^3
10^2
10
1
0
20
40
60
80
100

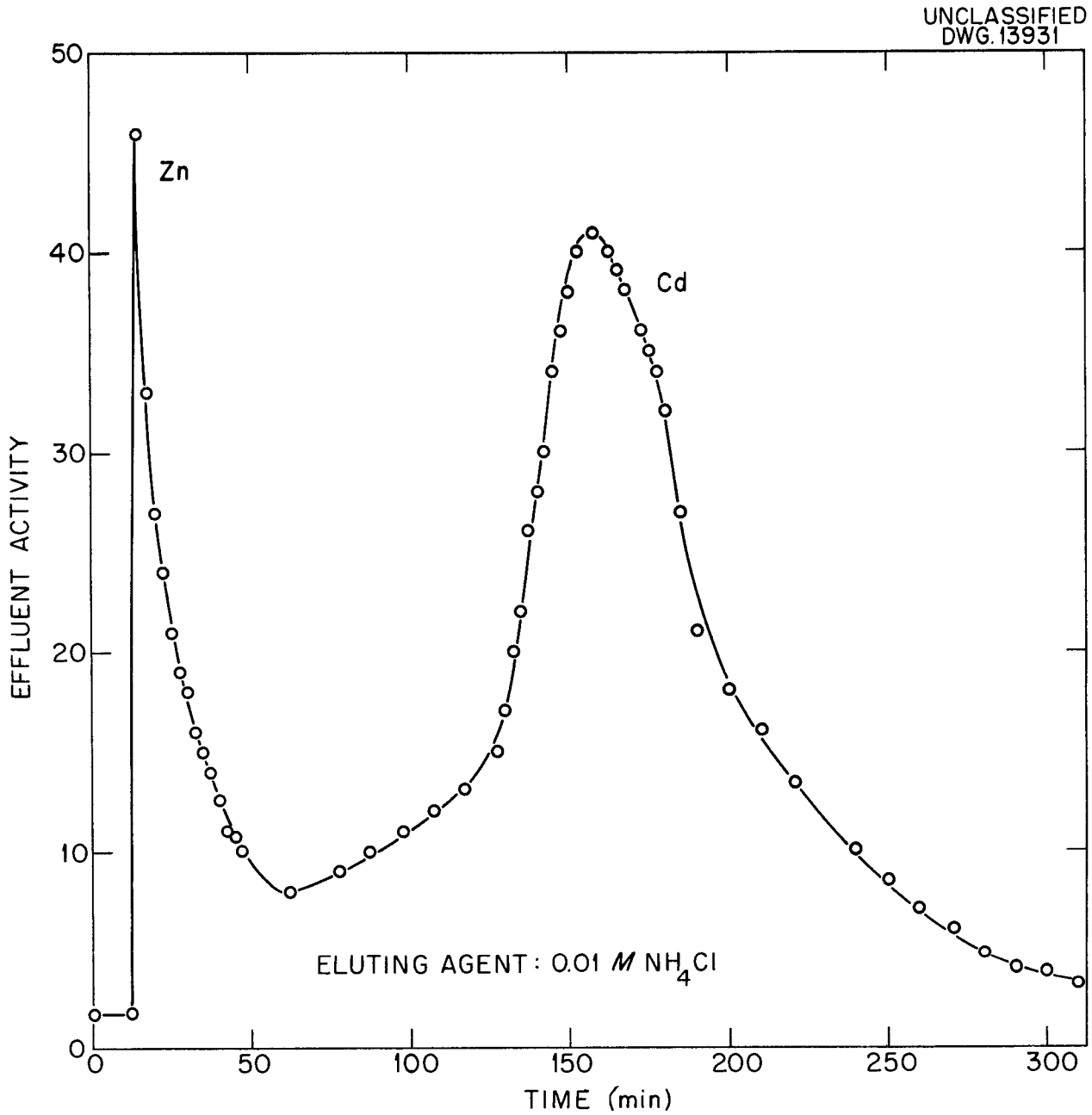


Fig. 26. Cadmium-Zinc Separation on Dowex-2.

CHEMICAL PHYSICS

NEUTRON DIFFRACTION STUDIES

H. A. Levy S. W. Peterson

Crystal Structure of Ammonium Chloride. Ammonium chloride at room temperature has been studied by neutron diffraction with powdered ND_4Cl and single crystals of NH_4Cl. The structure consists of disorderly oriented ammonium ions at the body centers of cubes of chloride ions, entirely similar to that of ND_4Br at room temperature.[1] The hydrogen atoms are distributed in space in a manner consistent with the concept that the ion undergoes a rotary oscillation of considerable amplitude. The parameters that describe the structure are given in Table 36.

TABLE 36

Structure Parameters of NH_4Cl and ND_4Cl

	NH_4Cl	ND_4Cl
N-H or N-D distance, *A*	1.03 ± 0.02	1.03 ± 0.02
Characteristic half-angle of oscillation (deg.)	12 ± 3	10 ± 3

An ordered structure for room-temperature ND_4Cl recently reported by Goldschmidt and Hurst[2] is clearly incorrect. The lambda-point transitions occurring at −30.4°C in NH_4Cl and −23.7°C in ND_4Cl have been demonstrated to be of the order-disorder type. A detailed account of this work is in preparation and will be submitted for publication at an early date.

Neutron Coherent Scattering Cross Sections of Nitrogen and Vanadium. The study of ammonium chloride, reported above, strongly suggested that the value 9.1 barns[3] for the coherent scattering cross section of nitrogen was too low. Higher values of 11 and 9.7 barns have been reported from neutron reflection measurements.[4]

The compound vanadium nitride, VN, has been prepared by this group for an independent measurement of the cross section. Vanadium nitride was chosen because its simple structure (NaCl type), its chemical properties, and the very small coherent cross section of vanadium[3] make a precise determination of the nitrogen value possible. Chemical and spectrographic analyses and x-ray diffraction examination proved the material to be essentially pure. From measurement of the intensities of three odd-index and four even-index reflections, the value of the coherent cross section of nitrogen was evaluated as 11.1 ± 0.4 barns. This value was confirmed by examination of the neutron-diffraction pattern of potassium azide, KN_3.

The neutron-diffraction pattern of VN showed that the phase of the vanadium scattering was negative opposite to that of nitrogen. A contrary result has been given by neutron-reflection experiments.[5] As a check on the above result, the pattern of vanadium carbide was also examined, and the phase of vanadium

(1) H. A. Levy and S. W. Peterson, "The Nature of the Second-Order Transition in ND_4Br," *Phys. Rev.* **83**, 1270 (1951).

(2) G. H. Goldschmidt and D. G. Hurst, "The Structure of Ammonium Chloride by Neutron Diffraction," *Phys. Rev.* **83**, 88 (1951).

(3) C. G. Shull and E. O. Wollan, "Coherent Scattering Amplitudes as Determined by Neutron Diffraction," *Phys. Rev.* **81**, 527 (1951).

(4) A. W. McReynolds and R. J. Weiss, "Coherent Neutron Scattering Cross Section of V^{51}," *Phys. Rev.* **83**, 171 (1951).

(5) A. W. McReynolds, "Neutron Refraction in O_2, N_2, He, A Gases," *Phys. Rev.* **84**, 969 (1951).

scattering again appeared clearly negative. The vanadium cross-section values given by the nitride and carbide are 0.029 ± 0.01 and 0.026 ± 0.01 barns, respectively. An account of this work is being prepared for publication.

EXPERIMENTS IN CHEMICAL KINETICS WITH MOLECULAR BEAMS

S. Datz E. H. Taylor

Improvements have been made during this quarter in the techniques to be used for measuring bromine and potassium in the contemplated molecular-beam experiments. Potassium is to be measured by the surface ionization gage, and the background from the hot tungsten filament of the gage has been reduced, by suitable outgassing of the filament, to an ion current equivalent to about 2×10^4 atoms per second. Earlier experiments showed a background of about 10^8 to 10^9.

Tests of a newly available scintillation counter with a low-absorption liner show that the counting rate for identical radiobromine samples was greater by about a factor of 7 than with the previous, brass-lined counter. This increase in the counting rate occurs because the new instrument counts the 37-kv and part of the 11-kv x rays in addition to the harder gamma rays. With the new counter x- and gamma-ray counting of radiobromine becomes about as sensitive as proportional counting of the beta rays, and source preparation is not so difficult as for precise beta counting.

RADIO-FREQUENCY SPECTROSCOPY

R. Livingston

Magnetic Moment of Technetium^{99}. A sample of 156 mg of Tc^{99} as NH_4TcO_4 was prepared by W. Martin and observed in a nuclear induction apparatus at Y-12, in collaboration with H. Walchli. The Tc^{99} resonance was found and its frequency compared with that of the deuteron in the same magnetic field, giving $\nu(Tc^{99})/\nu(D) = 1.46628 \pm 0.0001$. The computed nuclear magnetic moment of Tc^{99} with a diamagnetic correction of 0.411% is

$$\mu(Tc^{99}) = + 5.6805 \pm 0.0004 \quad .$$

Further details will be published elsewhere.[6]

Piezoelectric Spectra. A new type of spectrum in crystalline solids was reported in the last quarterly report. The spectra are present only in piezoelectric substances and are the result of mechanical oscillation of the individual crystallites. D. F. Smith (K-25) suggested this explanation. Several piezoelectric substances were selected at random and all showed the effect. The materials were sea sand (quartz), potassium dihydrogen phosphate, tartaric acid, ammonium dihydrogen phosphate, and ammonium fluoride. Additional tests with sea sand showed that the number of lines observed depended on the number of grains of sand present. Also, the lines were more intense when the sample was placed in the condenser part of the spectrometer oscillator circuit in contrast to location in the coil part of the circuit. This is in keeping with the concept that the absorption process is probably electric (dipole) rather than magnetic.

Some of the observations of piezoelectric spectra, however, are still unexplained. In some substances the lines disappear at temperatures at which the substances are still

[6] H. Walchli, R. Livingston, and W. J. Martin, "The Nuclear Magnetic Moment of Tc^{99}," *Phys. Rev.* **85**, 479 (1952).

supposed to be piezoelectric. Thus, in cooling NH_4Cl the lines appear below the lambda-point transition (-31°C) where the substance is known to be piezoelectric, but they disappear near -160°C although the substance is still piezoelectric.

Pure Quadrupole Spectra. A paper on the detection and measurement of pure quadrupole spectra was given at a meeting of the New York Academy of Sciences and will be published soon.[7]

The chlorine quadrupole spectra of a number of compounds have been observed. These include most of the chloroethanes, *cis*- and *trans*-dichloroethylene, isopropyl chloride and *tert*-butyl chloride. As soon as a few additional substances are observed, the results will be prepared for publication elsewhere.

CALORIMETRY OF RADIOACTIVITY

G. H. Jenks F. H. Sweeton

As reported previously[8] a determination of a quantitative relationship between the half life and average beta energy of C^{14} decay has been carried out by measuring: (1) the power generated by a given amount of a mixture of $C^{14}O_2$ and normal CO_2, and (2) the abundance of $C^{14}O_2$ in the mixture. To complete the determination, a test of the aliquoting procedures followed in the measurements is being made by determining the relative radioactivity of the different samples. An ionization chamber into which the respective gases are introduced is used in these measurements. To date, the activity of the gas contained in one of the two calorimetric samples has been compared with that of a given volume of the gas used in the abundance measurement. The value for the amount of C^{14} in this calorimetric sample, calculated from the results, is in good agreement with that determined previously, and the accuracy of the aliquoting procedures is tentatively established.

From the results of the various measurements made in this study, some conclusions may now be drawn concerning the values for the half life and average beta energy of C^{14} decay. As pointed out above, a quantitative relationship has been established between these two constants of the decay. To date, some uncertainty exists in the experimental values for both these quantities. Several determinations of the half life have been reported[9] but the results have varied considerably. However, the most recent measurements, which are probably the most reliable, have all given values of 5400 to 5600 years, except one made at Chalk River that gave a value of about 6400 years. No measurements of the average energy as such have been reported, but evidence that the beta-ray spectrum of the decay has an allowed shape has been found by Feldman and Wu[10] and by Berggren and Osborne.[11] Other investigators[9] have found slight deviations of the Fermi plot from that for an allowed shape. If the shape of the spectrum is allowed, the average beta energy can be computed with confidence since the maximum beta-energy is well known. Ketelle

(7) R. Livingston, "Detection and Measurement of Direct Nuclear Quadrupole Transitions," *Ann. N. Y. Acad. Sci.*, in press.

(8) "Calorimetry of Radioactivity," in *Chemistry Division Quarterly Progress Reports*, ORNL-1153, p. 70; ORNL-1036, p. 60; and ORNL-1053, p. 112.

(9) W. F. Hornyak, T. Louritsen, P. Morrison, and W. A. Fowler, "Energy Levels of Light Nuclei.III," *Rev. Modern Phys.* **22**, 333 (1950).

(10) L. Feldman and C. S. Wu, "Beta-Ray Spectra of C^{14}" *Phys. Rev.* **75**, 1286 (1949).

(11) J. L. Berggren and R. K. Osborne, "The Beta-Ray Spectra of C^{14} and S^{35}," *Phys. Rev.* **74**, 1240 (1948).

of ORNL carried out this computation and obtained a value of 48.7 kev.

If the computed value for the average energy is assumed to be correct, the results of the present study yield a value of about 6000 years for the half life, i.e., 7 to 11% greater than the majority of those recently published. Conversely, if the correct half life is assumed to be 5500 years, the average energy calculated from the present results is about 45 kev.

A complete report of the measurements made in this study and of the results is being prepared.

RADIATION CHEMISTRY

GAS PRODUCTION IN AQUEOUS REACTOR SOLUTIONS

J. W. Boyle C. J. Hochanadel
J. A. Ghormley W. F. Kieffer
T. H. Handley A. C. Stewart
T. J. Sworski

The yield of gas from pile decomposition of aqueous uranyl sulfate and uranyl fluoride solutions has been measured as a function of total dose, enrichment, concentration, temperature, and added solute. The observed yield is the net result of the yield for decomposition modified by a radiation-induced back reaction. At high temperatures the yield is also modified by a thermal back reaction. What are believed to be nearly true yields for decomposition were measured under conditions in which back reactions were minimized.

EXPERIMENTAL

Irradiations. Carefully degassed solutions in fused silica ampoules were exposed in hole 12 of the X-10 graphite pile. The desired temperature was maintained during irradiation by an electric furnace. In studies at 120°C on the effect of concentration and enrichment, about 0.5 ml of solution was used. Other ampoules contained about 2 ml of solution with an equal gas space. For irradiations above 150°C, 1- and 2-mm-ID, thick-walled, silica capillary ampoules containing about 0.1 ml of solution were used. The capillary ampoules were similar to those designed by Ghormley and Allen[1] for measuring pressure in the ampoule without opening it and thereby allowing a number of effects to be studied on the same sample. Gamma irradiations were made by using a Co^{60} source at an intensity of about 4000 r per minute.

The total energy absorption in pile-irradiated solutions was determined by calorimetric measurements, as reported previously.[2] The fission energy absorbed in solution was calculated from the thermal flux determined with a manganese monitor. For all experiments at 120°C, about 25 mg of 0.7% Mn, Al-Mn-Co alloy was irradiated with each sample and the Mn^{56} activity counted after about 2 hr of decay. Energy input for these samples was calculated from the following expression:

$$\text{total ev/ml} = \text{specific monitor activity} \times [(\text{mg of } U^{235} \text{ per ml}) \times 3.446 + 0.5804] \times 10^{15} .$$

Analyses. The products formed are H_2, O_2, and peroxide. Yields are reported as G_{H_2} = molecules H_2 per 100 ev absorbed. In most cases a small amount of CO_2 was found, which probably resulted from oxidation of traces of organic impurities. Evolved gases were analyzed by using the Saunders-Taylor[3] semimicro technique in which H_2 and O_2 are burned on a platinum filament. Peroxide in solution was determined both from the stoichiometric excess of H_2 and also by direct analysis of the solution by using a spectrophotometric method. This method is a modification of one reported previously.[4] The reagent consisted of a mixture of equal volumes of (1) a solution containing 2 g of NaOH, 66 g of KI, 0.2 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 1 liter of distilled water and (2) 20 g of potassium acid phthalate in 1 liter of distilled water. One milliliter of uranyl

(1) J. A. Ghormley and A. O. Allen, *Decomposition of Tritium Oxide Under Its Own Radiation*, ORNL-128, Sept. 1, 1948.

(2) J. A. Ghormley, T. J. Sworski, and C. J. Hochanadel, "Radiation Chemistry of Aqueous Reactor Solutions," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1951*, ORNL-1153, p. 74.

(3) K. W. Saunders and H. A. Taylor, "The Photolysis of Acetone in Presence of Mercury," *J. Chem. Phys.* 9, 616 (1941).

(4) A. O. Allen, T. W. Davis, G. V. Elmore, J. A. Ghormley, B. M. Hainea, and C. J. Hochanadel, *Decomposition of Water and Aqueous Solutions Under Pile Radiation*, ORNL-130, Oct. 11, 1949.

sulfate solution (44 g of uranium per liter) was mixed with 2.5 ml of reagent, diluted to 5 ml, and the optical density measured at 3750 Å. A blank was prepared with reagent and UO_2SO_4 solution in the same concentration as the sample, but it contained no peroxides. Optical densities of the sample (D_s) and blank (D_b) were measured separately in the same absorption cell by using transmission through air as a reference. The micromolar concentration of peroxide in the original solution was

$$(D_s - D_b) \times 57 \times Diln. \text{ per path length in cm,}$$

where *Diln.* is the ratio of the volume of the final mixture to the volume of the original sample. The wavelength 3750 Å was chosen because UO_2SO_4, with added peroxide reagent, has minimum absorption in this region and triiodide absorption is only slightly lower than at its peak at 3500 Å. The absorption was found to follow Beer's law over a forty-fold range of concentration (10^{-4} to 4×10^{-3} *M*).

Effect of Uranyl Sulfate Concentration on Gas Yield. Over the range studied, the yield of H_2 decreased with increased UO_2SO_4 concentration. This was most clearly shown for enriched solutions containing 37.7 mg of U^{235} per ml in which the yield of hydrogen dropped from 1.5 at 40 mg of U per ml to 0.5 at 800 mg of U per milliliter. Hydrogen production vs. energy input for these solutions is shown in Fig. 27. It may be noted that hydrogen production is linear with energy input. This is typical for enriched uranium solutions in which fission recoils contribute more than 95% of the total energy input.

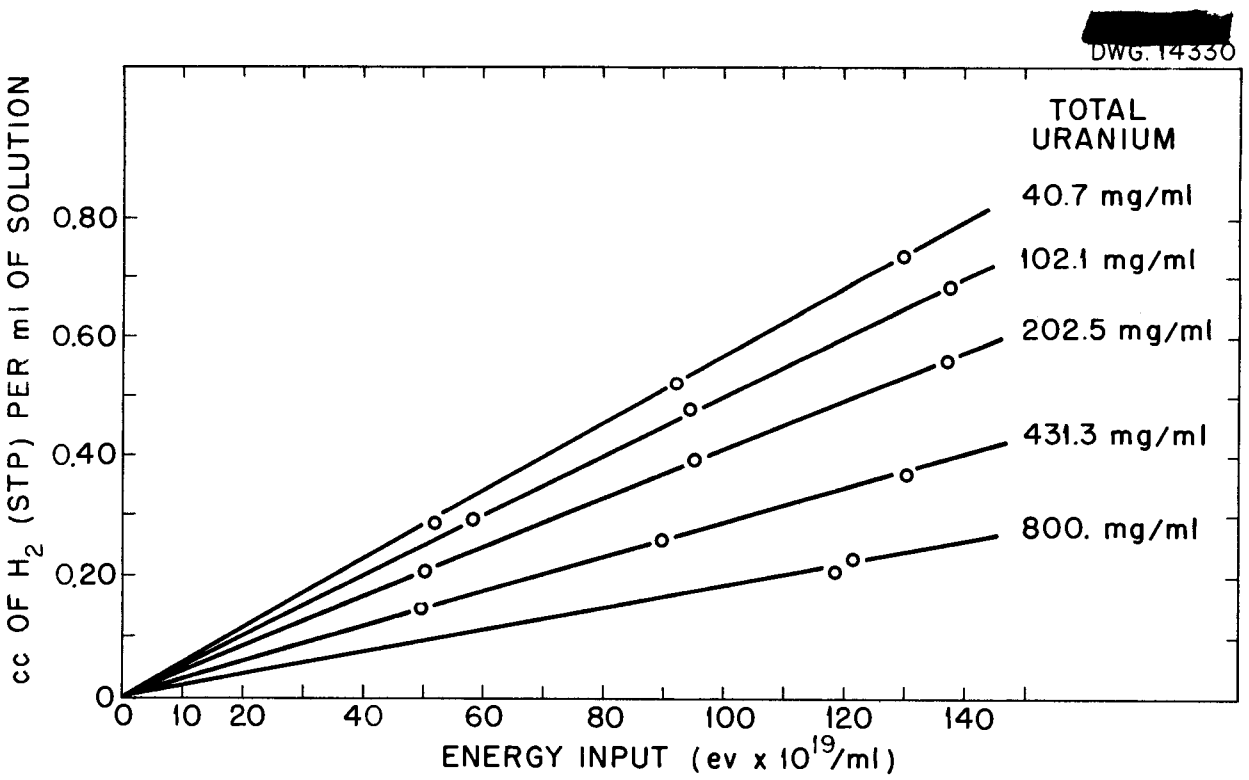


Fig. 27. Hydrogen Gas Production of UO_2SO_4 Solutions Containing 37.7 mg of U^{235} per ml of Solution by Pile Irradiation at 120°C. Ratio of fission energy to total energy = 0.995.

Figure 28 shows the contrasting behavior of depleted uranium solutions in which fission recoils contributed less than 50% of the total energy input. The tendency to level off at relatively low H_2 concentration indicates the importance of radiation-induced back reaction in these solutions. This was also indicated by the dependence of yield on liquid-to-gas volume in the ampoules. Yields for decomposition were taken from initial slopes of these curves.

Hydrogen yields obtained at several UO_2SO_4 concentrations and enrichments are listed in Table 37 and plotted in Fig. 29. Each value represents an average of three to six determinations. In addition to the decrease in yield with increasing concentration, the results show an increase in yield with enrichment until the U^{235} concentration is such that 99% of the total energy absorbed in solution is from fission recoils. This increase with enrichment is more pronounced at lower total uranium concentrations.

Effect of Added Bromide Ion on Gas Yields. It had been shown that bromide ion effectively inhibits radiation-induced reactions involving H and OH free radicals.[4] Its effectiveness as an inhibitor for radiation-induced back reaction had been shown by linear hydrogen build-up with dosage in either pile or gamma irradiation of KBr solutions. The effect of added bromide ion on hydrogen yields from pile-irradiated UO_2SO_4 and UO_2F_2 solutions is shown in Table 38. Each value represents the average of three or more determinations. Figure 30 shows typical curves for gas production vs. pile dosage at several temperatures with and without added bromide ion. The effect of bromide

[redacted]

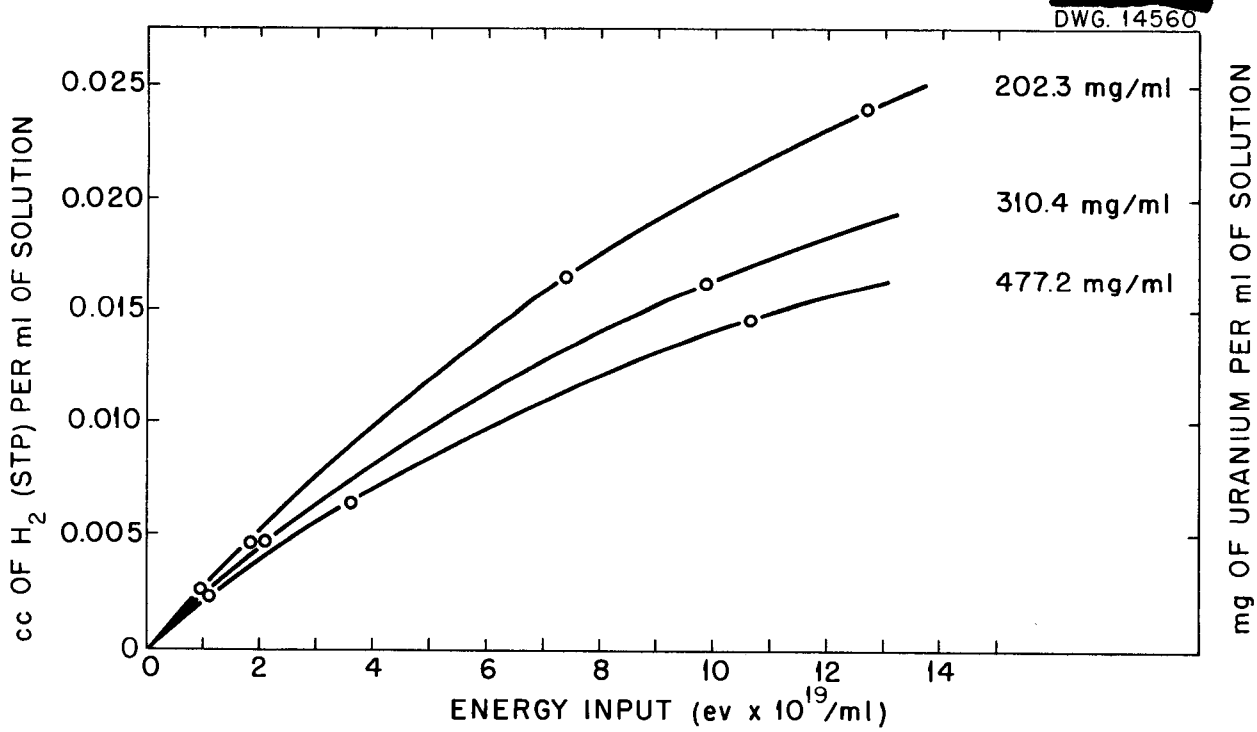


Fig. 28. Hydrogen Gas Production of Depleted UO_2SO_4 Solutions by Pile Irradiation at 120°C.

ion is also indicated in Figs. 31 and 32, which show pressure changes in some typical capillary type of ampoules subjected to various treatments. The results show that for solutions in which fission recoil contributed less than about 93% of the total energy, the yields were greatest for solutions containing bromide ion. For enriched solutions (99% recoil energy), the added bromide ion had little effect. The effect was greater as the ratio of recoil energy to total energy became less. Also the increase in yield with added bromide ion was greater at higher temperatures. These results are consistent with the view that the relative yield of free radicals to ultimate product molecules increases as the linear intensity of ionization of the radiation decreases. Therefore the effect of bromide ion is greatest for gamma irradiation in which radical yield and hence back reaction are most significant. The converse is true for densely ionizing fission-recoil particles.

The effect of bromide ion is clearly demonstrated in Fig. 31, which compares gamma-ray-induced back reaction in a solution containing no bromide ion with that in a solution containing bromide ion in which the pressure increased and indicated not only inhibited back reaction but also additional decomposition by gamma rays. The yield for gamma-ray decomposition of aqueous bromide solutions decreased upon adding UO_2SO_4 from $G_{H_2} = 0.46$, with no added uranium, to $G_{H_2} = 0.22$, with 44 mg of U per ml, and to $G_{H_2} = 0.11$, with 300 mg of U per milliliter. The added bromide ion had little or no effect on pile-irradiated enriched UO_2SO_4 solutions and indicated that

TABLE 37

***G* Values for Hydrogen Production from Aqueous Uranyl Sulfate Solutions Irradiated at 120°C**

G (moles of H_2 per 100 ev)	TOTAL U (mg of U per ml)	U^{235} (mg of U^{235} per ml)	ENRICHMENT (%)	FISSION ENERGY vs. TOTAL ENERGY
1.66	4.03	3.76	93.2	0.957
1.51	40.7	37.9	93.2	0.995
1.34	102.1	37.4	37.0	0.995
1.11	202.5	37.6	18.6	0.995
1.11	203.4	189.6	93.2	0.999
0.77	431.3	37.8	8.75	0.995
0.56	713.5	33.5	4.7	0.995
0.49	796.0	37.4	4.7	0.995
0.73	436.8	3.1	0.72	0.949
1.48*	18.6	1.63	8.75	0.906
0.94	227	1.63	0.72	0.906
0.80	386	1.63	0.42	0.906
0.95*	38.1	0.274	0.72	0.619
0.69*	202.3	0.063	0.031	0.273
0.62*	310.4	0.096	0.031	0.364
0.56*	477.2	0.148	0.031	0.467

*Calculated from estimated initial rate of gas production.

[redacted]

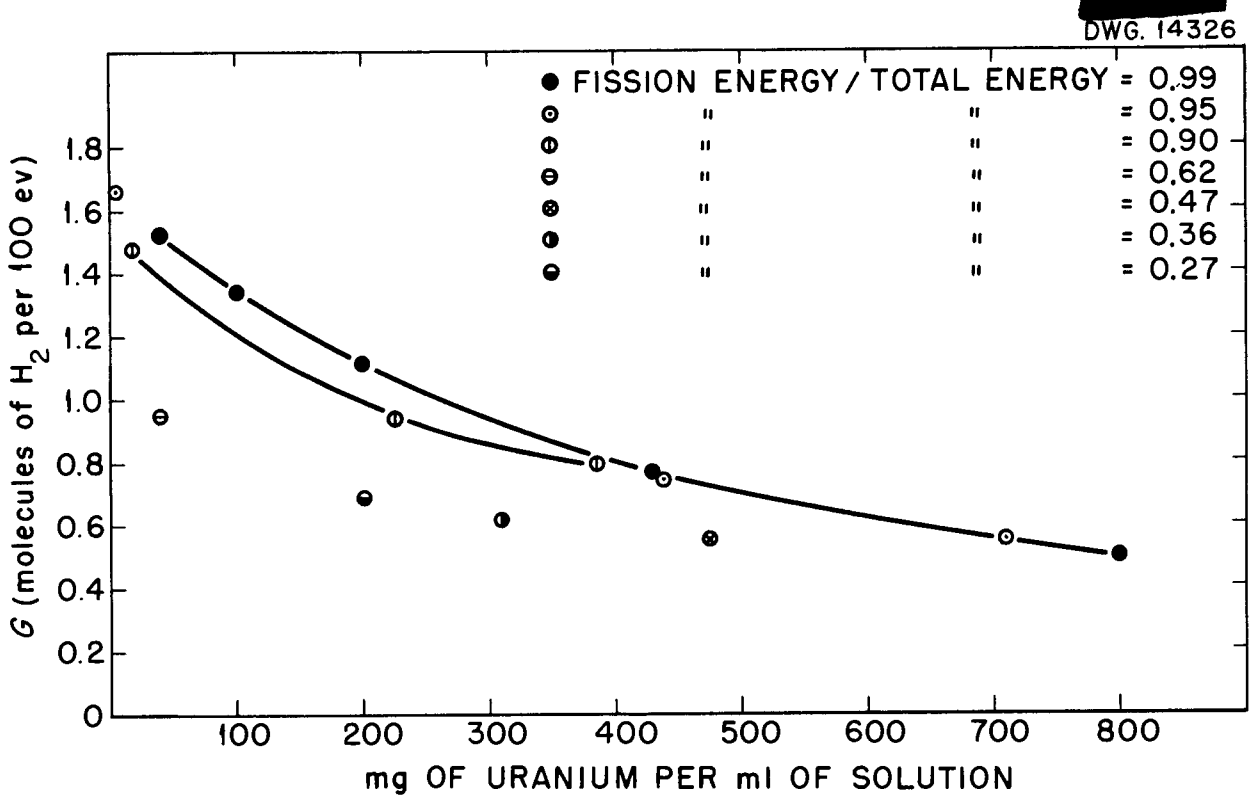


Fig. 29. Hydrogen Gas Production of UO_2SO_4 Solutions by Pile Irradiation at 120°C. The effect of the total uranium concentration and the ratio of fission energy to total energy are shown.

TABLE 38

Effect of Added Bromide Ion on Hydrogen Yields from Pile-Irradiated UO_2SO_4 and UO_2F_2 Solutions

SOLUTION	mg of U per ml	mg of U^{235} per ml	FISSION ENERGY vs. TOTAL ENERGY	KBr ADDED (*M*)	G_{H_2} 30°C	G_{H_2} 150°C	G_{H_2} 250°C
UO_2SO_4	44.6	0.316	0.653		0.98*	0.76	
	44.6	0.316	0.653	0.01	1.23*	1.17	
	40.7	37.9	0.995			1.5	1.4
	40.7	37.9	0.995	0.02		1.6	1.6
	297	2.11	0.924		0.84	0.72	~0.5
	297	2.11	0.924	0.02	0.95	0.90	0.85
UO_2F_2	44.6	0.316	0.653			0.64*	
	44.6	0.316	0.653	0.01		1.32*	
	297	2.11	0.924			0.67	0.42
	297	2.11	0.924	0.02		1.17	0.91

*Yields by gas analysis. Other yields by measurement of pressure in sealed ampoules.

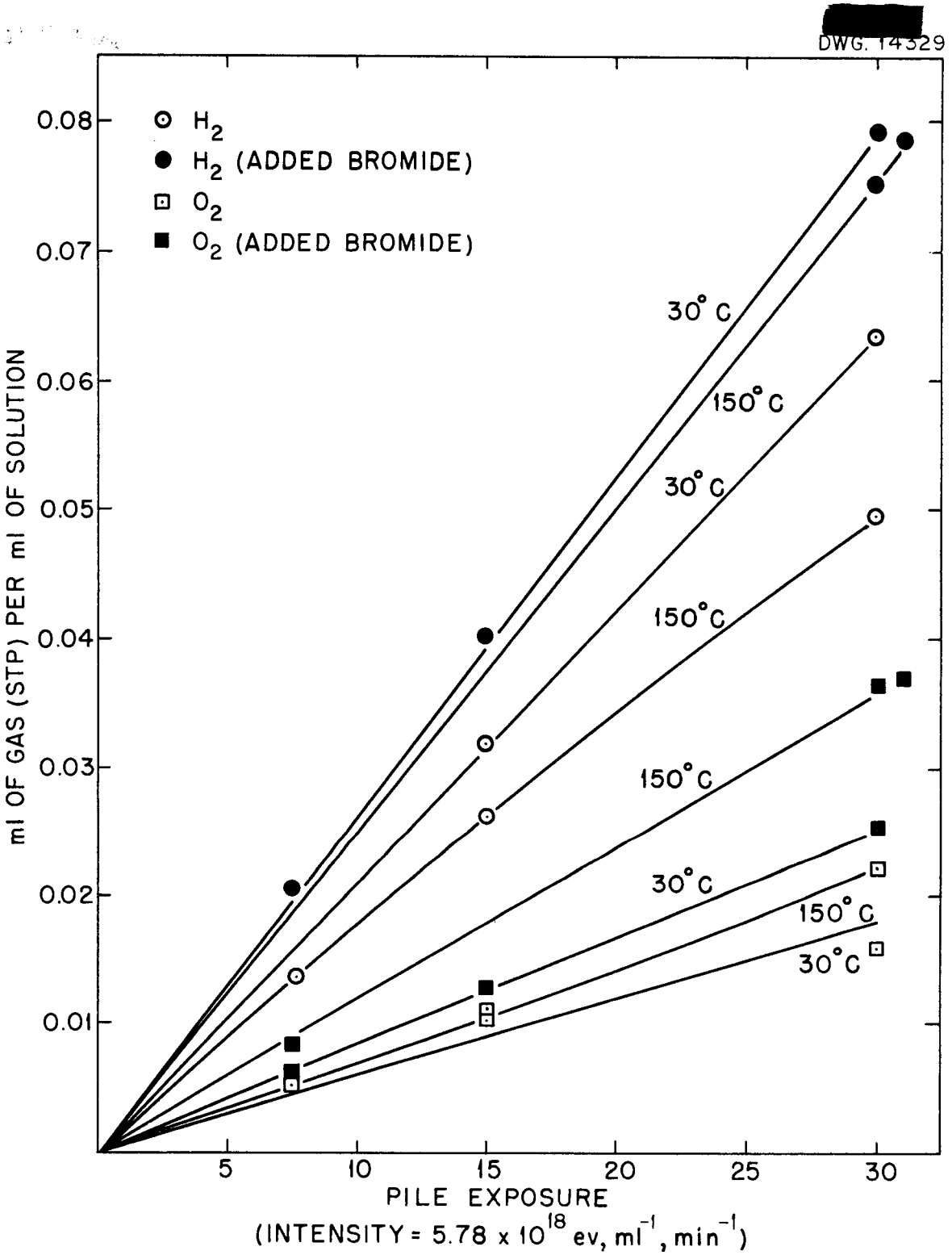


Fig. 30. Effect of Added Bromide Ion on Yields of Products from Pile-Irradiated UO_2SO_4 Solutions Containing 44.6 mg of Natural Uranium per ml of Solution.

back reaction did not significantly lower the yield in these solutions. The greater effect of bromide ion at higher temperatures indicates a temperature-sensitive back reaction.

Effect of Temperature on Gas Yields. By studying enriched solutions in which the radiation-induced back reaction is negligible and the rate of gas production is large compared with

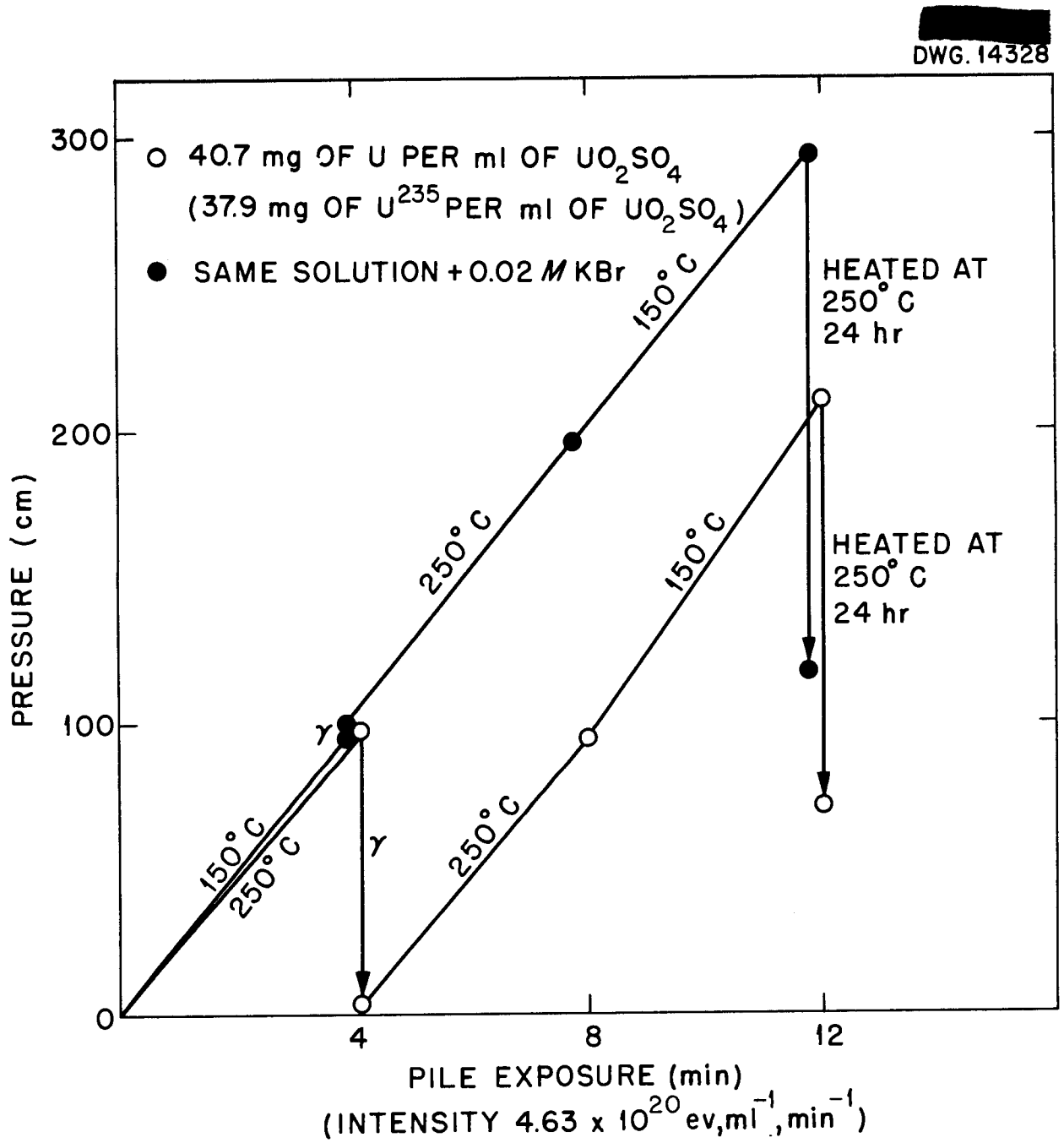


Fig. 31. Pressure Changes in Pile-Irradiated Ampoules Containing Enriched UO_2SO_4 Solutions.

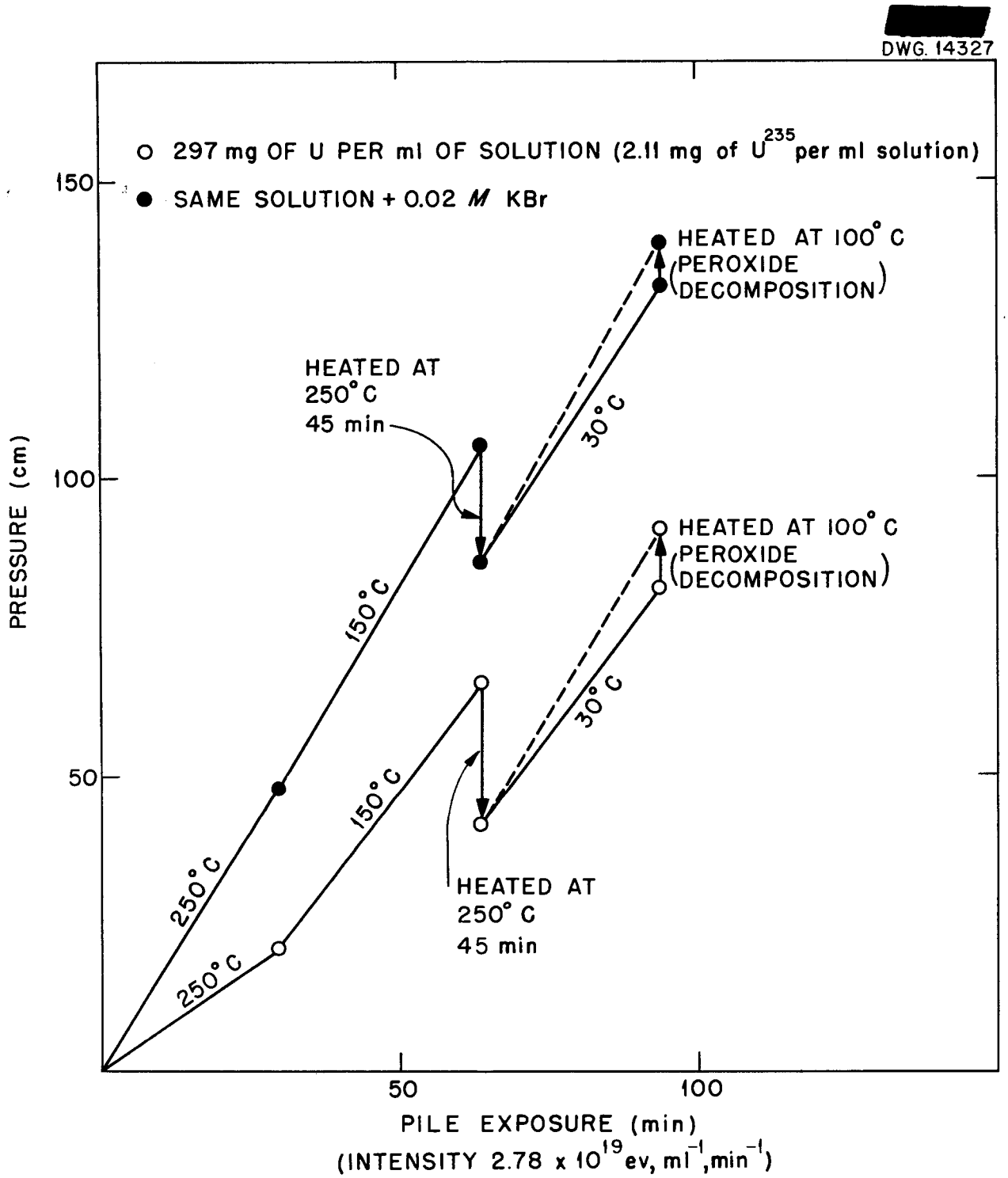


Fig. 32. Pressure Changes in Pile-Irradiated Ampoules Containing UO_2SO_4 Solutions.

the rate of thermal recombination, it was shown that the yield of gas is independent of temperatures up to 250°C. This is shown in Fig. 31, in which pressure increases in two typical ampoules, both irradiated at 150 and 250°C, are plotted. The importance of thermal recombination at 250°C during irradiation is indicated for enriched solutions in Fig. 31 and for natural uranium solutions in Fig. 32.

Peroxide Formation. A series of deaerated UO_2SO_4 solutions (44 mg of U per ml) irradiated in hole 12 at 50°C for between 1/2 and 8 min and analyzed for peroxide gave a constant yield of 0.86 molecule of peroxide per 100 ev. Previous calculations of peroxide on the basis of gas analysis data (Fig. 30) indicated a much lower yield of 0.5 molecules per 100 ev. A possible cause of this discrepancy is the decomposition of H_2O_2 after irradiation, since the peroxide determinations were made about 24 hr after irradiation, whereas the gas analyses in the earlier work were made three or four days after irradiation.

The low concentrations of H_2O_2, as indicated by gas analysis, for samples irradiated above 100°C are assumed to be the result of rapid decomposition of peroxide at the higher temperatures.

STUDIES ON THE RADIATION DECOMPOSITION OF CRYSTALLINE $KBrO_3$

G. E. Boyd J. W. Cobble

Two earlier papers[5,6] presented a discussion of a study of the Szilard-Chalmers enrichment of 35.9-hr Br^{82} produced by irradiation of pure crystalline $KBrO_3$ in the X-10 graphite pile. Two concurrent processes were found that acted to lower the specific activity of the radiobromine^{82} released in the crystal by the gamma-ray recoil following neutron capture: (1) a radiation-induced reaction that returned the recoiled Br^{82} to BrO_3^-, and (2) a radiation decomposition of $KBrO_3$ that released nonradioactive bromine isotopes which diluted the chemically separated active bromine. The present research was done to determine the causes for the radiation decomposition and to assess their relative importance. Some of the causes necessarily considered were (1) the gamma rays from uranium fission, resultant fission products, and neutron capture in pile materials, (2) the fast and epithermal neutrons, (3) the heavy-particle recoil following thermal-neutron capture, and (4) the energetic electrons from activated nuclides in the crystal and/or from the walls of the vessels containing the $KBrO_3$. It was possible to rule out contributions from fission-product recoils and from heavy-particle recoil.

The total or gross radiation decomposition constant, k_T, was taken as the sum of the constants for processes (1), (2), and (4):

$$k_T = k_\gamma + k_n + k_\beta \ .$$

This assumption seemed to be justified by the observation that the pile decomposition was linear with time and proportional to the intensity (power) (Fig. 33).

Radiation decomposition determinations were also conducted on $KBrO_3$ shielded from the pile radiations by various materials (Fig. 34). The decrease in the decomposition rate

(5) G. E. Boyd, J. W. Cobble, and S. Wexler, "Recoil Reactions with High Intensity Slow Neutron Sources. I. The Szilard-Chalmers Enrichment of 35.9 h Br^{82}," *J. Am. Chem. Soc.* **74**, 237 (1952).

(6) J. W. Cobble and G. E. Boyd, "Recoil Reactions with High Intensity Slow Neutron Sources. II. The Retention of Radiobromine by Crystalline $KBrO_3$," *J. Am. Chem. Soc.* **74**, 1282 (1952).

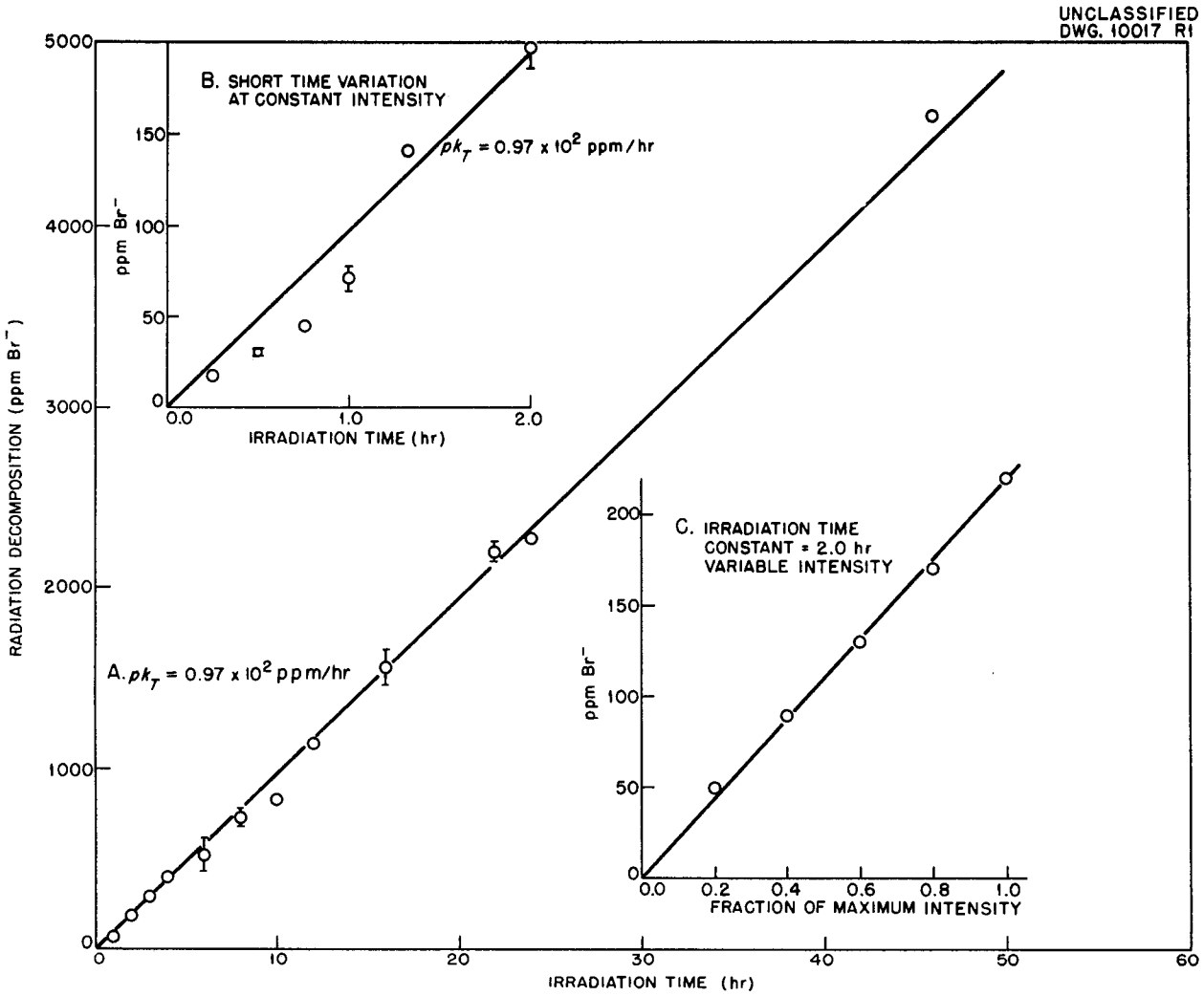


Fig. 33. Radiation Decomposition vs. Irradiation Time and Intensity.

effected by shielding with 1.5 g of Pb per cm^2 may be attributed to the removal of incident-energetic electrons (E_{max} = 3.01 Mev) emitted by the 2.30-min Al^{28} formed in the walls of the pneumatic tube used to transfer the sample to a point near the center of the pile,[7] plus the removal of about 13% by absorption of pile gamma rays that were estimated to show an average energy of 0.8 Mev (from the work of Richardson[8]). The further reduction of the decomposition rate to 54 ppm/hr by 13.2 g of Pb per cm^2 shielding may be explained by additional gamma-ray absorption. The reduction resulting with boron shielding came chiefly from the elimination of the external beta rays. Only about 2 ppm/hr of the decomposition could be assigned to the slow neutrons, which

[7] The authors wish to thank G. Jenks of the Chemistry Division, ORNL, for pointing out the importance of this effect to them, as well as to express appreciation for other helpful discussions during the course of this study.

[8] D. M. Richardson, *Colorimetric Measurement of Radiation Energy Dissipated by Various Materials Placed in the Oak Ridge Pile*, ORNL-129 (1948).

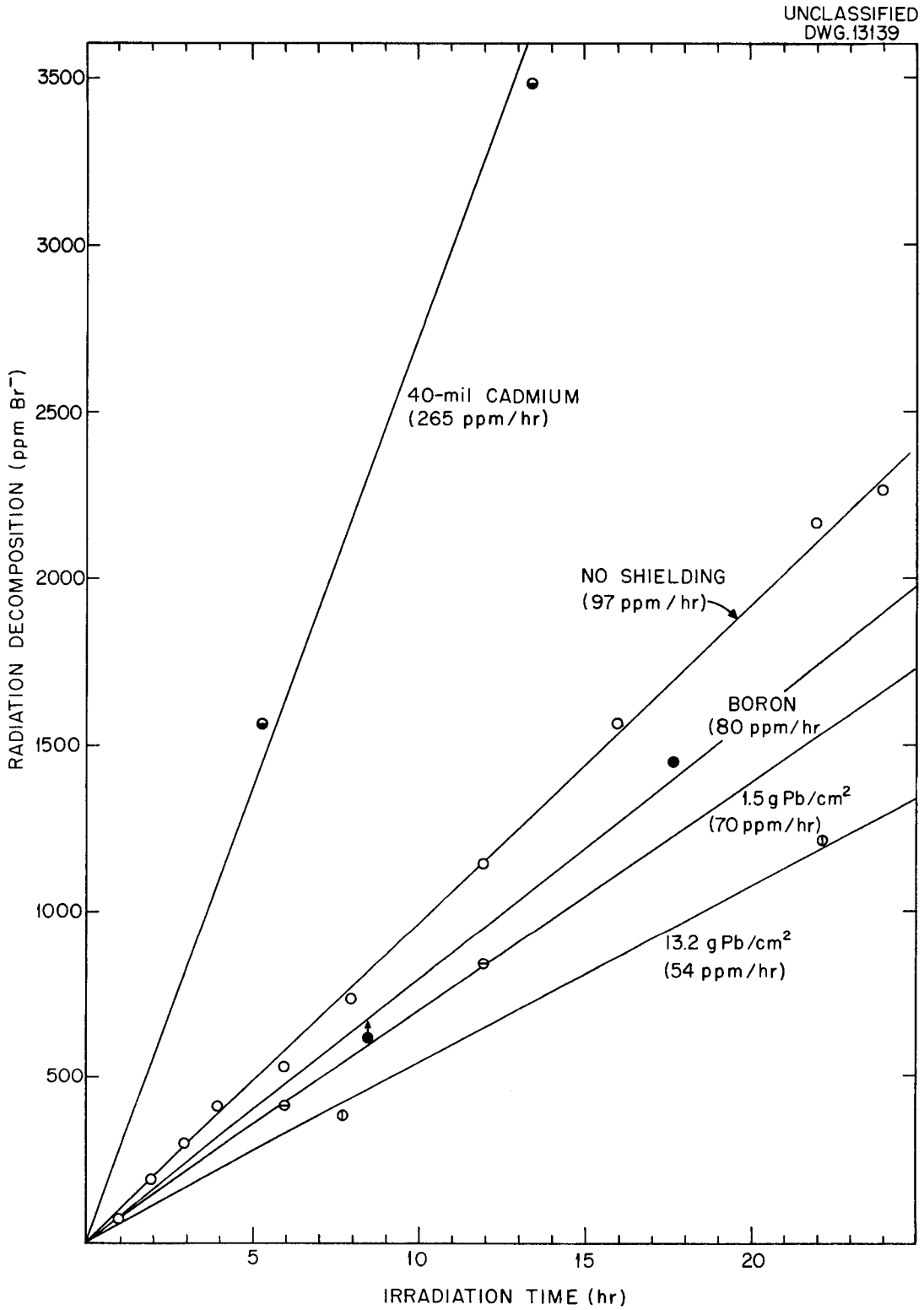


Fig. 34. Radiation Decomposition of $KBrO_3$ in the X-10 Graphite Pile.

indicated a very small self-bombardment of the crystal by beta and gamma rays from activated nuclei in the crystal or by recoiling heavy particles from the (n,γ) process. The nearly threefold increase observed in the cadmium shielding experiment was unexpected. The effect can be shown *not* to be caused by energetic cadmium-capture gamma rays; a plausible explanation is that numerous low-energy quanta (gamma or x rays), which have a large energy absorption coefficient in $KBrO_3$, are emitted by the radiative-capture process in cadmium.

TABLE 39

Decomposition of Pure, Crystalline $KBrO_3$ upon Exposure to Co^{60} Gamma Radiation at 25°C

Source Intensity = 4910 r/min

IRRADIATION TIME (hr)	DECOMPOSITION (ppm Br^-)
15.8	322
24.1	520
25.7	533 (80°C)
43.2	852
64.3	1332
111.7	2253

k_γ = 20.3 ppm/hr

Quantitative measurements of gamma-ray decompositions were made by using the experimental Co^{60} source (E_{avg} = 1.15 Mev) constructed by Ghormley and Hochanadel.[9] The decomposition was linear with time and seemed temperature-independent (Table 39).

After correcting for differences in gamma-ray flux between the Co^{60} source and the pile, it was estimated that about 41% of the total decomposition near the center of the X-10 graphite pile was induced by gamma rays.

The most difficult problem was the evaluation of the decomposing action of fast and epithermal neutrons. Owing to the neutron energy dependence of the decomposition it was necessary to conduct measurements with several fast-neutron sources. Results from an irradiation in the Los Alamos fast reactor at a bombardment position where the average neutron energy was 0.6 Mev are presented in Fig. 35.[10] A measurement at an average neutron energy of 1.6 Mev was made by using a U^{235} converter in the thermal column of the fast reactor, and the decomposition at an average of 6.1 Mev was obtained with neutrons produced by 15-Mev deuterons[11] on beryllium.[12] From the known gamma-ray yields, the effects of gamma rays (also present in all the fast-neutron sources) could be estimated to be negligible. A summary of all the fast-neutron decompositions is shown in Fig. 36. By using the fast-neutron spectrum determined by Bopp and Sisman[13] for the X-10 graphite pile, an estimate could be made of the expected decomposition of $KBrO_3$ from fast and epithermal neutrons. This amounted to approximately 42% of the total observed decomposition.

(9) J. A. Ghormley and C. J. Hochanadel, "A Cobalt Gamma-Ray Source Used for Studies in Radiation Chemistry," *Rev. Sci. Instr.* **22**, 473 (1951). The authors wish to thank Ghormley and Hochanadel for allowing them to use this convenient, calibrated radiation source.

(10) The authors wish to express their appreciation to R. W. Spence and J. Sattizahn of the Radiochemistry group and to C. Zabel and E. Swickard of the Physics Division, Los Alamos, for their assistance in conducting these measurements.

(11) C. E. Falk, *Technical Report No. 5*, Carnegie Institute of Technology, July 1950.

(12) The authors wish to express their thanks to D. Cowie and P. H. Abelson of the Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, D. C. for use of the 60-in. cyclotron.

(13) C. D. Bopp and O. Sisman, *The Neutron Flux Spectrum and Fast and Epithermal Flux in Hole 19 of the ORNL Reactor*, ORNL-525, July 28, 1950.

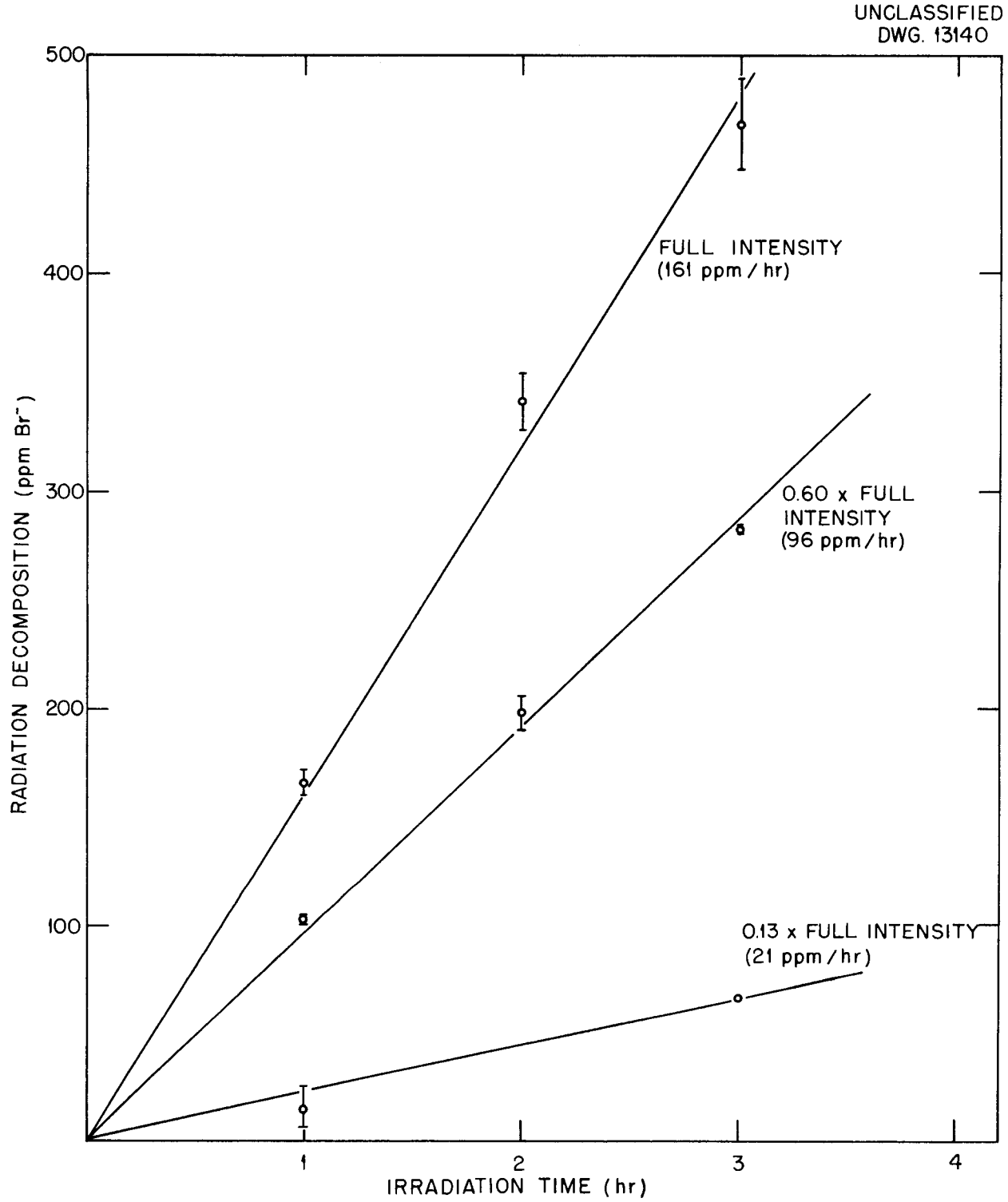


Fig. 35. Radiation Decomposition of $KBrO_3$ in the Los Alamos Fast Reactor.

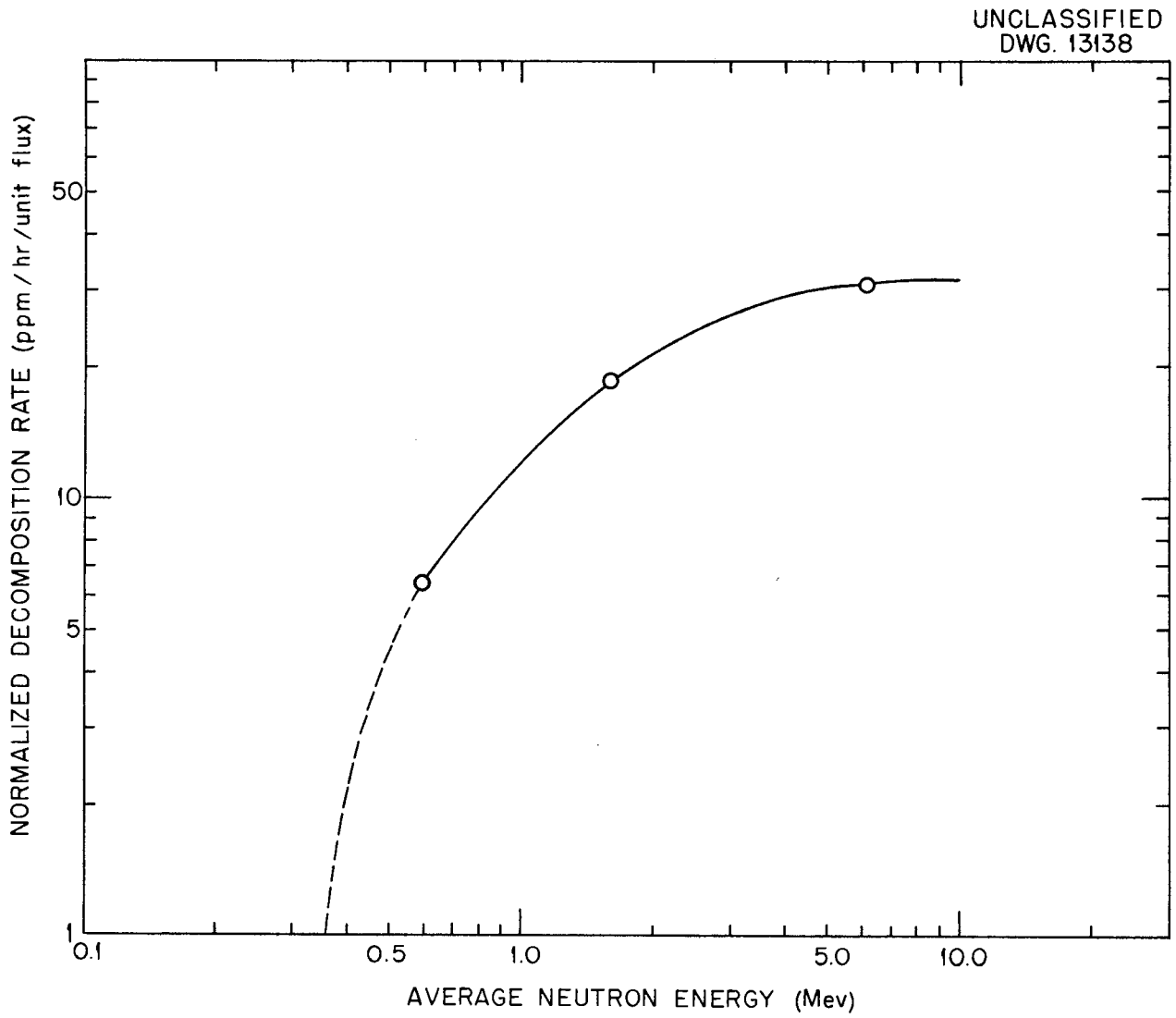


Fig. 36. Energy Dependence of the Fast Neutron Decomposition of $KBrO_3$.

A summary of the relative contributions of the various pile irradiations considered in this work is given in Table 40.

The yield value given in the last column of Table 40 shows that the energetic-neutron component is responsible for a sizable fraction of the total decomposition. A *G* value of 1 molecule per electron volt absorbed denotes relatively good decomposing efficiency – with gamma rays or electrons, approximately 33 ev per molecule are required ($G = 33$). The reason for the difference between the efficiencies for these two types of radiations probably lies in the decomposition mechanisms involved. The energy loss of neutrons occurs by actual collisions with the nuclei of molecules rather than by interaction with their electrons as with gamma rays and electrons. Since the latter may give rise to molecular excitation and subsequent emission of radiation

TABLE 40

Radiation Decomposition of Crystalline $KBrO_3$ Irradiated in the X-10 Graphite Pile

RADIATION TYPE	AVERAGE ENERGY (Mev)	DECOMPOSITION (ppm/hr)	RELATIVE DECOMPOSITION (%)	YIELD (ev/molecule)
External beta rays	1.3	15	15	~40
Gamma rays	0.8	40	41	33
Thermal neutrons	0.022 ev	2	2	
Epithermal neutrons	1 ev to 1 Mev	17	18	1.1 ± 0.3
Fast neutrons	≥ 1.0	23	24	
	Gross decomposition	97	100	

TABLE 41

Reactivation of a Radiation-Deactivated ZnO Catalyst

TREATMENT	TOTAL TIME OF IRRADIATION (hr)	ACTIVITY TOWARD HYDROGENATION OF $1C_2H_4 + 2H_2$ AT 0°C. (1.00 g of ZnO, 50 cm^3 of gas, t = 1/2 hr)
Evacuated at 390°C overnight		45
Evacuated at 0°C, 2 hr Irradiated, 12,000 r/min	144	53
Evacuated at 0°C, 2 hr Irradiated, 12,000 r/min	238	65
Evacuated at 0°C, 2 hr Irradiated, 12,000 r/min	1216	89
Evacuated at 0°C, 2 hr Irradiated, 12,000 r/min	1884	156
Evacuated at 0°C, 2 hr Irradiated, 12,000 r/min	2386	326
Evacuated at 390°C, 990 min		57
Evacuated at 0°C, 2 hr		59

without decomposition, a large part of the energy absorbed may not be effective. This does not appear to be the case with neutrons where the energy absorbed is dissipated with frequent molecular rupture.

EFFECT OF RADIATION ON HETEROGENEOUS CATALYSTS

J. A. Wethington E. H. Taylor

Further evidence has been obtained that the decrease in catalytic activity of ZnO exposed to gamma radiation is probably not a poisoning through radiation decomposition of tightly adsorbed reactants or products. A sample reduced severalfold in activity toward ethylene hydrogenation by irradiation with Co^{60} gamma rays for about 2000 hr at about 12,000 r/min was reactivated to nearly its initial activity by the usual activation technique - evacuation overnight at about 390°C. Table 41 gives some detailed results.

It seems unlikely that the final evacuation would have removed so nearly completely any radiation-produced poison that might be assumed to be the cause of the decrease in activity upon irradiation.

CHEMISTRY OF THE SOLID STATE

HIGH-TEMPERATURE X-RAY DIFFRACTION

M. A. Bredig

A spectrometer has been used to search for a face-centered-cubic, high-temperature structure in uranium dicarbide, UC_2, and lanthanum dicarbide, LaC_2. In these compounds, members of a series of dicarbides tetragonal at room temperature, the metal ion has an increasing number of valence electrons whose effect on the lattice energy is of interest.[1] The identification of a new, high-temperature structure in these compounds is difficult because a very slight amount of surface oxidation prevents penetration of the x-ray beam to the carbide. Earlier attempts to obtain photographically recorded, high-temperature x-ray patterns of uranium dicarbide were abandoned for that reason.

In the present experiments, a surface oxidation occurred at intermediate temperatures and prevented the observation of the carbide structure upon heating. Instead, the pattern of cubic uranium dioxide was obtained. Since the crystal lattice constant of UC_2 must be expected to be fairly similar to that of cubic UO_2, a_0 = 5.45 Å, proof that UO_2 rather than cubic UC_2 was being observed came from the fact that neutron diffraction[1] had shown the tetragonal phase to be still present at 1250°C. In addition, upon cooling, the cubic structure persisted, whereas in analogy to calcium dicarbide the cubic structure is expected to transform instantaneously, upon cooling, into the tetragonal low-temperature form. However, an x-ray pattern taken at an increased temperature of 1850°C (at which temperature uranium oxide reacts with excess carbon according to the equations $UO_2 + 4C = UC_2 + 2CO$ and, partly, $UO_2 + 3C = UC + 2CO$) showed the presence of a face-centered-cubic structure with a_0 = 5.45 ±0.1 Å, that is, intermediate between the tetragonal constants 4.95 and 5.95 Å and larger than the constant of UC, a_0 = 4.95 Å. This structure did not persist even upon relatively rapid cooling; it changed into the tetragonal phase. Here then, the cubic form of UC_2 was actually observed directly for the first time. However, it must be pointed out that the chemical composition of the phase observed at 1850°C may be somewhat different from that of pure UC_2. It may contain UC in solid solution. Mallett, Gerds, and Nelson[2] have shown that such solid solutions exist.

It is one of the objectives of the present investigation to establish the conditions of temperature and carbon content at which the cubic phase changes into the tetragonal phase. This phase change is interesting also because of the comparatively large change (approximately 10%) in specific volumes occurring in the rapid transformation. The change in specific volume would be important in consideration of the compound as a high-temperature fission fuel, since stability of both mechanical structure and neutron interaction is desirable. It is considered likely that even in a solid with the maximum carbon content (that is, a composition very closely corresponding to UC_2) the transition, tetragonal to cubic, occurs at a high temperature.

Future attempts may be directed toward determining this temperature

(1) M. A. Bredig, "High-temperature Crystal Structure of Uranium Dicarbide," *Physics Division Quarterly Progress Report for Period Ending September 20, 1950*, ORNL-865, p. 81-83.

(2) M. W. Mallett, A. F. Gerds, and H. R. Nelson, *The Uranium-Carbon System*, AECD-3226, Apr. 1, 1951.

by recording x-ray patterns as the temperature is gradually lowered from 1850°C. However, in order to avoid the difficulties of surface oxidation, a high-temperature vacuum furnace for neutron-diffraction measurements at temperatures in excess of 1300°C appears to be preferable and is now in the planning stage.

The lanthanum dicarbide investigated was prepared by heating pellets of a mixture of lanthanum oxide and carbon for only a few minutes in a small, rectangular carbon crucible supported inside the x-ray-diffraction vacuum furnace. The pattern of the known tetragonal structure recorded at room temperature changed to that of the hexagonal oxide at intermediate temperatures. At 1750°C, through reaction with excess carbon, a cubic carbide phase was formed, which upon rapid cooling reverted to the common tetragonal carbide form. The lattice constant of the cubic phase observed, $a_0 = 6.0 \pm 0.1$ Å, is, as in the case of UC_2, intermediate between the tetragonal constants $a_0 = 5.54$ and $c_0 = 6.53$ Å. This was expected because the cubic structures of these compounds, which are probably of the pyrite (FeS_2) type, are entirely analogous to CaC_2, SrC_2, and BaC_2.

In these experiments difficulties were still encountered with the mechanical structure of the sample support because of the extreme temperatures to which it was exposed. The sample support is now being replaced with a water-cooled shaft.

REMOTELY CONTROLLED X-RAY-DIFFRACTION SPECTROMETER

M. A. Bredig

B. S. Borie, Jr.
Metallurgy Division

G. E. Klein and F. A. Sherrill
Physics of Solids Institute

Work on the spectrometer was at a standstill during this period because it was found impossible to operate the sealed-off G-E x-ray diffraction tube with the Hilger high-voltage generator. A new Norelco apparatus will soon be available for this purpose and work will be resumed.

CRYSTAL STRUCTURE OF THE ALPHA MODIFICATIONS OF SOME A_2BX_4 COMPOUNDS

M. A. Bredig R. D. Ellison

The nature of the chemical binding between beryllium and fluorine in complex alkali metal-beryllium fluorides is of interest in connection with the irradiation stability of melts of such compounds. A determination of the crystal structure of the hexagonal, high-temperature alpha form and, in particular, of the atomic distances between beryllium and fluorine seems desirable. As a start, a check of the structure determination[3] of glaserite was undertaken. The glaserite used had the approximate composition $K_3Na(SO_4)_2$, and it was isotopic. The alpha modifications were similar to those of the complex beryllium fluorides – that is, they were stable immediately below their melting points.[4] In glaserite, in contrast to the fluorides, the high-temperature structure can be easily preserved and conveniently studied at room temperature.

The cell size, without refinements for greatest accuracy, was found to agree with that given for glaserite by Gossner.[3] The S-O distance in the $SO_4^=$ ion that Gossner's structure proposal demands is 1.35 Å, which is approximately 0.25 Å smaller than usually found in sulphates. A check of the intensities of the $h01$ reflections confirms the thought that the

[3] B. Gossner, "The Crystal Structure of Glaserite and Potassium Sulfate," *Neus Jahrb. Miner. Geol.* **57A**, 89-116 (1928).

[4] M. A. Bredig, "Phase Relations in the Systems Ca Orthosilicate-orthophosphate," *Am. Mineral.* **28**, 594-601 (1943).

structure, as proposed, is not entirely correct. The diffraction symmetry and the linear Fourier synthesis of the electron density suggest that the errors are not very great and may probably be corrected by a slight change in the orientation of the sulphate ions and simultaneous expansion. A two-dimensional ($hk0$) Patterson synthesis is expected to yield the desired refinement of the atomic positions.

EFFECT OF RADIATION ON CRYSTAL STRUCTURE

M. A. Bredig

The irradiation of lead monoxide in the Chalk River reactor for approximately one month at a flux of 6.4×10^{19} fast neutrons per square centimeter led to a partial transformation (25%) of the yellow form into the red modification.[5,6] The exposure was repeated in the LITR, and, surprisingly, the result entirely contradicted the result from the Chalk River exposure. After an exposure to 3.6×10^{19}[7] fast neutrons per square centimeter in the water-cooled torpedo of the LITR, no trace of the tetragonal red form was observed in the two yellow specimens. One possible, though not as yet satisfactory, explanation is the following: The temperature of the lead monoxide in the Chalk River test, even though the specimen was cooled by an air stream of 25°C, may have risen considerably above that of the coolant because of gamma-ray absorption and poor heat transfer through the loose powder and the glass walls of the ampoule. The heat transfer may have been better in the LITR experiment in which the heat transfer medium was water at approximately 80°C. Further experiments, which will include monitoring both temperature and neutron flux, are needed to explain the discrepancy between the two tests before the tentative conclusions drawn from the first, apparently positive, results can be considered invalid. No transformation was observed in the LITR test with the calcite and aragonite forms of calcium carbonate.

MISCELLANEOUS X-RAY-DIFFRACTION WORK

M. A. Bredig R. D. Ellison

Identification work was performed on specimens submitted by various members of the HRE Project staff and by others. Preparations are being made for a study of x-ray-diffraction effects of concentrated thorium nitrate solutions in tributyl phosphate (for J. E. Savolainen, Chemical Technology Division).

METAL-METAL HALIDE SYSTEMS

M. A. Bredig J. W. Johnson

As a preliminary to the investigation of systems that are of special interest as reactor coolants and fuel mixtures, a few experiments were undertaken in the system cadmium–cadmium chloride, including x-ray-diffraction studies of the quenched melts. These studies showed agreement with data found in the literature[8]—that is, about 12 mole % of the metal dissolves in the melt, but even upon fast cooling it is precipitated without formation of a solid subchloride, CdCl or Cd_2Cl_3. Magnetic susceptibility measurements[9] have shown the

(5) *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1951*, ORNL-1116.

(6) *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1950*, ORNL-1036.

(7) This figure was supplied by T. H. Blewitt and R. R. Coltman who kindly included these specimens in the charge of a torpedo, which they designed and operate. It is based on a comparison of the amount of damage produced in a single copper crystal in the X-10 graphite pile and the LITR.

(8) R. E. Hedger and H. Terrey, "Suboxides and Subhalides of Cadmium," *Trans. Faraday Soc.* **32**, 1614-16 (1936).

(9) J. Farquharson and E. Heymann, "Magnetic Properties of Solutions of Cadmium in Molten Cadmium Chloride and of Molten Calomel," *Trans. Faraday Soc.* **31**, 1004-10 (1935).

absence of paramagnetic ions, such as Cd^+, in the melt.

Quenching experiments in the system calcium-calcium chloride followed by determination of alkalinity and hydrogen evolution on dissolving the solidified salt phase in water led to an apparent value of 40 mole % for the solubility of calcium metal in its dichloride. This value is much higher than the 20 mole % reported in comparatively recent investigations by Cubicciotti and Thurmond,[10] but it is in seemingly better agreement with the much older data by Woehler and Rodewald.[11] They reported a value of 50 mole %. It seems very possible, however, that small amounts of the hexahydrate present in the dichloride had supplied a sufficient quantity of water for the formation of CaO and CaH_2 according to the equation

$$CaCl \cdot 6H_2O + 12Ca = CaCl_2 + 6CaO + 6CaH_2.$$

The two compounds would, upon dissolution in water, produce both alkalinity and hydrogen evolution corresponding to that of dissolved calcium metal or calcium subchloride. The reaction, upon dissolution in water,

$$CaO + CaH_2 + 3H_2O = 2Ca(OH)_2 + 2H_2,$$

gives the same ratio of $Ca(OH)_2$ to H_2 as the reactions

$$2Ca + 4H_2O = 2Ca(OH)_2 + 2H_2,$$

or

$$4CaCl + 4H_2O = 2CaCl_2 + 2Ca(OH)_2 + 2H_2.$$

These equations demonstrate the need for extreme care in preparing truly anhydrous calcium dichloride. Such dehydration and purification are now under way.

Experiments with the system sodium in molten sodium chloride have led to a solidified salt phase containing 10 mole % of sodium, after quenching from 850°C, and to another one containing 4 mole %. Intense blue coloration, known to be caused by collodially dispersed sodium metal, was observed in the rapidly cooled part of the melt near the crucible wall. The wide variation of these two values and their discrepancy with a literature value[12] of 15 mole % for this temperature require further investigation.

(10) D. D. Cubicciotti and C. D. Thurmond, "Metal-salt Interactions at High Temperatures: the Solubilities of Some Alkaline Earth Metals in their Halides," *J. Am. Chem. Soc.* **71**, 2149-53 (1949).

(11) L. Woehler and G. Rodewald, "Known and New Subhaloids," *Z. anorg. Chem.* **61**, 54-90 (1909).

(12) R. Lorenz and R. Winzer, "The Solubility of Sodium and Calcium in their Chlorides and Chloride Mixtures," *Z. anorg. allgem. Chem.* **183**, 121-6 (1929).

INSTRUMENTATION

A NEW LINEAR AMPLIFIER FOR SCINTILLATION SPECTROMETRY

E. Fairstein

The basic developmental work on a new amplifier has been completed and a model is now being constructed. The novel feature of the amplifier is the pulse shaper. The shaper consists of two identical, shorted, delay lines. The lines are cascaded at the input of the amplifier and cause the output-pulse shape to be the second derivative of the photomultiplier voltage pulse. On an oscilloscope the output is a flat-topped pulse of approximately 0.6-μsec duration followed by an undershoot of equal amplitude and duration. The advantages of this pulse shape over the usual one will become apparent from the following discussion.

In the usual RC-coupled pulse amplifier, the time constant of one of the coupling networks is made very much smaller than that of any of the others. If the usual detector pulse is applied to such an amplifier, the output pulse will have a rapid rise and a longer exponential decay. The rate of decay will depend upon the time constant of the smallest coupling network. The pulse will also undershoot the base line. The peak amplitude of the undershoot compared with the peak of the first part of the pulse will never exceed the ratio of the shortest time constant to the next shortest, but it will approach it for time-constant ratios less than 0.05. Since an RC-coupled amplifier can pass no direct current, the long-time average of any given pulse must be zero - that is, the integrated area of the pulse on one side of the line must be numerically equal to that on the other. It is evident that a pulse whose peak undershoot is small compared with that of the primary pulse must be of long duration compared with that of the primary pulse.

Under actual counting conditions where pulses occur at a random rate, it is a common situation for pulses to occur in the troughs of the undershoot of earlier pulses. These pulses will appear to have lower amplitudes than those of their neighbors. It can also be observed that the average value of all the pulses appears smaller than their true average value by an amount that is numerically equal to the duty cycle of the counting process, where the duty cycle is defined as the ratio of the total measured primary pulse area to the total possible primary pulse area for a unit time interval of measurement. As a consequence of these effects, if an attempt is made to obtain the pulse height distribution of a monoenergetic emitter, for example, it is found that as the counting rate increases the peak will broaden and shift toward the zero-energy axis.

It appears that the only solution to the problem is the extreme of making the undershoot as large as the primary pulse. When this is done, the duration of the undershoot is the same as that of the primary pulse. The operating conditions of the counting system can be chosen so that a pulse is either recorded correctly, or not at all. The dead time of the system need not be more than twice that of the older method using the same primary pulse width, and the usable counting rate can probably be increased by a factor of 10 or more.

The signal shaping can be accomplished by RC, LC, or delay-line networks. Delay-line networks give much better results than the RC or LC networks and are being used in the present amplifier. No difficulties with reflections are experienced if care is taken in termination. The expected characteristics of the new amplifier are as follows:

Primary pulse width	0.6 μsec
Maximum dead time	Less than 2.0 μsec
Dynamic range	Greater than 300 to 1
Blocking characteristics	Nonblocking
Output-pulse height	100 volts into 1,000 ohm or greater load
Pulse-height selector	Built-in, single-channel, differential discriminator
Gain	50,000
Preamplifier	Gain of one may be used with 100 ft of 100-ohm cable without pulse-shape degradation
Usable counting rate	Depends upon permissible counting loss. There will be no energy spread or baseline shifts with high counting rates or overloads

A LOGARITHMIC SWEEP CIRCUIT FOR USE IN PULSE-HEIGHT ANALYSIS

E. Fairstein

A photographic method for determining the energy distribution of a radioactive source has been known for some time. The radiations from the sample are converted to electrical pulses whose amplitudes are proportional to the energy of the radiations. The pulses are shaped to have a flat top and are then applied to the *Y*-axis terminals of an oscilloscope. A linear sweep is triggered by each of the pulses. The controls are set so that the pulses appear on the screen as a series of straight lines parallel to the *X* axis. A light filter is then placed over the screen, and a long-time exposure photograph is taken of the pulses. The characteristics of the filter are such that the rate of light absorption in the *X* direction increases logarithmically. The absorption in the *Y* direction is constant. Evidently, those regions where the pulse rate is high will appear to penetrate further into the area of high absorption than those regions where the pulse rate is low. On the finished photograph, a light contour will represent a graph of pulse rate vs. pulse amplitude. The pulse amplitude corresponds to the *Y*-axis displacement, and the logarithm of the pulse rate corresponds to the *X*-axis displacement. If high-contrast film is used and successive copies of the photograph are made on high-contrast film or paper, a line of demarcation between regions of high and low light intensity will be quite apparent. This line represents the desired contour of pulse rate vs. amplitude.

The most serious limitation to the technique is the problem of

obtaining sufficient light intensity for a good photograph in a reasonably short-time exposure. It was suggested by H. Zeldes that this limitation could be overcome by using a logarithmic sweep for the *X* axis rather than an absorption filter over the face of the cathode-ray tube. In the case of a two-cycle sweep, the improvement in light intensity is approximately fiftyfold.

A unit was built that provides the necessary sweep voltage and offers the user some additional conveniences as well. A counting circuit is included to disconnect the input after a predetermined number of pulses have been recorded. The number can be set for 1,000, 2,000, 5,000 or 10,000 pulses. This is necessary for producing identical exposures of samples with different disintegration rates. A flat-topped pulse is provided to turn on the cathode-ray tube beam at the start of the sweep. A pulse stretcher is provided so that the pulses from an A-1 amplifier may be properly shaped. The sweep duration can be set for 5, 10, 25, or 50 microseconds. Two cycles are displayed for all sweep-duration settings. The pulse-stretching time and the beam-gate duration are also controlled by the setting of the sweep-duration switch. A pulse-height selector is provided to suppress the zero of a pulse-height distribution.

The unit has been tested electrically, but no photographic measurements have yet been made with it.

PHOTOMULTIPLIER DETECTION OF IONIZING EVENTS IN A GAS

R. Stone C. J. Borkowski

Energy in the form of light quanta is emitted when an ionized or excited atom of a gas drops to a lower level of excitation. An investigation is being made of the feasibility of detecting ionizing events in gases by the measurement of this light.

The method has been to attach an end-window photomultiplier to a gas chamber containing an alpha source. A suitable gas is continuously passed through the chamber. When argon is used, nearly 100% of the alpha particles passing through the gas is detected.

Only in monatomic gases has sufficient light been emitted to observe single alpha ionizing events. The pulse height in neon is about twice that in helium, and in argon it is three times that in helium. Since the alpha-particle range exceeded the chamber dimensions when helium and neon were used, the relative pulse heights do not indicate the relative light production in the gases for equivalent alpha-energy expenditure.

All the pulses are small, with those in argon giving about 1/500 the height of sodium iodide pulses for the same dissipation of energy. About 100-kev alpha-energy dissipation in argon is required to release a single photoelectron from the photocathode.

A considerable amount of self-absorption of light apparently takes place in the counting gas, since the largest pulses are obtained when the sample can be collimated so that the ionization takes place quite close to the photocathode. A very small amount of air or polyatomic gas is sufficient to quench all pulses. The quenching action is similar to that which takes place in a Geiger-Mueller counter discharge.

In a single check, little difference was found between the response of a 5819 photomultiplier (down 90% at 3000 Å) and a C-7140A photomultiplier

(down 90% at 2200 Å) when the tubes were equalized for the same peak response. This result could be expected because of the wide emission spectrum of argon.

Figure 37 was drawn from an oscilloscope record of the gas pulses, by using a sweep speed equal to 0.1 μsec/cm. The general pulse shape is shown and a rise time of about 0.15 μsec is indicated. Considerably more light would be emitted if lower pressures of gas could be used, since, at atmospheric pressure, excited argon atoms lose a large fraction of their energy in thermal collisions with neighboring atoms before photon emission takes place. Because of the small amount of light emitted, practical application of the detection of ionizing particles by this method is limited to densely ionizing events produced by alpha particles, fission fragments, and high atomic number cosmic-ray particles. Possible applications might be the assay of intense sources of polonium or the counting of fission pulses in the presence of intense alpha and beta activity. For example, a fission counter of this type might be considered for use as a neutron-flux monitor in a reactor. The light could be piped out to an external photomultiplier, and thus the electrical leads to conventional detectors, such as pulse ion counters, could be eliminated. Furthermore, no deterioration of the gas would be expected, as would be the case if organic or inorganic phosphors were used.

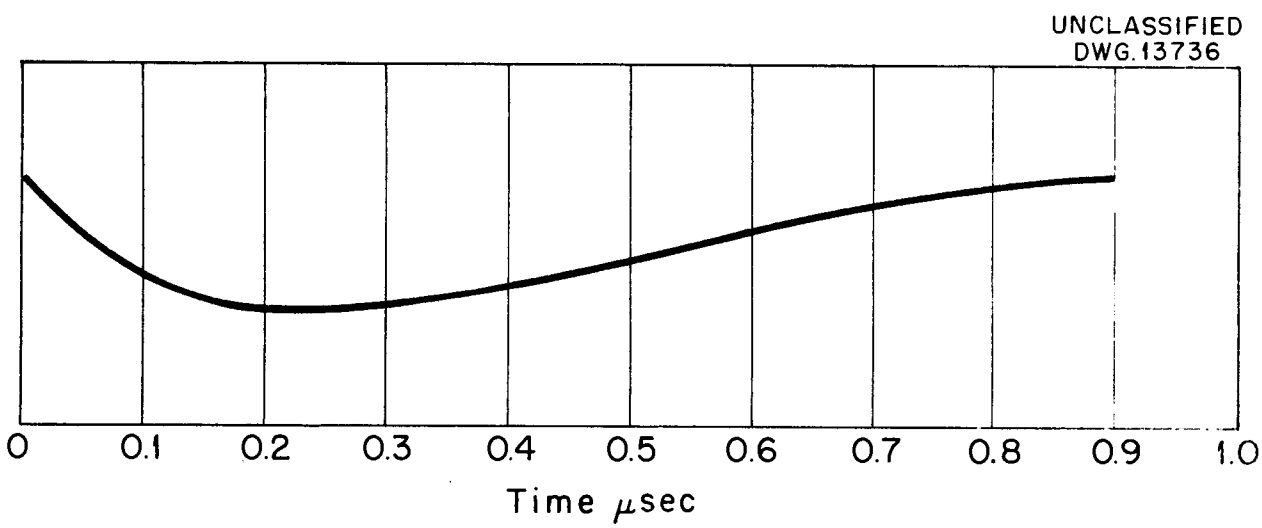


Fig. 37. Typical Shape of Gas Pulse.

REACTOR CHEMISTRY

STABILITY OF PLUTONIUM IN SOLUTIONS OF URANYL SULFATE AND URANYL FLUORIDE

K. S. Warren H. W. Wright

The preliminary stability investigation of plutonium sulfate in 1.26 *M* UO_2SO_4 (reported in detail previously[1]) indicated a hydrolysis solubility of about 0.005 g of plutonium per liter at about 200°C. A study has been initiated on the rate of precipitation of plutonium(IV) from a uranyl sulfate solution at temperatures from 100 to 200°C. The data obtained indicate that equilibrium is not reached after ten days below 140°C. Further work is needed on reaction rates above 140°C before the equilibration times can be predicted.

Samples of uranyl fluoride solution containing a small amount of plutonium fluoride were used in similar hydrolysis-rate experiments at 130°C. The stability of plutonium fluoride with respect to precipitation under these conditions does not differ appreciably from that of plutonium sulfate.

A cell was constructed for electrolytic oxidation of plutonium(IV) to plutonium(VI). A trial electrolysis showed that practically complete conversion to the higher valence state is obtained in two days or less. All investigations will be reported in detail in the next Homogeneous Reactor Project quarterly progress report.

FISSION-PRODUCT SOLUBILITIES IN AQUEOUS URANYL SULFATE SOLUTIONS AT ELEVATED TEMPERATURES

E. V. Jones

Studies have been completed on yttrium and lanthanum sulfate solubilities in 0.126 and 1.26 *M* UO_2SO_4 between 150 and 300°C. This work was reported in the last Homogeneous Reactor Project quarterly progress report.[2] A summary of current investigations is given below and details will appear in the next HRP report.

Cesium Sulfate. The silica-tube synthetic method has been used to determine the solubility of cesium sulfate in 1.26 *M* UO_2SO_4 from 170 to 290°C and in 0.126 *M* UO_2SO_4 from 55 to 180°C. These studies are practically complete. The temperature coefficient of solubility was positive.

The solubility of cesium sulfate in 0.126 *M* UO_2SO_4 at 180°C is only slightly less than it is in water at the same temperature, as determined by Lietzke and Stoughton,[3] but it is more than two hundred times less soluble in 1.26 *M* UO_2SO_4 than in water and, therefore, a double-salt formation is indicated in the latter system.

Ceric Sulfate. Preliminary tests show that ceric sulfate is only slightly soluble in 1.26 *M* UO_2SO_4 at room temperature and has a negative temperature coefficient of solubility. Therefore no attempt was made to study it by the silica-tube synthetic method.

Molybdenum Oxide. Molybdenum(VI) oxide was found to be appreciably soluble in 1.26 *M* UO_2SO_4 at room temperature. Heating to about 75°C did not appreciably change the solubility; above this temperature a white

(1) W. L. Marshall, R. D. Brown, H. O. Day, J. S. Gill, E. V. Jones, K. S. Warren, and H. W. Wright, "Solution Chemistry," *Homogeneous Reactor Project Quarterly Progress Report for Period Ending November 15, 1951*, ORNL-1221, p. 97.

(2) *Ibid.*, p. 99.

(3) M. H. Lietzke and R. W. Stoughton, *The Measurement of the Solubility of Fission Product Sulfates at High Temperatures and Pressures*, ORNL-970, March 13, 1951.

precipitate formed slowly. At higher temperatures the amount of precipitate decreased and at 190°C disappeared. Upon cooling, the white precipitate reappeared at about 115°C and remained at room temperature. At 250°C, 1% or more of molybdenum oxide was completely soluble in 1.26 *M* UO_2SO_4.

Zirconium Sulfate. Two exploratory measurements were made on the solubility of zirconium sulfate in 1.26 *M* UO_2SO_4 with samples containing 6.53 and 11.15%, respectively, of zirconium sulfate.

Both samples dissolved completely below 200°C, but at higher temperatures an irreversible change occurred and yielded many masses of fine, white precipitate that remained when the tubes were cooled to room temperature.

Composites of Cesium, Lanthanum, Molybdenum, Yttrium, and Zirconium Sulfates. Five exploratory runs were made at 250°C with composites of the above metal sulfates in 1.26 *M* UO_2SO_4. The initial concentration of each salt was about 50% (or lower) of the predetermined solubility for the individual systems. By an elimination process, both molybdenum and zirconium sulfates were found to be causing the precipitation. The mechanism possibly involved complex-salt formation.

Cadmium Sulfate. The solubility of cadmium sulfate in 1.26 *M* UO_2SO_4 has been studied from 25 up to approximately 250°C. Cadmium sulfate shows a negative temperature coefficient of solubility and exhibits considerable supersaturation. The solubility varied from 31.62 wt % at 23°C to 22.51 wt % at 248°C. Lietzke and Stoughton[3] found the solubility of cadmium sulfate in 0.126 *M* UO_2SO_4 to be 2.8 wt % at 251°C.

Silver Sulfate. The study of the solubility of silver sulfate in 1.26 *M* UO_2SO_4 from room temperature up to 263°C is nearing completion. Silver sulfate showed a positive temperature coefficient of solubility, and the solubility varied from 2.36 wt % at 52°C to 17.25 wt % at 263°C. The latter sample was heated above 260°C for several hours without showing signs of instability. The solubility of silver sulfate in 0.126 *M* UO_2SO_4 also is under study.

CUPRIC FLUORIDE SOLUBILITY IN AQUEOUS URANYL FLUORIDE SOLUTION

E. V. Jones J. S. Gill

The findings of H. F. McDuffie and his group on cupric-ion-induced homogeneous recombination of hydrogen and oxygen in uranyl sulfate solution led to an exploratory study of cupric fluoride solubility in uranyl fluoride solution. The investigation, complete with experimental data, was reported in the past Homogeneous Reactor Project quarterly progress report.[4] Solubilities at 250°C were greater than 0.19 *M* cupric fluoride in 0.126 *M* uranyl fluoride and greater than 0.59 *M* in 1.26 *M* uranyl fluoride.

CONDUCTIVITY OF AQUEOUS URANYL SULFATE AND URANYL FLUORIDE SOLUTIONS

R. D. Brown

Conductivity studies on uranyl sulfate solution have continued, and data are now available on aqueous solutions of this compound in concentrations from 0.0001 to 6 *N* at 0, 25, and 50°C. Some of these data and other details of the study were given in the last Homogeneous Reactor Project quarterly progress report.[5]

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[4] Marshall, Brown, Day, Gill, Jones, Warren, and Wright, *op. cit.*, ORNL-1221, p. 103.

[5] *Ibid.*, p. 103.

Uranyl sulfate is a weak electrolyte; its equivalent conductivity increases rapidly with increasing dilution. There is also an increase in equivalent conductivity with increasing temperature that averages approximately 60% from 0 to 25°C and 30% from 25 to 50°C at moderate dilutions (e.g., 0.05 *N*).

The conductivities of uranyl fluoride solutions in concentrations from 1 *N* to 0.0001 *N* were measured at 0 and 25°C. The equivalent conductivity at 0°C is only 15 to 20% of that for uranyl sulfate at 0°C and increases much more rapidly with increasing temperature; the conductivity at 25°C is approximately twice as great as at 0°C.

A full account will be given in the next Homogeneous Reactor Project quarterly progress report.

VAPOR PRESSURES OF AQUEOUS URANYL SALT SOLUTIONS

H. O. Day J. S. Gill

High-temperature vapor pressures of solutions of uranyl sulfate and uranyl nitrate were determined with a Baldwin pressure gage. The results were fully discussed in the last Homogeneous Reactor Project quarterly progress report.[6]

The solutions contained dissolved air, and there was a free air space above the solution in the bombs. Calculations were made to estimate the effect of the air on the pressure measurements. Since the geometry of the bomb was known as well as the volume of solution, the original quantity of air present could be estimated. The values of the densities of uranyl sulfate solutions at the elevated temperatures and of the solubility of air in the solutions at these temperatures had to be assumed, because there were no experimental data available for determining these values. It was assumed that the density of a solution of particular concentration at some elevated temperature would be as much greater than that of pure water at this temperature as the density of uranyl sulfate at 25°C of the same concentration is larger than that of pure water at 25°C.

The solubility of O_2 and N_2 in pure water at elevated temperatures is given by Pray, Schweickert, and Minnich.[7] The classic literature gives the solubility of these gases in potassium sulfate and sulfuric acid solutions at room temperature. It was assumed that the fractional lowering of solubility by these solutions was the same at all higher temperatures, up to 350°C. It was next assumed that the solubility of O_2 and N_2 in uranyl sulfate solutions of any particular concentration, thermodynamic activity, and temperature would be equal to the average of the solubilities in K_2SO_4 and H_2SO_4 solutions of equal activity and temperature. Activity data for uranyl sulfate solutions have been given by C. H. Secoy.[8]

With the data obtained, the partial pressures of O_2 and N_2 were calculated and subtracted from the experimental pressures. The corrected values obtained are given in Table 42.

At present full attention is being given to the determination of very accurate vapor-pressure data of uranyl salt solution at lower temperatures (50 to 165°C).

(6) *Ibid.*, p. 105.

(7) H. A. Pray, C. E. Schweickert, and B. H. Minnich, *The Solubility of Hydrogen, Oxygen, Nitrogen, and Helium in Water at Elevated Temperatures*, BMI-T-25, May 15, 1950.

(8) J. R. Coe and E. H. Taylor, *Report on the Chemistry Division for the Months December 1947 and January and February 1948*, CNL-37, p. 33.

TABLE 42

Vapor Pressure Data of Uranyl Salt Solutions

TEMPERATURE (°C)	VAPOR PRESSURE (psia)		
	LITERATURE VALUES OF PURE WATER	6.84 wt % URANYL SULFATE	32.82 wt % URANYL SULFATE
200	225.54	$223._3$	$216._2$
225	369.90	$366._2$	$361._6$
250	576.91	$576._4$	$559._7$
275	862.80	$860._3$	$850._1$
300	1246.12	$1243._1$	$1234._2$
325	1748.39	$1742._9$	$1698._2$
350	2398.39	$2388._2$	

ANALYSIS FOR SULFATE IN URANYL SULFATE SOLUTIONS – AN ION-EXCHANGE METHOD

H. O. Day
J. S. Gill
E. V. Jones
W. L. Marshall

A study has been made to find a more accurate method for sulfate analysis than the conventional barium sulfate gravimetric procedure, which was found to give erratic results that were as much as 1 to 2% high. An ion-exchange process was developed in which uranium was removed on a Dowex-50 ion-exchange column and sulfate ion in the effluent was quantitatively titrated with standard base. The analytical values obtained were within titration accuracy, or about ±0.2%. This work has been reported in detail in the Homogeneous Reactor Project quarterly progress report.[9]

EFFECT OF RADIATION ON AQUEOUS REACTOR SOLUTIONS

J. W. Boyle
E. L. Compere
T. H. Handley
W. E. Hill
H. F. McDuffie
J. F. Manneschmidt
D. M. Richardson
C. H. Secoy
M. D. Silverman
A. W. Smith
H. H. Stone
F. H. Sweeton
L. F. Woo

Hydrogen-Oxygen Recombination in Solutions. Earlier work on homogeneous recombination of hydrogen and oxygen in solutions in the absence of radiation has been presented in the quarterly progress reports of the Chemistry Division[10] and the Homogeneous Reactor Project.[11] Efforts since the last report have been devoted to (1) a study of the copper catalysis of the recombination, (2) a study of the effect of temperature and uranyl sulfate concentration on the recombination reaction, (3) exploratory experiments to find ions that exhibit significant catalysis of the reaction, (4) refinement of the experimental techniques, (5) interpretation of results, and

(9) *Ibid.*, p. 107.

(10) "Radiation Stability," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1951*, ORNL-1153, p. 93.

(11) "Radiation Stability," *op. cit.*, ORNL-1221, p. 122.

(6) design and construction of improved apparatus.

The order of the recombination reaction with respect to copper sulfate concentration is of major interest. A series of replicated experiments has been carried out at 250°C, in the absence of uranyl sulfate, in which copper sulfate concentrations of 0.0010, 0.0025, and 0.0100 *M* were used. The recombination rates were directly proportional to the copper ion concentration and indicated that the reaction is probably first order with respect to copper. The rate constants agreed at a particular copper concentration within about 15%, although copper concentration was varied tenfold. It should be noted that the experimental showing of first order does not agree with the prediction of second order, based on the assumption previously made[10] that the reaction of hydrogen with copper may be represented as

$$H_2 + 2Cu^{++} \longrightarrow 2H^+ + 2Cu^+ .$$

The exact mechanism cannot be elucidated until further experimental data are available.

Recombination rates have been determined at various temperatures in the range 210 to 290°C for uranyl sulfate concentrations of 0.0625, 0.125, 1.25, and 2.5 *M*. For each concentration, consistent temperature effects were observed and an activation energy of about 15 kcal was indicated. Furthermore, the rate was much faster than for water alone, which clearly indicated that uranyl sulfate exhibits a moderate degree of catalysis. However, at a given temperature, the variation of concentration did not cause a significant change in reaction rate.

It is tentatively postulated that the catalytic activity of the uranyl sulfate is constant over this concentration range, and thus lower concentrations must be investigated to permit observation of an effect on the rate. Such experiments are in progress.

It is likely that the catalytic activity is related to the thermodynamic activity of uranyl ion. However, only room temperature data are available on the thermodynamic activity of uranyl sulfate.[8] At room temperature the activity coefficient drops sharply with increasing concentration, displays a broad minimum from 0.4 to 2.0 *M*, and then rises quite rapidly. The range between room temperature and the 250°C level is too great to permit any but the most general application to concentration data.

In general, the separation of a solution into two liquid phases results when the activity of components goes through a maximum as the mole fraction increases, so more than one composition may have a given activity.[12] The proximity of the two liquid-phase regions in the uranyl sulfate–water system indicates that such a maximum is being sought by the system and implies that the thermodynamic activity of uranyl sulfate may be relatively constant over a broad range of composition.

Previously reported inpile irradiation experiments in which enriched uranyl sulfate solutions contained in stainless steel capsules were irradiated at temperatures of 250 to 290°C have demonstrated an anomaly in the time-dependent pressure curve. The pressure curve initially rose rapidly to an equilibrium value and then the equilibrium pressure gradually lowered and left a "hump." The equilibrium is now understood as a balance between gas production (via fission recoil

[12] S. Glasstone, *Textbook of Physical Chemistry*, Van Nostrand, New York, 2d ed., p. 722 (1946).

decomposition of water) and gas recombination (catalyzed by ions present in the solution). The slow shift in equilibrium is believed to be caused by the gradual accumulation of fission products that have catalytic activity for gas recombination. Since the concentration must be extremely low, the specific activity of such catalysts must be very high. Therefore a necessary part of the recombination reaction study will involve an effort to identify these materials and to characterize their activity.

Some exploratory experiments have been carried out with a number of ions. Apparently active ions include Fe, Tl, Ce, Sn, V, and Ti. The nickel ion does not appear to be significantly active. It has been postulated that ion couples might work better than either ion alone. Thus, A^{++} might react rapidly with H_2 to give A^+; B^+ might react rapidly with O_2 to give B^{++}; and A^+ might react rapidly with B^{++} to regenerate A^{++} and B^+. Some preliminary evidence has been obtained and a thorough study is contemplated.

The recombination reaction has been studied by following the rate of decrease in total pressure. A solution is placed in a small (10 or 30 ml) stainless steel bomb connected by capillary pressure tubing to a valve block connected to a water filled Baldwin SR-4 pressure cell attached to a pressure recording system that is sensitive to ±5 psi. Oxygen gas and hydrogen gas are added from cylinders until the desired pressures are obtained, normally 300 psi oxygen and 600 psi hydrogen at room temperature. The bomb is rapidly heated to the desired temperature, in the 210 to 290°C range, and the temperature is then held to within 1°C. The pressure and temperature are automatically recorded as recombination occurs and the pressure drops.

In order to interpret the rate of pressure drop in terms of a recombination rate of the dissolved gases, the following equations may be used:

$$\frac{dP_{H_2}}{dt} = k\, P_{H_2} F$$

or

$$\frac{d(\pi - A)}{dt} = (kF)\,(\pi - A)\ ;$$

integrated to

$$\ln(\pi - A) = -(kF)\,t + \ln(\pi_0 - A)\ ,$$

where

P_{H_2} = partial pressure of hydrogen, psi,

k = solution recombination rate constant, hr^{-1} (includes all catalytic and thermodynamic activity factors),

π = observed total pressure, psi,

A = pressure of nonreacting gases, psi (H_2O, O_2, N_2, excess O_2 over stoichiometric, etc.),

F = moles of hydrogen dissolved per moles of hydrogen in the system.

The factor F depends largely on the geometry of the system, the temperature, and the nature of the gases. However, it is substantially independent of pressure under the conditions of interest and so is constant for a given experiment.

Adequate evaluation of F requires that an adequate material balance be made for hydrogen in the system. In carrying out such a balance, the

following factors are to be taken into account:

1. solubility of gases in liquid,
2. evaporation and vapor pressure of liquid,
3. thermal expansion of liquid,
4. thermal expansion of bomb,
5. compressibility of liquid in bomb,
6. nonideality of gaseous mixture in bomb,
7. effect of cold external volumes (dead space in lines, valves, etc.),
8. increase in external volume by dilation of strain gage,
9. increase in external volume by compressibility of water in strain gage,
10. effect of total pressure on the vapor pressure of water,
11. effect of salt concentration on gas solubility,
12. volume of gas,
13. volume of liquid.

The majority of these effects are significant. Evaluation of F is laborious under these circumstances, since material balances must be made and pressures estimated and corrected to consistent values by successive approximations for each substance present in each step of the charging process. As a result, no explicit formula for F is presented.

The above treatment is an elaboration of the earlier treatment,[10] in which

$$F = \frac{\dfrac{V_L}{V_G}}{\dfrac{V_L}{V_G} + \dfrac{\alpha}{RT}}$$

and only factors 1, 2, 3, 12, and 13 were considered. A value of $F = 0.124$ found by the simple equation to be applicable to 250°C operating conditions may be compared with a value of 0.083 found by the more elaborate treatment. Thus from given observations of the rate of pressure drop caused by recombination, the estimated recombination rate constants would differ by a factor of up to 1.5 depending on the elaborateness of the F factor calculation.

Several experiments using water, hydrogen, and oxygen have been made with the experimental procedure described above to check the ability to carry out material balances. When factors 1 through 13 are considered, the balances are good to within 1 to 3%, so knowledge of the F factor now appears to be reasonably firm. Since the relative effects of the external factors influencing F can be greatly reduced by increasing bomb size, 30-ml bombs are now being used instead of 10-ml bombs in the out-of-pile studies.

No values for the solubility of hydrogen and oxygen in uranyl sulfate solutions at elevated temperatures and pressures have yet been determined, so the values published in BMI-T-25[7] for the solubility in pure water have been used as the best available approximation.

Some effort has been devoted to a consideration of apparatus factors (other than the *F* factor discussed above) influencing precision and accuracy of the recombination rate constants obtained by observing the rate of pressure drop. Pressure observation appears to be accurate and reliable – that is, sensitive to within 5 psi at the 2000-psi level. On the other hand, factors concerned with temperature control and heat transfer appear capable of refinement to advantage.

In the experiments to date, temperature control has been achieved by placing the reaction bomb in a small aluminum can within a cylindrical, nichrome and ceramic, heating element contained in a stainless steel beaker with Vermiculite poured in to surround and cover the bomb and heater for insulation. Thermocouples between bomb and can were attached to a 200 to 300°C Brown recorder for temperature recording and to a Minneapolis-Honeywell Pyro-vane controller that operated by adding a small external resistance in series with the heater circuit when the temperature was above the desired level. An experiment was carried out to determine the accuracy of temperature measurement and control, by using a 10-ml bomb that contained 5 ml of water and was fitted with an internal thermocouple. Temperatures inside the bomb were 1°C lower than indicated by the outside thermocouple and fluctuated over a 1°C range. Steam pressures indicated temperatures still lower by 1 to 2°C. It was concluded that no major temperature error was involved, that temperature fluctuations could and should be minimized by improved apparatus, and that a cool spot that served to lower the pressure existed within the bomb, probably near the connector at the top. Tests indicated that the cool spot was as much as 10°C lower in the 30-ml bombs, presumably because the longer bomb was less perfectly enclosed by the heater.

An aluminum block heater has been designed and fabricated that will completely enclose three 30-ml bombs. Experiments on a prototype indicate that control of temperature may be to ±0.2°C. With this system, a reproducibility of the rate constant to ±3% appears likely, except for being affected by chemical factors. By using two such assemblies it will be possible to carry on six experiments simultaneously. Future work on the following items is being considered:

1. continued investigation of copper catalysis,
2. continued investigation of effect of uranyl sulfate concentration on recombination,
3. evaluation of effect, if any, of increased metal surface on reaction,
4. evaluation of effect of varying the hydrogen-to-oxygen ratio,
5. evaluation of effect of varying hydrogen pressure,
6. search for and evaluation of other ions with catalytic effect,
7. variation of geometric factors to demonstrate knowledge of *F* factor.

Kinetics of Uranyl Sulfate-Peroxide Solutions. Irradiations of both natural and enriched uranyl sulfate solutions have been made in the X-10 graphite pile by two groups of investigators at ORNL – Boyle and Kieffer, and Ghormley, Hochanadel, Stewart, and Sworski. In these experiments the uranium concentration was varied from 0.00168 to 3.39 *M*, the enrichment from 0.71 to 93.2%, and the temperature from 30 to 120°C. Analyses

of the gases produced during bombardment were made. Experiments by the second group indicate that the peroxide produced during bombardment is approximately equivalent to the excess hydrogen found from gas analysis when analyses for both are run at the same time.

The data obtained from a total of 45 such experiments have been correlated by assuming that the excess hydrogen gas analyses give the amount of peroxide present. On the basis of the estimated amount of peroxide and the known concentration of uranium, calculations were made to determine whether the solubility product of uranyl peroxide,

$$K_{S.P.} = 1.3 \times 10^{-3} \pm 15\% ,$$

had been exceeded during the experiments. Although the effects of sulfate complexing, activity coefficients, and a temperature coefficient of solubility were neglected, the experimental results confirm the calculated values for precipitation – that is, in three experiments at 100°C, in which precipitation was observed, calculations showed that the solubility product had been exceeded by a factor of 4. Duplicate experiments at 120°C failed to give the precipitates that were expected from the calculations. Six experiments, indicated by calculations to be borderline cases, did not show precipitation.

In every experiment checked, some thermal decomposition of peroxide must have occurred in the time interval (at least 10 min) between removal of the sample from the pile and observation; furthermore, considerable time elapsed (several days) before gas analyses were completed on the bombarded samples. Hence, the results reported for peroxide formation always tend to be low.

Out-of-pile experiments on peroxides have been devised to simulate pile conditions. By controlling the rate of addition of hydrogen peroxide to uranyl sulfate solutions at various temperatures, it is possible to approximate the rate of formation of peroxide in pile-bombarded solutions. Of particular interest are peroxide decomposition and uranyl peroxide solubility as functions of concentration, temperature, and time. The thermal decomposition of uranyl peroxide has been known for some time.

Radiation Studies of Gas Production and Recombination at High Temperatures and Pressures. As stated in the previous Chemistry Division quarterly progress report,[10] plans were made to test the ability of copper ions (dissolved $CuSO_4$) to catalyze the recombination of hydrogen and oxygen, by using gas generated *in situ* by the action of fission recoils from enriched uranyl sulfate solutions exposed to a neutron flux of 5×10^{11} in the X-10 graphite pile. The effect of copper was to be measured by a lowering of the equilibrium gas pressure at a chosen temperature as compared with experiments in which no copper was added to the uranyl sulfate solution. Such experiments have now been carried out and the predicted behavior was demonstrated convincingly.

When 10 ml, type-347 stainless steel bombs containing 5 ml of uranyl sulfate solution (40 g of U per liter, 93.2% enrichment) and small quantities of dissolved copper sulfate (0.00625 and 0.009 *M* in Cu) were held at a series of temperatures in the full flux (5×10^{11}) of hole 12 in the X-10 graphite pile, a corresponding series of equilibrium pressures was obtained. These values are listed in Table 43.

TABLE 43

Equilibrium Pressures

RUN	COPPER (*M*)	TEMPERATURE (°C)	PRESSURE (psi)		
			STEAM	TOTAL (observed)	EQUILIBRIUM
363	0.009	194	200	1850	1650
		209	270	1130	860
		229	400	700	300
		239	475	660	185
		249	567	670	103
		259	670	730	60
360	0.00625	209	270	2200	1930
		229	400	1100	700

When values of log P_{equil} are plotted against temperature, a smooth trend is noted, which can be attributed primarily to the activation energy for the rate-determining reaction (Fig. 38). The value of 5000 psi for run 283, without copper, provides a clear indication of the magnitude of the effect. The actual pressures observed experimentally (steam pressure plus equilibrium gas pressure) fall through a wide minimum as the temperature increases and finally begin to rise again as steam pressure becomes the dominant factor (Fig. 39). This temperature dependence of total pressure was observed first by Boyle and Secoy[13] in 1950 when using systems not containing copper; in those systems the minimum is found at higher temperatures and pressures.

A suitable mathematical framework for describing the kinetics of both radiation and nonradiation recombination studies has been found in the simple differential equation

$$\frac{dN_{H_2}}{dt} = \{k_1 - k_2 [Cu^{++}] [H_2]\} V_L$$

$$= \left\{ k_1 - k_2 [Cu^{++}] \frac{P_{H_2}}{a} \right\} V_L$$

where

$\frac{dN_{H_2}}{dt}$ = change in moles of hydrogen in the system per unit time (hr),

k_1 = rate of production of hydrogen, a function of flux, *G* value, U^{235} concentration, and fission cross section and energy release per fission (moles of H_2 per hr per liter),

[13] C. H. Secoy, report at Homogeneous Reactor Project Information Meeting, 1950.

k_2 = specific rate constant for the homogeneous recombination of hydrogen and oxygen catalyzed by copper ions,

$[Cu^{++}]$ = molar concentration of copper ions,

$[H_2]$ = molar concentration of dissolved hydrogen,

V_L = volume of liquid phase in liters,

P_{H_2} = partial pressure of hydrogen gas (psi, approximated as 2/3 the total gas pressure exclusive of steam pressure),

$\alpha = \dfrac{P_{H_2}}{[H_2]}$, from date in BMI-T-25.[7]

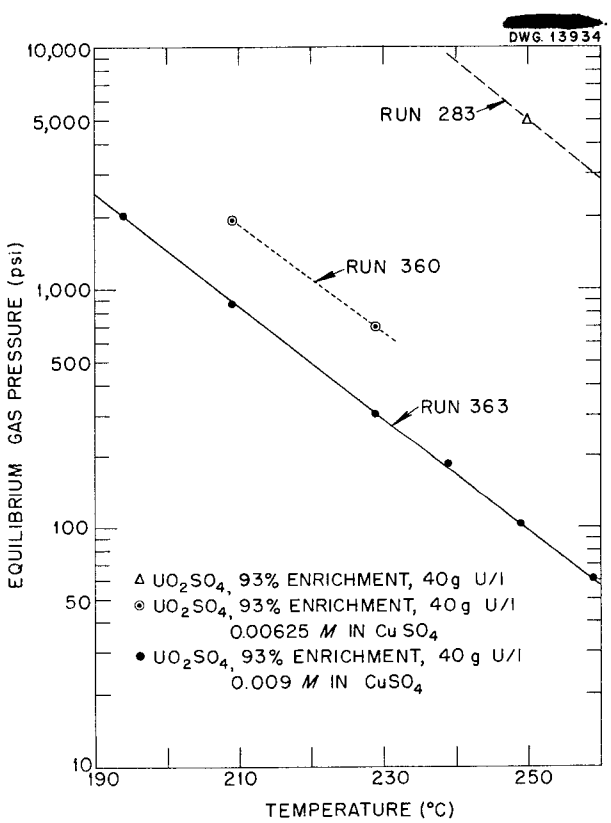

Fig. 38. Effect of Temperature and Copper on Equilibrium Gas Pressure. Irradiated at full flux in hole 12 of X-10 graphite pile.

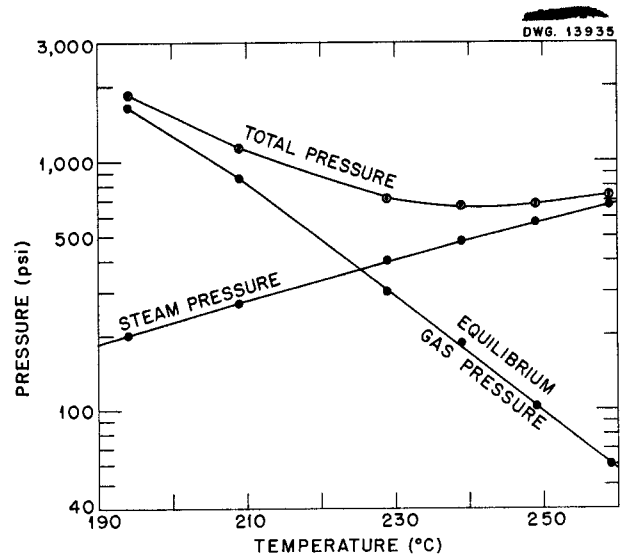

Fig. 39. Effect of Temperature on Pressure for the System Aqueous Uranyl Sulfate plus Copper Sulfate. Data from run 363.

The equation may be converted as follows for direct application to experimental data (measurement of total pressure), as discussed in the previous section on "Hydrogen-Oxygen Recombination in Solutions,"

$$\frac{dP_{H_2}}{dt} = \left\{ k_1 - k_2 \, [Cu^{++}] \frac{P_{H_2}}{\alpha} \right\} V_L E$$

where

$$\left(\frac{dN_{H_2}}{dt} \right) (E) = \frac{dP_{H_2}}{dt}$$

This equation is of the form

$$\frac{dP}{dt} = k_1' - k_2' P ,$$

which is an equation for a straight line. When values of dP/dt (readily obtainable during the course of an experiment) are plotted against P, straight lines are actually obtained.

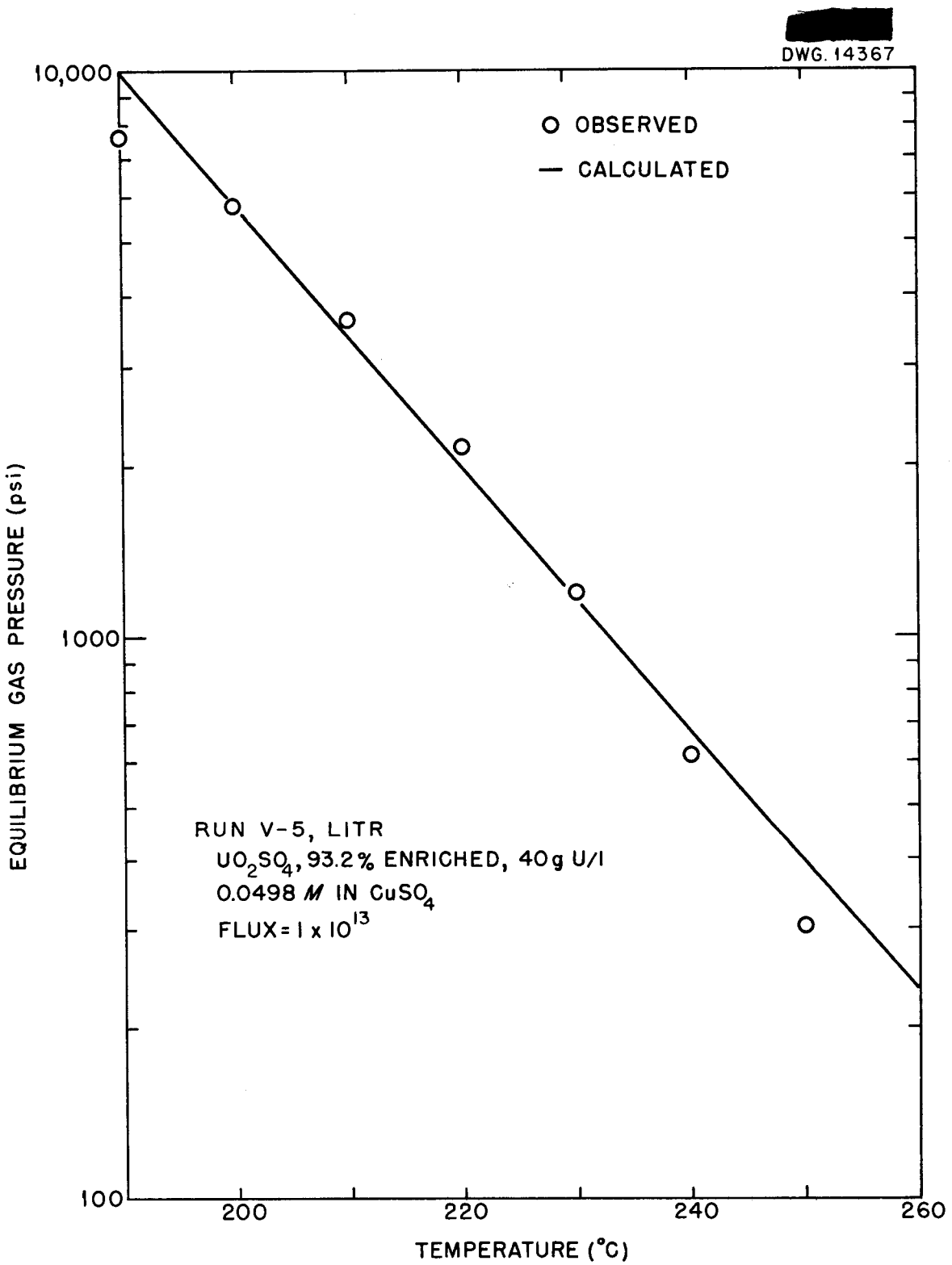

Fig. 40. Effect of Temperature on Equilibrium Gas Pressure at High Flux on Enriched Uranyl Sulfate Solutions Containing Copper Sulfate.

The intercept on the P axis, where $dP/dt = 0$, is the pressure at equilibrium and is equal to k_1'/k_2'; the intercept on the dP/dt axis, where $P = 0$, provides a value for k_1'; and the slope of the line is $-k_2'$. When an experiment is in progress, points at different temperatures should fall on lines of different slope. Operations at different levels of flux should affect only the position of the k_1' intercept and P_{equil} and leave the slope of the line unchanged. These values make possible a test for the validity of the G values and the specific recombination rates obtained in separate experiments (described in previous sections).

As a further test of the adequacy of this treatment, prediction can be made of equilibrium pressures expected at fluxes, temperatures, and copper concentrations other than those already studied. Based on data obtained in the X-10 graphite pile at a flux of 5×10^{11} and a copper concentration of 0.009 M (Figs. 38 and 39), calculations were made of expected equilibrium pressures for experiments in the LITR at a flux of 1×10^{13} and a copper concentration of 0.05 M. Figure 40 shows the agreement obtained when the experiment was subsequently carried out. Figure 41 shows actual experimental data obtained at a temperature of 230°C, and Fig. 42 shows the experimental lines obtained for several temperatures between 190 and 250°C.

By using the treatment that *at equilibrium* gives

$$k_1 = k_2 \, [Cu^{++}] \frac{P_{H_2}}{\alpha},$$

values of

$$k_2 = \frac{\alpha k_1}{P_{H_2} \, [Cu^{++}]}$$

may be obtained for a series of temperatures. Since k_1 is considered practically independent of temperature, a value for ΔH may be obtained from a plot of log k_2 vs. $1/T$(°K), which gives a line whose slope is $-\Delta H/2.303\,R$. In this way ΔH was found to be 20.2 kcal by using the data from experiments at fluxes of 5×10^{11} and 1×10^{13} (Table 43 and Fig. 42).

The required copper concentration in moles per liter for steady-state operation at temperature T, flux ϕ, and steady-state gas pressure (exclusive of steam pressure or added oxygen pressure) P_g, is given by the expression

$$M_{Cu} = \frac{K_T \phi}{P_g},$$

which can be evaluated by using empirical values of K_T determined from run 363 at 5×10^{11} flux (listed in Table 44).

TABLE 44

Values of K_T at Four Temperatures

t (°C)	T (°K)	α	K_T* $\times 10^{10}$
175	448	17,000	1.125
200	473	14,840	0.290
225	498	10,800	0.076
250	523	7,900	0.020

*Subsequent recalculation indicated that these values of K_T were 10% high.

From these values of K_T and the value of ΔH, an expression for K_T at various temperatures can be established:

$$\log K_T - \log \alpha = \frac{\Delta H}{2.303\,RT} - C$$

and with numerical simplifications introduced

$$\log K_T - \log \alpha = \frac{4420}{T} - 24.0454 \ .$$

The description of the kinetics of gas production and recombination given here contains no terms involving the effect of radiation on the recombination of hydrogen and oxygen, although

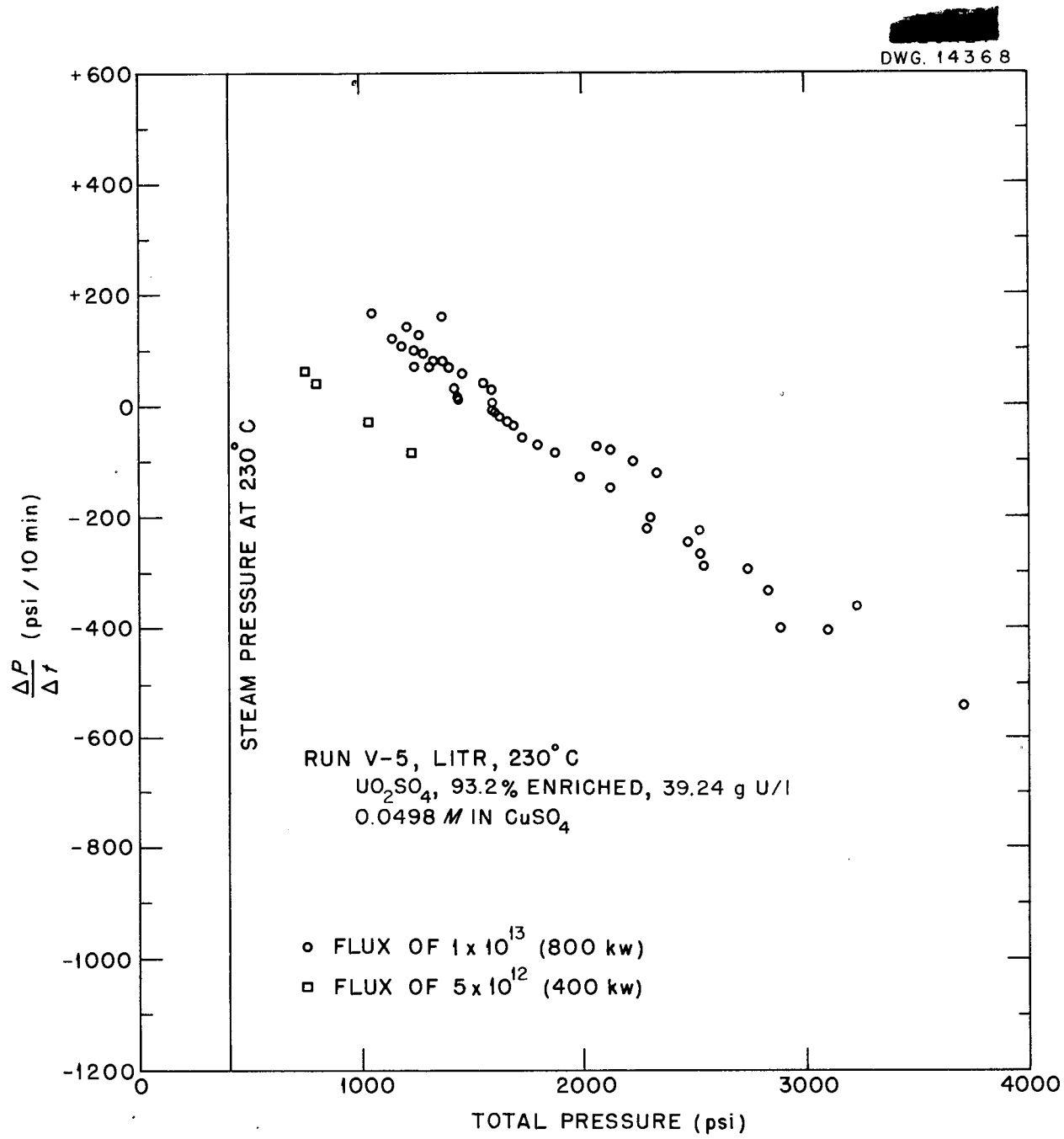

Fig. 41. Experimental Values of $\Delta P/\Delta t$ vs. P.

[redacted]

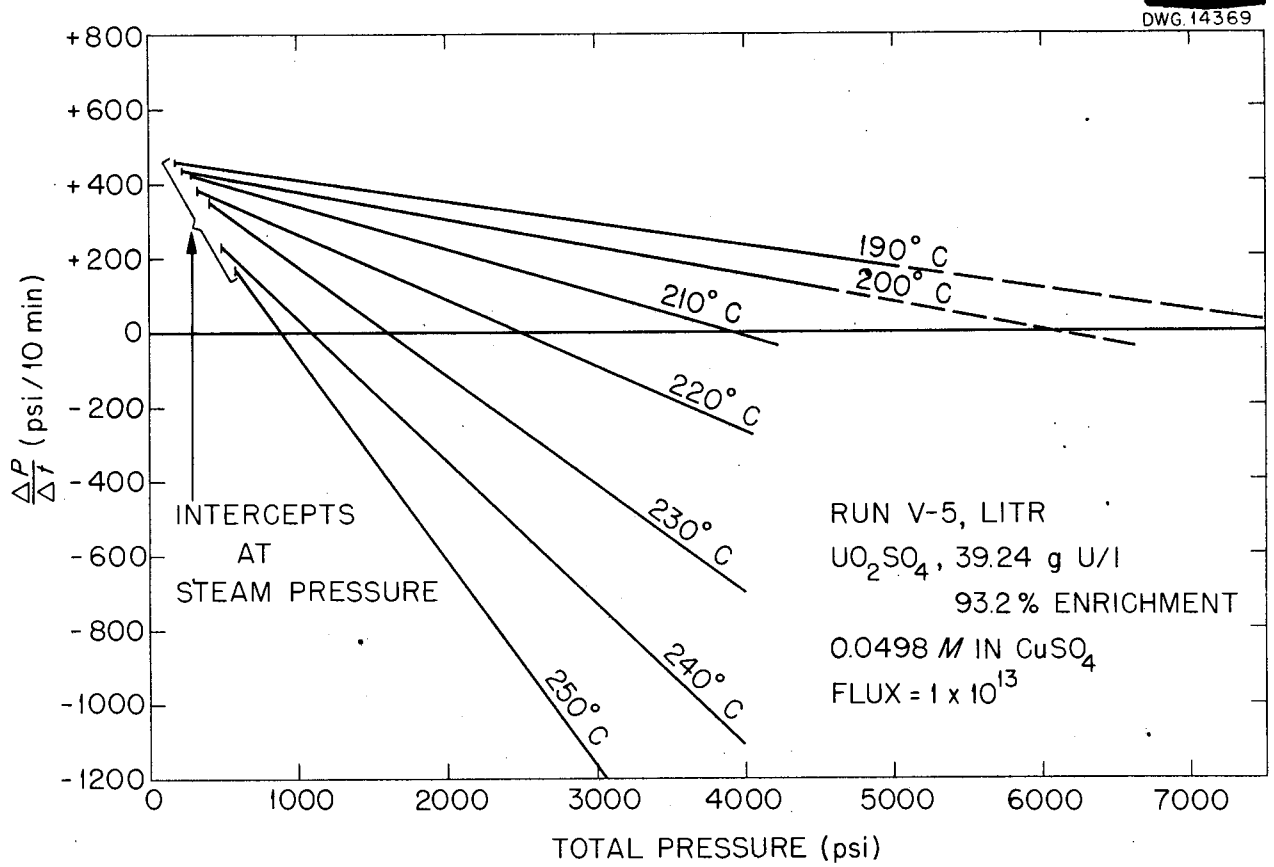

Fig. 42. Relationship Between $\Delta P/\Delta t$ and P at Various Temperatures.

the effect of gamma radiation on this reaction is considered important in the determination of G values and in studies of radiation effects upon aqueous solutions in the absence of fission recoils. Three experiments were carried out to determine whether this effect might be of sufficient magnitude to require consideration for practical reactor operation.

1. A 10-ml stainless steel bomb containing 5 ml of distilled water was placed in a cobalt gamma source emitting 9000 r/hr and pressurized to 990 psi with 2:1 H_2-O_2. During a period of 48 hr the pressure (at 16°C) fell to 950 psi (20 psi per day).[14] During the next 164 hr the temperature was held at 100, 200, 250, 285, and 290°C for approximately equal periods. At the end of this time the temperature was lowered to 10°C and the pressure read as 725 psi (a drop of 225 psi in 164 hr or 33 psi per day).

2. The above assembly (at 725 psi) was transferred to hole 12 of the X-10 graphite pile and held at full flux for 48 hr (16 hr at 290°C, 8 hr each at 250, 210, 150, and 100°C), at the end of which the temperature was reduced to 30°C and the pressure found to be 490 psi (a drop of 235 psi in 48 hr). Of this, 170 psi occurred in the 16 hr at 290°C, and 65 psi occurred in the remaining 32 hr (49 psi per day).

3. A similar experiment in the LITR with higher thermal-neutron fluxes

[14] C. J. Hochanadel calculated 14 psi per day from low-pressure ampoule data.

and tenfold higher ratios of gammas and fast neutrons to slow neutrons than are available in the X-10 graphite pile gave similar results – recombination was either very slow or apparently just overbalanced by decomposition. This possibility may be investigated later in connection with fundamental studies of radiation decomposition of water at high flux; more detailed study was not considered of practical importance to the reactor program at the present time.

In comparing these slow recombination rates with the rates of gas production and recombination of interest to the HRE, the value of dP/dt found in the LITR (run V-5), seen from Fig. 42 to approach 500 psi per 10 min for systems having similar geometry, is so much greater that leaving the radiation effect out of any explanation of gas production and recombination in uranyl sulfate solutions is fully justified.

AN ATTEMPT TO DEVELOP A HIGH-TEMPERATURE REFERENCE ELECTRODE

M. H. Lietzke R. W. Stoughton

A series of experiments was performed in an attempt to develop a high-temperature reference electrode. It was hoped that such an electrode would be useful in studying passive films on stainless steel, such as will be used in the HRE. Also, it is of fundamental interest to measure the potentials of various half-cell combinations at high temperatures (i.e., above 100°C), and to compare the values so obtained with thermodynamic calculations. Apparently such a study has not been made previously.

The electrode compartments were sealed in a stainless steel bomb that was fitted with electrically insulated leads. The bomb wall was passivated so that measurements of the film potential could be made against the reference electrodes. The electrodes were mounted in quartz tubes that were sealed at one end and fitted at the other end with Teflon plugs through which platinum wires were passed. The wires leading to the electrodes were coated with Teflon paint to insulate them from the solution in the bomb proper. The solution in the electrode compartment communicated with the solution in the bomb by means of a quartz capillary sealed to the side of the quartz compartment. The potential measurements were made with a vibrating-reed electrometer and recorded on a Brown recording potentiometer.

In the first experiment, Pb(amalg.)-$PbSO_4$ and Ag-Ag_2SO_4 electrodes were tried. The lead electrode was prepared by using a 5 wt % lead amalgam with a platinum lead-in wire, and the quartz compartment was filled with a 0.1 M H_2SO_4 solution saturated with $PbSO_4$. The Ag-Ag_2SO_4 electrode had a silver wire dipping into 0.1 M H_2SO_4 solution saturated with Ag_2SO_4. Both the $PbSO_4$ and the Ag_2SO_4 were prepared by precipitation from solutions of the corresponding nitrates, and the precipitates were washed by decantation. The cells were evacuated before filling.

At equilibrium the cell combination 5% Pb-Hg, $PbSO_4$ || Ag_2SO_4, Ag gave a potential reading of 997 mv at 23°C. This compares with a value of E° = 1.012 v estimated from the free energy values given in Latimer's tables.[15] The entropy change for the reaction at 25°C from Latimer's tables indicated a value of −0.17 mv/°C for $\partial E/\partial T$. At 100°C, values of 1.00 v for the cell potential and −0.16 mv/deg for $\partial E/\partial T$

[15] W. M. Latimer kindly loaned K. A. Kraus a copy of the "Tables of Free Energies and Heats of Formation and Entropies" to be published in the forthcoming edition of *Oxidation Potentials*.

are obtained by calculation; whereas, at 250°C the corresponding values are 0.976 v and −0.16 mv/°C. Figure 43 shows values of the potentials obtained by measurement as a function of temperature. The curve gives a value of $\partial E/\partial T = -0.59$ mv/°C, which is about 3½ times higher than the calculated value.

The discrepancy of 15 mv at 25°C may result partly from the leads having a lower activity than pure lead because of the solubility of mercury in solid lead. The discrepancy in the values of $\partial E/\partial T$ may result from the change in the activity of the lead in the amalgam because of the large solubility change with temperature. (The solubility of lead in mercury is about 3.5% at 25°C and about 60% at 250°C.)

To check the low value of 997 mv for the cell potential at room temperature, another set of electrodes was prepared by using a 57.4 wt % lead amalgam and 0.05 *M* H_2SO_4. The new set of electrodes gave exactly the same value for the cell potential. A Pb-$PbSO_4$ electrode containing a lead wire and no amalgam was also tried, but even after one week the cell did

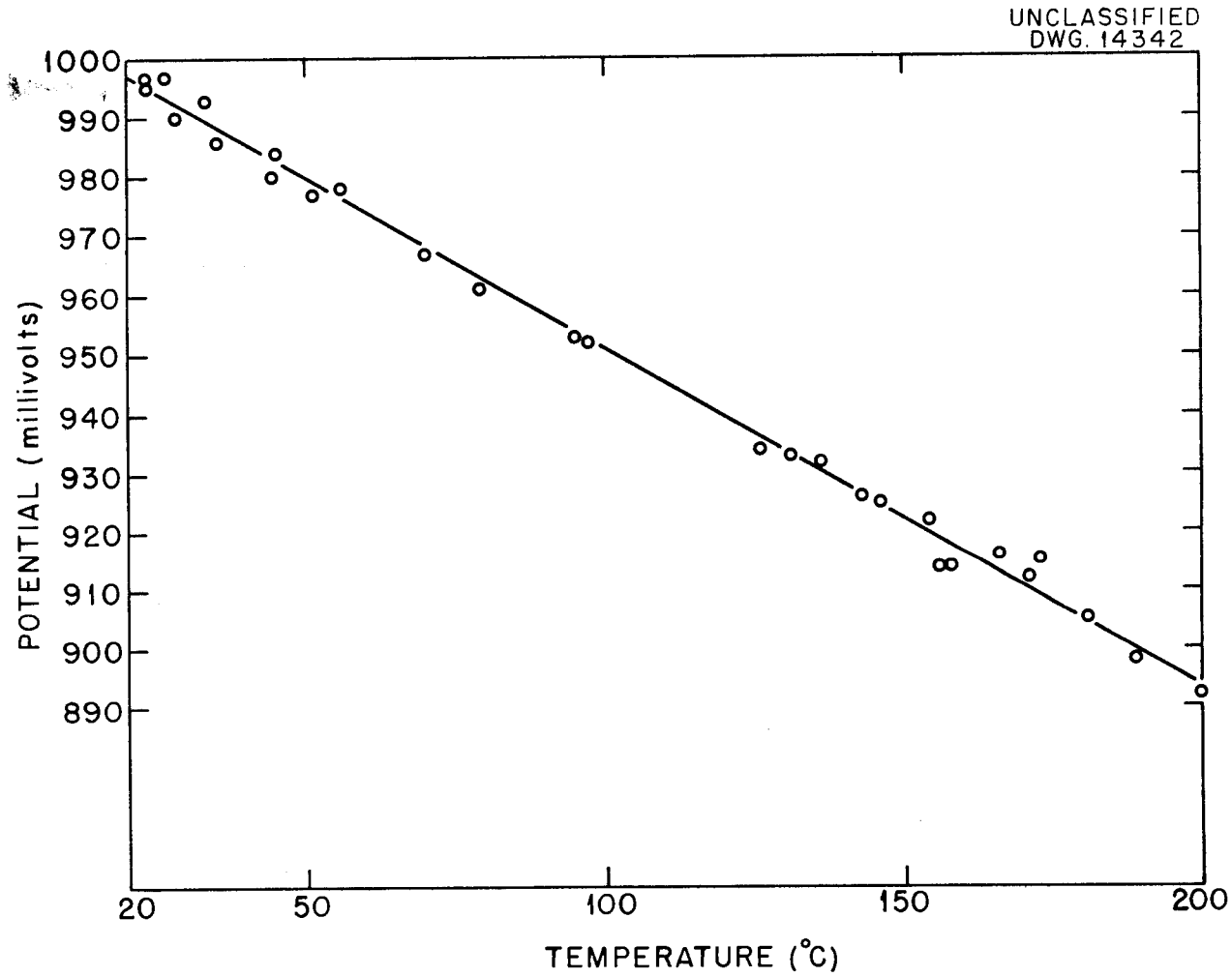

Fig. 43. Potential vs. Temperature Curve for the Pb-$PbSO_4$ and Ag-Ag_2SO_4 Electrodes in 0.1 *M* H_2SO_4.

not come to equilibrium; the potential for this cell vs. a $Ag-Ag_2SO_4$ electrode was only about 500 millivolts.

In order to determine how the electrodes would function in UO_2SO_4 solution, three electrodes were prepared as follows:

1. Ag, Ag_2SO_4

   (electrode solution consisting of 0.13 *f* UO_2SO_4 solution saturated with Ag_2SO_4),

2. Pt, 3.9% Pb-Hg, $PbSO_4$

   (electrode solution consisting of 0.13 *f* UO_2SO_4 solution saturated with Ag_2SO_4),

3. Pt, 57.4% Pb-Hg, $PbSO_4$

   (electrode solution consisting of 0.13 *f* UO_2SO_4 solution saturated with Ag_2SO_4).

The electrodes were placed in the bomb (which had previously been passivated with 1% HNO_3 at 250°C for 24 hr) in 0.13 *f* UO_2SO_4 solution. Figure 44 shows the potentials obtained as a function of temperature. When the bomb containing the three electrodes was opened it was found that reduction of the UO_2SO_4 had taken place in the electrodes containing the amalgams. However, the $Ag-Ag_2SO_4$ electrode was unchanged.

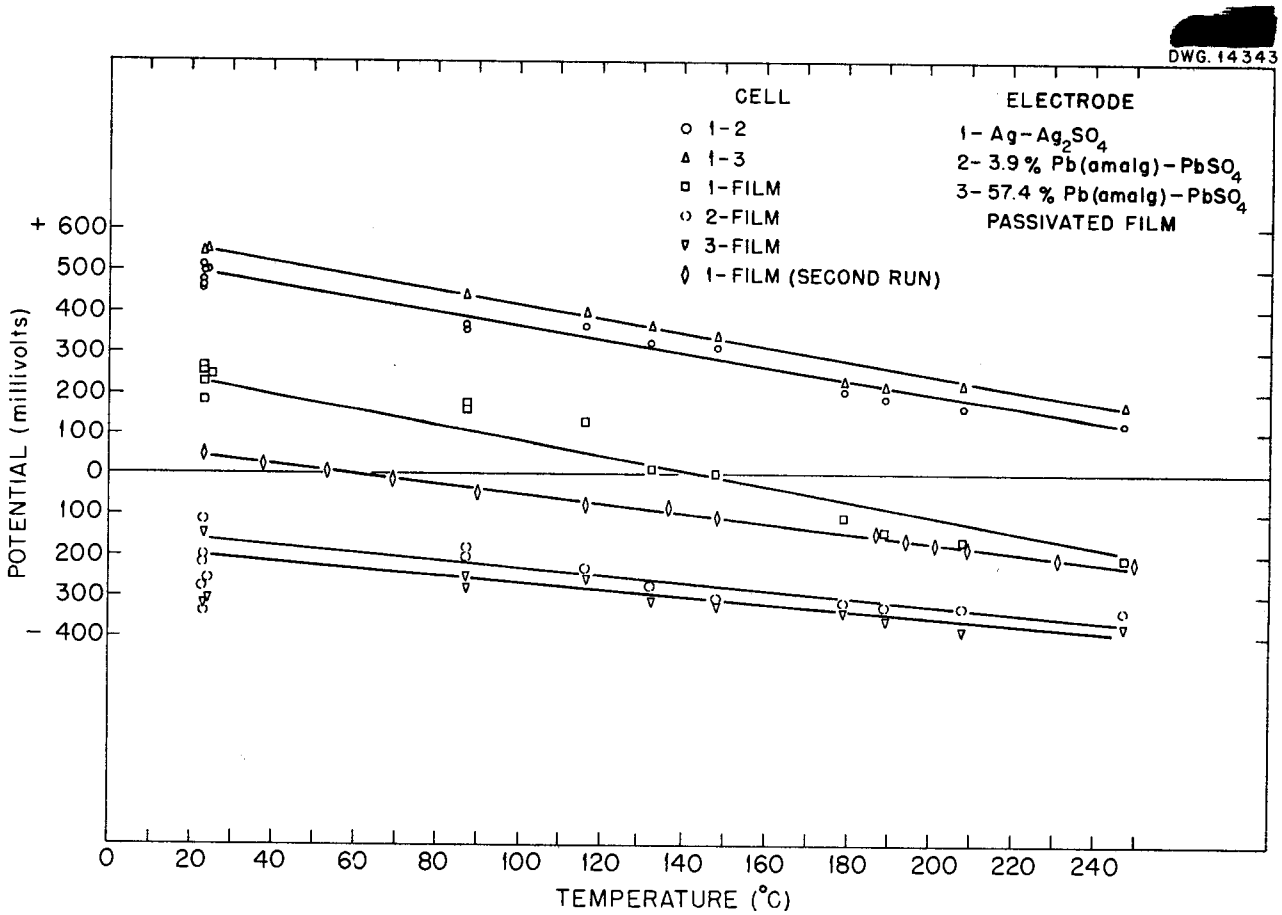

Fig. 44. Potential vs. Temperature Curves for Various Electrode Combinations in 0.13 *f* UO_2SO_4 Solution.

Since it appeared that the $Ag\text{-}Ag_2SO_4$ electrode might serve satisfactorily as a reference electrode in UO_2SO_4 solution, another run was made with just the $Ag\text{-}Ag_2SO_4$ electrode in the passivated bomb. The potentials obtained in this case as a function of temperature are also indicated on Fig. 44. The absolute values of the potentials of the $Ag\text{-}Ag_2SO_4$ electrode vs. the passive film obtained in this run differ from the corresponding values obtained in the first run, although the slopes of the curves are nearly parallel. This indicates that the absolute values of the potentials shown by films which have been made at different times cannot be directly compared and interpreted. Only the behavior of a given film toward the reference electrode may be meaningful.

Future work will include a study of several other electrodes both in H_2SO_4 and in UO_2SO_4 solutions, as well as further work with the electrodes already tried.