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QUARTERLY PROGRESS REPORT

FOR PERIOD ENDING JUNE 30, 1952

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CHEMISTRY DIVISION

QUARTERLY PROGRESS REPORT

for Period Ending June 30, 1952

S. C. Lind, Acting Director

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

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CHEMISTRY DIVISION QUARTERLY PROGRESS REPORT

SUMMARY

INORGANIC CHEMISTRY

The method of measuring activity coefficients by ultracentrifugation has been found to be satisfactory. The data agree with the data found in the literature for aqueous cadmium iodide solutions.

The thermodynamic constants for the equilibrium between the two complexes of manganese(III) with 2,4-pentanedione in aqueous solution were determined.

NUCLEAR CHEMISTRY

The assignment of mass 93 to the 7-h molybdenum activity was confirmed by the bombardment of niobium with 20.1-Mev protons.

A method for the preparation of kilocurie quantities of Xe^{135} for use in an extension of the determination of the neutron cross section has been designed and is described in detail. Two possible sources are covered, namely, a fuel element of the LITR, and the off-gas from the homogeneous reactor.

RADIO-ORGANIC CHEMISTRY

The products of irradiation of C^{14}-labeled acetic acid are being identified.

The rearrangements of 2-phenyl-2-(*p*-tolyl)ethylamine nitrite in three different solvents have been studied under three completely different sets of conditions. The same approximate mixtures of carbinols are obtained in all three cases.

Isotope-effect studies are reported for five *para* substituted benzoic esters and the extent of the effect in each case has been correlated with the *para* substituent. A mathematical study of the methods used in evaluating isotope-effect experiments is included.

Model experiments for the synthesis of 3-methylphenanthrene-9,10-C_1^{14} have been completed.

Samples of biphenyl have been placed in the ORNL Graphite Reactor and in the LITR for periods up to one week. Less than 1% total decomposition has been observed, as evidenced by hydrogen evolution and by melting-point depression of the biphenyl samples.

CHEMISTRY OF SEPARATION PROCESSES

Because of the decomposition of the anion-exchange resin by the alkali liberated during the reaction, the determination of equivalent weights of inorganic and organic salts are less accurate by the anion-exchange method (± 5%) than by the use of cation-exchange resins (± 1%). Attempts to prepare dioctylpyrophosphoric acid, a possible constituent of an extraction solvent for uranium, from solutions in orthophosphoric acid were unsuccessful.

A specially designed isopiestic apparatus has been used for the determination of moisture up-take isotherms for the hydrogen, lithium, sodium, potassium, ammonium, cesium, and zinc salt forms of variously cross-linked Dowex-50 type of cation exchangers. Several thermodynamic treatments were applied to the data.

A program of experimental study of the electrochemical properties of coherent ion-exchange materials such as membranes and rods has been initiated. Techniques for accurate measurement of resin-membrane conductances, transport numbers, equilibrium Donnan electrolyte partition, moisture, and exchange capacity have been developed. Membrane-potential determinations employing the concentration cell $Ag;AgCl(a_I)||AgCl(a_{II});Ag$ (a_I and a_{II} are mean ionic activities of electrolyte) are reported. The decrease in permaselectivity with increased sodium chloride concentration is reflected by the decrease of the transport number of Na^+ and connected with the higher rate of penetration of the chloride ions into the membrane.

In a study of radiation damage to the CR-51 type of ion-exchange-resin membranes, the exchange capacity was found to be only slightly affected and therefore to be a poor criterion of the damage. On the other hand, moisture and specific electrical conductances show significant changes.

CHEMICAL PHYSICS

By measurements on aluminum phosphide, the coherent neutron-scattering cross section of phosphorus was found to be 3.14 barns, with a positive phase.

Shifts in the frequency of quadrupole resonance lines of the order of 1 in 10,000 for a pressure of 2500 psi have been observed in sodium and potassium chlorates.

CHEMISTRY OF THE SOLID STATE

A surprisingly large increase with temperature of the solubility of sodium metal in molten sodium chloride was measured up to 1000°C where it is 20 mole % or 10 to 20 times greater than near the melting point, with no indication of a reversal of the trend. A tentative hypothesis connects this observation with possible changes of coordination of the ions in the melt.

A smaller temperature dependence seems indicated in tests covering the solubility (of the order of 6 to 10 mole %) of alkali metal in ternary eutectic melts of the fluorides of lithium, sodium, and potassium.

RADIATION CHEMISTRY

In a study of gamma-ray induced oxidation in sulfuric acid solution, uranium(IV) was found to be oxidized completely to uranium(VI) at a rate that decreases with increasing dosage, the initial yield being approximately 3.6 equivalents per 100 ev for both 10^{-2} and 10^{-3} *M* uranium(IV) solutions.

The effect of pH on hydrogen peroxide yields in aqueous solution containing helium, oxygen, hydrogen plus oxygen, and benzene plus oxygen was found to be very pronounced at a pH of less than 2.

Electrical conductivity peaks attributed to release of trapped electrons or positive holes have been observed in sodium chloride on heating at a constant rate after exposure to gamma rays. The temperatures of the conductivity peaks correspond with those at which glow-curve peaks are observed. A previously reported decrease in ionic conductivity produced by irradiation of alkali halides has been confirmed.

REACTOR CHEMISTRY

The solubility of excess UO_3 in UO_2SO_4 solutions at 250°C, expressed as the solubility ratio of U to SO_4,

was found to increase with increasing UO_2SO_4 concentration to a maximum value of 1.30 at 1.81 *M* UO_2SO_4.

Temperatures of separation into two liquid phases in the system UO_3-$UO_2SO_4 \cdot H_2O$ were determined for U-to-SO_4 ratios of 1.00, 1.10, and 1.20.

The solubility of barium sulfate in uranyl sulfate solutions was found to increase logarithmically with the square root of the concentration of uranyl sulfate. In a 1 *M* uranyl sulfate solution it is 42 times greater than in water.

The solubility of silver sulfate in 0.126 and 1.26 *M* uranyl sulfate solutions was determined between 25 and 260°C.

The tendency of either plutonium(III) or plutonium(VI) in aqueous and uranyl sulfate solutions to revert to plutonium(IV) is greatly enhanced by the presence of either gamma rays from a Co^{60} source or by reactor radiation.

Solutions of plutonium in uranyl sulfate can be stabilized by amounts of phosphoric acid which, in regard to neutron economy, compare unfavorably with comparable uranyl sulfate-sulfuric acid solutions.

The equivalent conductivity of aqueous uranyl sulfate solutions was measured at 200°C in a bomb type of cell.

Clearly defined end points were obtained in conductometric titrations with sulfuric acid at 25°C of UO_2SO_4 solutions containing an excess of UO_3. It is concluded that UO_3 behaves as a weak base and that because of the small difference in conductivity between solutions of U-to-SO_4 ratios of 1.2 and 1.0 the corrosion effect of the two should be approximately the same.

The vapor pressures of 0.592 and 2.09 *m* UO_2SO_4 solutions have been measured between 25 and 100°C.

Hydrogen gas production by irradiation of uranyl nitrate solution was found at low concentrations to be similar to that of comparable sulfate or fluoride solutions. In more highly concentrated solutions, nitrate decomposition produces oxygen and nitrogen gas, and a low hydrogen yield also results.

Low values for oxygen gas production on irradiation of $U(SO_4)_2$ solutions in the ORNL graphite reactor are satisfactorily accounted for by the conversion of uranium(IV) to uranium(VI). The hydrogen gas production of 1.5 moles of H_2 per 100 ev was found to be the same as in comparable uranyl sulfate solutions.

The thermal decomposition of hydrogen peroxide in uranyl sulfate solutions of varying degrees of purity has been measured at temperatures up to 100°C. Results are presented in terms of the Arrhenius equation. Determinations at various temperatures of the solubility of uranyl peroxide in uranyl sulfate solutions have been made; some of the determinations were made under steady-state conditions of (simulated) formation and decomposition of hydrogen peroxide. With an allowable peroxide concentration of 0.004 *M*, thus obtained, a minimum total power of 41 kw for the HRE is calculated.

INORGANIC CHEMISTRY

MEASUREMENT OF THE ACTIVITY COEFFICIENT OF CADMIUM IODIDE BY ULTRACENTRIFUGATION

J. S. Johnson K. A. Kraus

Details of the measurement of activity coefficients of UO_2F_2 by ultracentrifugation have been given in the previous quarterly report.[1] In order to evaluate the reliability of the method for the determination of activity coefficients, two ultracentrifuge experiments were conducted with cadmium iodide solutions (initial concentrations 0.3504 and 0.5324 *M*) and the results compared with the activity coefficients based on emf measurements, as reported in the literature.[2]

The experiments were carried out at 27.5 ± 0.5°C in 3- and 12-mm cells at 33,450 rpm. As discussed in the previous quarterly report, the refractive index gradients, dn/dx, in the cell were obtained from the displacements of the bar shadow, Z, and the optical constants of the centrifuge. By combining these with the refractive-index measurements of Getman and Gilroy,[3] which indicated that the refractive index, n, is a linear function of the concentration, c, the concentration gradient, dc/dx, was calculated as a function of x, the distance from the center of rotation. From the concentration gradient, dc/dx, a concentration c vs. x diagram was constructed by normalizing to the known quantity of solute in the cell. The partial specific volume $\bar{v}$ = 0.182 to 0.188 was obtained from the density data of Gibson[4] in the concentration ranges of the two experiments.

The mean activity coefficients, $y_\pm$ (molarity scale), were calculated from the equation

$$\ln \frac{y_\beta}{y_\alpha} = \frac{M(1 - \bar{v}\rho)\,\omega^2}{2RT\nu}(x_\beta^2 - x_\alpha^2) - \ln\left(\frac{c_\beta}{c_\alpha}\right) \quad (1)$$

where M is the molecular weight of the solute, ν the number of moles of ions per mole of solute, in this case 3, ρ the density of the solution, ω the angular velocity. The subscripts α and β refer to different radii of rotation.

To permit ready comparison of the activity coefficients with the data in the literature, the assignment $y_\pm$ = 0.0470 at c = 0.3529 was made for both solutions. The value was obtained from the data of Bates[2] by converting his values of $\gamma_\pm$ to $y_\pm$ and by interpolating to 27.5°C.

As shown in Fig. 1, agreement between the activity coefficients calculated from the centrifuge data and those of Bates is satisfactory throughout the concentration range studied. At the highest concentration, the centrifuge data appear to be 1.1% lower than those of Bates, which appear to be well within the expected experimental error of the method.

THERMODYNAMICS OF COMPLEX IONS

G. H. Cartledge

Study of the equilibrium between the two complexes of manganese(III)

(1) J. S. Johnson and K. A. Kraus, *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1952*, ORNL-1285, p. 8 (in press).

(2) R. G. Bates, *J. Am. Chem. Soc.* **63**, 399 (1941).

(3) E. W. Washburn (Editor-in-Chief), *International Critical Tables*, VII, 70, McGraw-Hill, New York, 1930.

(4) R. E. Gibson, *J. Am. Chem. Soc.* **59**, 1521 (1937).

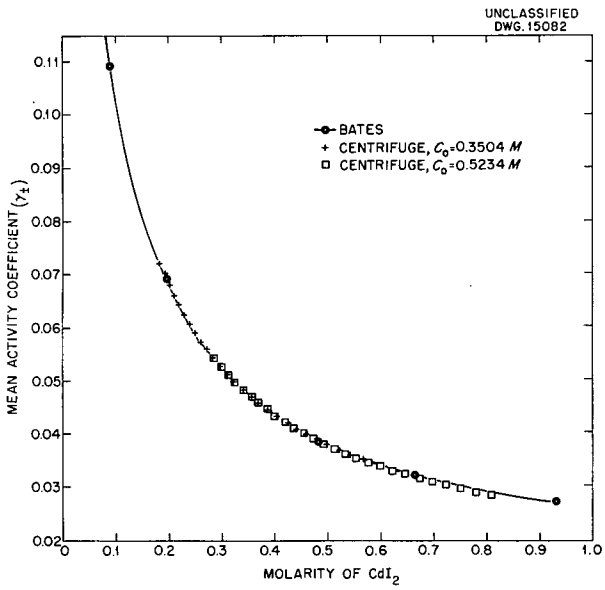


Fig. 1. Activity Coefficients of CdI_2.

with 2,4-pentanedione at different temperatures has been completed. If HPn represents the dione, thermodynamic constants for the reaction

$$MnPn_3 + 2H_2O \rightleftharpoons MnPn_2(H_2O)_2^+ + Pn^-$$

are: $K = 1.23 \times 10^{-4}$; $\Delta F^\circ_{298} = 5350$ cal; $\Delta H^\circ_{298} = 3030$ cal; $\Delta S^\circ_{298} = -7.7$ e.u. The measurements included a redetermination of the acidic ionization constant of pentanedione between 10 and 40°C. The values of K at 25°C is 8.99 ± 0.02 for the ionization reaction

$$HPn \rightleftharpoons H^+ + Pn^-;$$

$\Delta F^\circ_{298} = 12,300$ cal; $\Delta H^\circ_{298} = 4200$ cal; $\Delta S^\circ_{298} = -27.1$ e.u.

NUCLEAR CHEMISTRY

MASS ASSIGNMENT AND GAMMA RADIATIONS OF THE SEVEN-HOUR MOLYBDENUM ISOMER

G. E. Boyd R. A. Charpie[1]

The 7-h isomer activity in molybdenum produced by proton[2,3,4] and by deuteron irradiation of niobium,[3,5] by alpha-particle bombardment of zirconium,[3,6,7] and in very low yield by fast-neutron irradiation[7] of enriched Mo^{94} is of interest in that the assignment to mass 93 cannot be easily reconciled with predictions from the shell theory.

Some doubt concerning the mass assignment has persisted because, unexpectedly, it has not been possible to prepare the 7-h Mo^{93} by deuteron bombardment[7] of enriched Mo^{92} or by a (γ,n) reaction when enriched Mo^{94} was irradiated with 23-Mev gamma rays.[8] Numerous attempts to produce detectable amounts of a 7-h Mo activity by irradiating molybdenum enriched to 92.1% in mass 92 with slow neutrons in the ORNL Graphite Reactor have not been successful, and the 7-h period has not been observed as a daughter from the 2.75-h Tc^{93} produced by a (d,n) reaction on Mo^{92}. Finally, in recent bombardments of molybdenum with 20-Mev protons no 7-h molybdenum activity whatever was seen, although easily measurable quantities of the well-known 67-h Mo^{99} were formed by the energy-possible (p,pn) reaction.

To decide whether the 7-h period was actually produced by a $(p,2n)$

(1) Electromagnetic Research Division.

(2) G. T. Seaborg, *Rev. Mod. Phys.* **16**, 1 (1944) (private communication from L. Dubridge).

(3) D. N. Kundu and M. L. Pool, *Phys. Rev.* **70**, 111 (1946).

(4) J. P. Blaser, F. Boehm, P. Marmier, and P. Scherrer, *Helv. Phys. Acta.* **24**, 441 (1951).

(5) M. L. Wiedenbeck, *Phys. Rev.* **70**, 435 (1946).

(6) P. R. Stout and W. R. Meagher, *Science* **108**, 471 (1948).

(7) D. N. Kundu, J. L. Hult, and M. L. Pool, *Phys. Rev.* **77**, 71 (1950).

(8) R. B. Duffield and J. D. Knight, *Phys. Rev.* **76**, 573 (1949); also ref. 4.

reaction, a rough excitation curve was determined by using a stacked-foil technique in which 1-mil niobium foils interleafed with 5-mil aluminum and 2-mil silver foils were bombarded for 90 min with an approximately 50-μa beam of 20.1-Mev protons. First, however, an accurate half life was determined by measuring the decay of the gamma radiations emitted by a chemically purified molybdenum fraction separated from proton-irradiated niobium. The decay, which was exponential for more than 60 h, gave a value of 6.95 ± 0.05 h. Measurements of the gamma-ray energies were made (Fig. 2) by using a thallium-activated sodium iodide crystal scintillation-counter spectrometer. The energies observed appear to be in good agreement with recent magnetic-lens spectrometer measurements of conversion and photoelectron energies[9] except for the lowest energy transition, which differs appreciably.

In the stacked-foil experiment the gamma activities induced in the niobium foils were measured periodically in a calibrated 4π-geometry ionization chamber filled to 40 atm with argon gas.[10] The decay curves obtained could be resolved into only two periods: the 6.95-h Mo and the 10.2-d Nb^{92} formed by a (p,pn) reaction. The saturation amounts of each activity per milligram of niobium at the end of bombardment were computed, and by use of the accepted decay scheme[11] for the molybdenum isomer together with the known energy-efficiency curve for the ion chamber they were converted to absolute disintegration

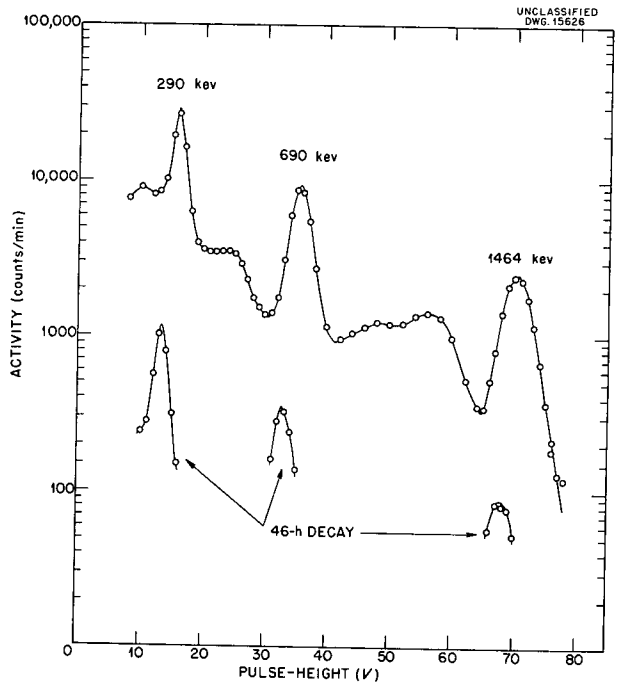


Fig. 2. Gamma-Ray Spectrum of 6.95-h Mo^{93} Measured by a Thallium-Activated Scintillation-Counter Spectrometer.

rates. Approximate reaction cross sections were then calculated from the proton-beam current and the areas of the niobium foils. The energy dependence of the cross section is given in Fig. 2 in which previously published[4] and more extensive measurements from 3.8 to 6.7 Mev are included. It is seen that the yield of 6.95-h Mo reaches a maximum at about 10 Mev and then remains constant or diminishes slightly with increasing energy. The yield curve for the formation of the 10.2-d Nb^{92} by a (p,pn) reaction, that may be expected to resemble that for a $(p,2n)$ reaction, is seen not to have reached a maximum even at 16 Mev. It seems necessary to conclude, therefore, that the 6.95-h Mo activity was formed by a (p,n) reaction and hence must be assigned to mass 93.

(9) L. Ruby and J. R. Richardson, *Phys. Rev.* **83**, 698 (1951); M. Goldhaber and A. W. Sunyar, *ibid.*, p. 906, Table 1.

(10) C. J. Borkowski, *Anal. Chem.* **21**, 348 (1949).

(11) M. Goldhaber and R. D. Hill, *Nuclear Isomerism and Shell Structure*, BNL-1157 (March 17, 1952); also ref. 2.

PROPOSED PREPARATION OF KILOCURIE QUANTITIES OF XENON-135

G. W. Parker G. E. Creek
G. M. Hebert

As a result of the general demand for an extension of the investigation of the xenon cross section,[12] a series of experiments have been proposed by ORNL physicists, Snell, Bernstein, and others to be performed with the aid of the new 84-channel velocity selector[13,14] located at the LITR.

As a contribution to the program, chemists in the Hot Laboratory group, with the collaboration of Brosi and Zeldes,[15] have undertaken the preparation of the sources using the new facilities of the Isotope Research Building.

Although refined spectrometer data are reportedly being sought in a separate program at Hanford, the unique situation of this Laboratory in having both the high-beam intensity of the LITR (greater than Hanford) and readily available kilocurie sources of xenon, warrants an attempt to obtain both an extension of transmission measurements to higher energies and a direct measurement of the scattering effect. With the possible exception of a special sample of higher specific concentration of Xe^{135} (obtainable only by growth from separated I^{135}) for a direct attempt at spin measurement by spectroscopy, the purity requirements of the gas permit its isolation by either of two methods involving only the separation of noble gases.

Method Involving Destruction of a LITR Fuel Assembly by Melting. The feasibility of outgassing aluminum-alloy fuel material and collecting the active rare gases has been reported by Siegel and Billington[16] who observed that the quantities of gas released at temperatures up to 550°C were negligible, whereas after melting (650 to 700°C) the gases were apparently all released. The authors have extended the threshold temperature to 600°C in vacuum without noticeable outgassing.

The procedure envisioned consists of removing a LITR alloy-fuel assembly from the reactor after a 24-hr irradiation at the 1 to 1.5 megawatt level and transporting it to a newly constructed Hot Laboratory cell where the melting operation may be safely performed. The mixed gases may be collected on coconut charcoal, separated, reduced in volume, and sealed in a thin copper sandwich conforming to the dimensions of the neutron beam.

Method Involving Stripping the Fuel Solution Off-Gas from the HRP. Since its conception, the Homogeneous Reactor has been regarded as the most attractive prospect for future large-scale rare-gas production. At 1 megawatt, the estimated equilibrium quantity of 9.2-h Xe held by the charcoal off-gas treatment system would approach 40,000 curies. Since the rate of decay approaches the rate of production after 18 hr, a collection over an 18-hr period at a power level as low as 20 kw should provide sufficient off-gas for a kilocurie source. The method is attractive because it utilizes a waste product instead of a currently

(12) S. Bernstein, A. R. Brosi, S. Freed, G. W. Parker, and M. M. Shapiro, *Status of the Investigation of the Total Cross Section of Xe^{135} as a Function of Energy*, ORNL CF-49-1-69.

(13) G. S. Pawlicki, *The ORNL Velocity Selector*, to be published.

(14) W. Selove, *A Rotating Shutter Time-of-Flight Neutron Spectrometer for the Resonance Region*, ANL-4392 (November 1949).

(15) H. Zeldes and A. R. Brosi, "Adsorption Column for the Separation of Radioactive Gases," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950*, ORNL-685, p. 53-61.

(16) S. Siegel and D. S. Billington, "The Effect of Reactor Radiation on Metals," *J. of Metallurgy and Ceramics* TID-66, p. 54 (Jan. 1949).

valuable fuel unit. In the operating program planned, the HRP is expected to reach the 20-kw power level easily, since a single fuel assembly will produce 20 kw in spite of being handicapped by a high burn-up of the xenon that is formed and held in the reactor.

The necessary equipment differs only in the first, or production step, for the two methods of obtaining the source. The transporting carrier, a tall lead cask weighing about 8 tons is designed to be used with either method. In the first method it will be used to shield the fuel assembly during transport; in the second it will contain an adsorbent column and a holder for a refrigerant such as liquid nitrogen.

Both a 20-kw resistance-type electric furnace and a 30-kw induction-type furnace have been tested for suitability in melting the approximately 20 lb of aluminum-uranium alloy in a LITR fuel assembly. Because of the burn-up of about 50% of the xenon during operation, a lengthy (6-to-8 hr) growth period is required after shutdown before the xenon returns to a maximum. By this time, most of the remote handling and preparation of the vacuum system should be accomplished. Melting requires only a short time, and it has been demonstrated that by adding helium into the top of the vertical, 6-in., stainless steel furnace tube the heavy gas is readily displaced out of the bottom of the furnace and held on 40 g of charcoal at liquid-nitrogen temperature (-195°C). The purification procedure is then identical to that described in the following for the alternate method.

The first step in the procedure for stripping xenon from the HRP off-gas involves pumping off the required amount of gas. The off-gas consists of 0.04 cfm of oxygen containing the rare gases, an indeterminant amount of radioiodine, bromine or unknown volatile fission products, a small amount of hydrogen, and perhaps even traces of the helium used in the leak-detector system. Because of the uncertainty of the contamination, a considerable portion of the effort will be spent in analyzing the first active gases produced. The plan of the equipment installed at the HRP site for the operation is illustrated in Fig. 3.

In addition to the gas-measuring and monitoring equipment, a dry-ice cooled silica-gel trap is provided for removing condensable contaminants other than rare gases. A water-displacement variable-speed pump for safe handling of the gas and a drying and precooling trap unit before the main adsorbent complete the installation.

Because of the well-recognized danger of adsorbing oxygen on charcoal, it is planned to use only silica adsorbents for removing contamination. The efficiency of silica-gel is generally one-third that of charcoal. However, by using the more convenient liquid nitrogen coolant on the main trap, the required capacity is easily obtained with silica gel. At liquid nitrogen temperature silica gel is more efficient by a factor of 30 than charcoal at solid-Co_2 temperature.

The plan of operation requires only that the pumping rate be approximately the same as the production rate of off-gas and that the coolant be replenished during the collection time. The excess off-gas will escape to the charcoal hold-up system and will be measured on a gas meter in series with the stack exhaust. At the end of a suitable period, the shield containing the adsorbent will be removed to the cell containing the remaining purification equipment.

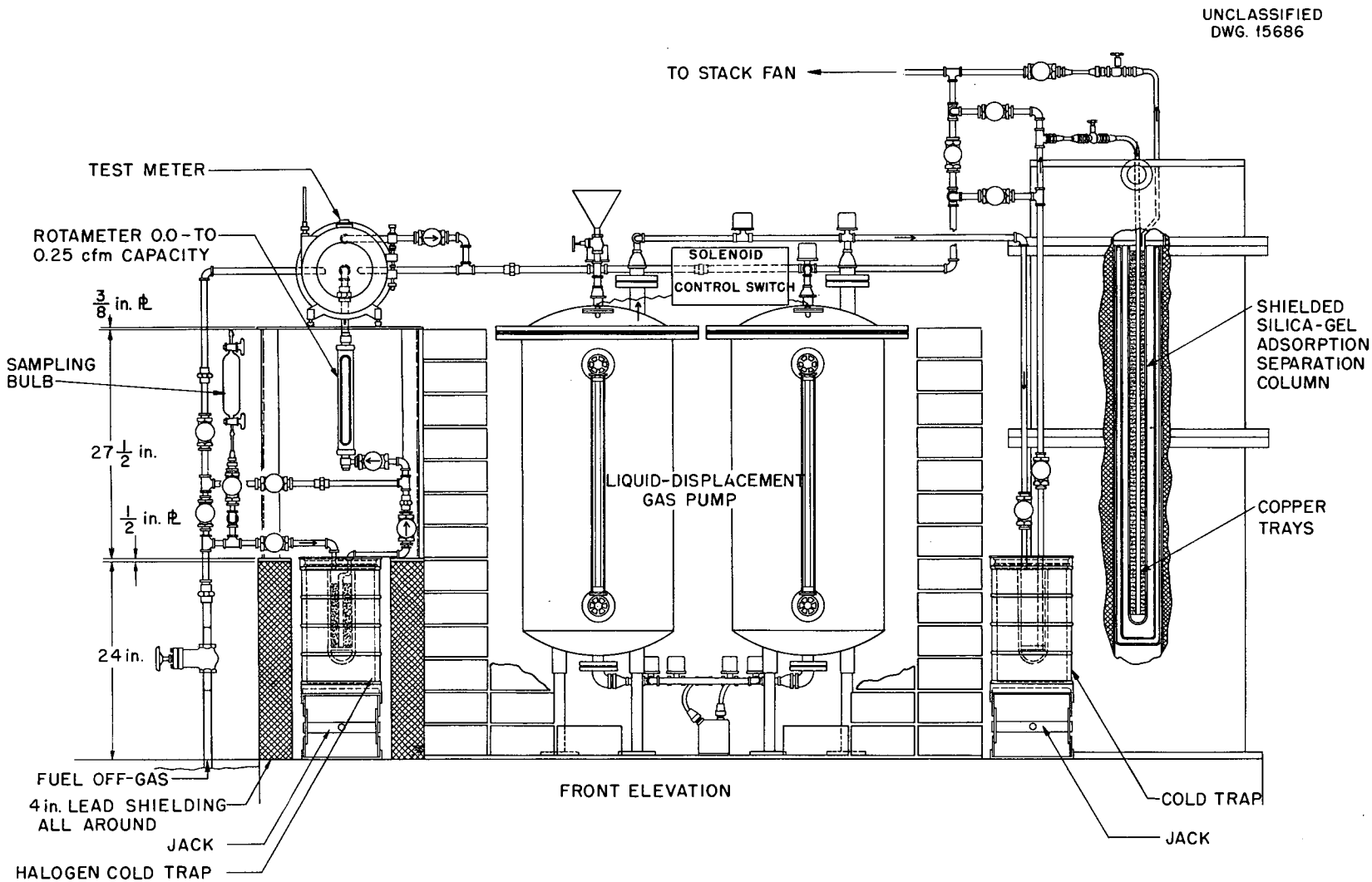


Fig. 3. HRP Off-Gas Collection Equipment.

Separation of 9.2-h Xenon from 3-h Krypton and Residual Gases. The limiting radiation from the rare-gas samples will occur in the hard gammas associated with 2.8-h Kr^{88}. The yield and decay rate make it a formidable activity in number of curies up to a cooling period of about 18 hr. In order to reduce the compressible volume of the sample to 1.0 cc, and to lower the radiation level, an effective adsorbent-column separation by the method of Zeldes and Brosi[15] will be performed in the cell. The shielded silica column will be attached to a hydrogen or helium gas stream where krypton and oxygen will be preferentially eluted at 0°C through an ion-chamber monitor that will detect only the hard radiation of Kr^{88}. The remaining xenon will then be displaced by additional hydrogen onto a minimum volume of charcoal from which lighter gases may be pumped off. Finally, the bed may be heated and outgassed by means of a Toepler Pump and a collecting bulb. Yield data and samples with suitable purity have already been obtained on column separations of gas from alloy samples in as little as 1 hour.

The 1.0-cc copper transmission chamber may be cooled by liquid nitrogen and filled by mercury displacement from the bulb. The small-bore stainless steel capillary tube connecting the bulb and sample holder will be flattened, sheared, and soldered before the specimen is tested for leakage. The source may then be placed in the beam position now used for stable specimens.

RADIO-ORGANIC CHEMISTRY

RADIATION AND ANALYTICAL CHEMISTRY

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

Work on the radiation chemistry of aqueous acetic acid has continued. After a number of preliminary experiments, 888 mg of the nonvolatile product formed by the irradiation of 910 ml of 0.25 *N* aqueous acetic-acid solution with 5.5×10^6 r of gamma radiation from Co^{60} was placed on a large Celite partition column and eluted with chloroform-butanol mixtures of increasing-butanol concentration. The column was eluted at a flow rate of 0.5 to 1.0 ml/min for a period of seven weeks. The eluate was titrated periodically with base and thus separated into fractions (Table 1). The fractions were in turn reconverted to the free-acid state and partitioned between ether and water. The ether

Table 1

PARTITION OF NONVOLATILE GAMMA-RADIOLYSIS PRODUCT FROM AQUEOUS ACETIC ACID WITH CHLOROFORM-BUTANOL-WATER

FRACTION	MILLIEQUIVALENTS
1	0.063
2	0.368
3	0.123
4	6.388
5	0.034
6	1.158
7	1.797
8	0.444
9	0.145
10	0.495
11	0.104
12	0.041
13	1.740*
14	11.862*

*Contains sulfuric acid.

eluate was collected in small fractions that were allowed to evaporate. The fractions were combined by visual analysis (Table 2), and ether-acetone solutions of the subfractions were made. Paper chromatographic analysis of the products is being made by direct comparison with known compounds.

MECHANISM OF THE ALIPHATIC AMINE-NITROUS ACID REACTION

P. S. Bailey[1] J. G. Burr, Jr.

It was stated in a previous quarterly report[2] that the migration ratios for several substituted aryl groups vs. phenyl, observed in the reaction of diarylethylamines with nitrous acid, were all close to 1.00 and strikingly different from the ratios of similar groups observed in the acid-catalyzed rearrangement of diarylethanols.

The reasons for the difference are now being investigated. The present method of attack is to study the thermal and acid-catalyzed rearrangement of several anhydrous diarylethyl ammonium nitrites. One of the compounds, 2-phenyl-2-(*p*-tolyl) ethyl-1-C^{14}-amine nitrite has been prepared and its thermal decomposition studied from three points of view.

Over-all Rate of Decomposition. Information has been obtained by carrying out the decompositions of the nitrite salt in a jacketed glass cell attached to a gas-burette system. Water from a constant-temperature bath was circulated through the jacket while the solution was stirred magnetically. The course of the reaction was followed by measuring the evolved nitrogen in the gas burette. The data thus obtained for three different solvents;

[1] Research participant from the University of Texas.

[2] L. S. Ciereszko and J. G. Burr, Jr., *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1952*, ORNL-1285, p. 54.

Table 2

PARTITION OF CHLOROFORM-BUTANOL FRACTIONS WITH ETHER-WATER

CELITE-BUTANOL FRACTION NO.	NO. OF SUBFRACTIONS (usual separation)	MELTING POINT OF SOLID IN SUBFRACTION	
		Subfraction No.	Melting Point (°C)
1	1 through 5	5	250
2	1 through 5	5	250
3	1 through 4		
4	1 through 4		
5			
6	1 through 6		
7	1 through 2	2	155 to 157
8	1 through 5	3	177 to 180
9	1 through 2	2	255 to 230
10	1 through 7		
11	1 through 5	3	250
12	1 through 4		
13			
14			

anhydrous ligroin (b.p. 90 to 100°C), anhydrous *n*-butanol, and water are summarized in Table 3 and Fig. 4.

Migration Ratios Observed for the *p*-tolyl Group Compared to the Phenyl Group. The migration ratios were obtained by isolating the reaction product, washing it with dilute hydrochloric acid (to remove any amine formed in the reaction) and oxidizing one-half of the product directly to terephthalic acid. The radioactivity of the terephthalic acid was a direct measure of the amount of *p*-tolyl group migration. The other half of the product was dehydrated with phosphorus pentoxide in benzene, and the resulting stilbene was isolated and then oxidized to terephthalic acid. There was very little difference in the activities of the two products, showing that a negligible amount of primary diarylethanol was formed in the rearrangement. Essentially the same procedure was used in the earlier work.[2]

Investigation of the Nature of the Reaction Product. One of the most unexpected observations in the rearrangements was that the product formed was not stilbene but the same mixture of rearranged carbinols in all three cases (ligroin, butanol, and water). Stilbene was the rearrangement product expected in the absence of any external source of hydroxyl ion, that is, an anhydrous salt suspended in an anhydrous medium. The product was a gum that gave a

Table 3

THERMAL REARRANGEMENT OF 2-PHENYL-2-(*p*-tolyl)ETHYL-1-C^{14}-AMMONIUM NITRATE[a] AT 70°C

RUN	SOLVENT	RATE CONSTANT (k)[b]	MIGRATION RATIO (as % *p*-tolyl migration)
1	Ligroin[c]	0.0306	48
2	Ligroin[c]	0.0290	
3	Water[d]	0.0132	47
4	Water[d]	0.0135	
5	*n*-Butanol[e]	0.0109	(43)[f]

[a]Nitride prepared by precipitation of amine hydrochloride as oil from water solution. Product removed by centrifugation, dried in ether-alcohol solution, and recovered as tan solid by vacuum evaporation over P_2O_5. M.p. (indefinite) 90°C. Calcd. for $C_{15}H_{18}N_2O_2$: N, 10.8. Found: N, 10.4. C^{14}, 1.63 μc/mmole. Sample wt, 1.00 g.

[b]All reactions gave good first-order plots (see Fig. 4).

[c]Ligroin (b.p. 90 to 100°C) dried over Na. Drierite (2.0 g) added with nitrite salt to absorb water formed by reaction. Salt first formed suspension, then as reaction proceeded quickly (10 to 15 min) liquefied and formed viscous oil that clung to walls of vessel. Liquefaction presumably marked by abrupt break in plot of log ($V^0 - V$) vs. time.

[d]Solvent dried by distillation (b.p. 116°C). Nitrite salt and reaction products both soluble giving homogeneous reaction. Drierite (2.0 g) present.

[e]Nitrite salt soluble in water: reaction products insoluble. Increasing amount water-insoluble product appeared during reaction.

[f]Preliminary value.

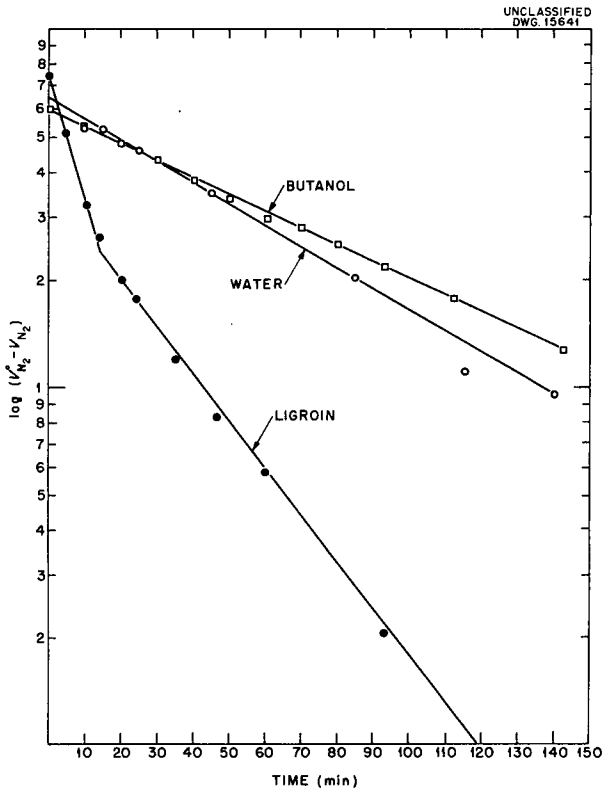
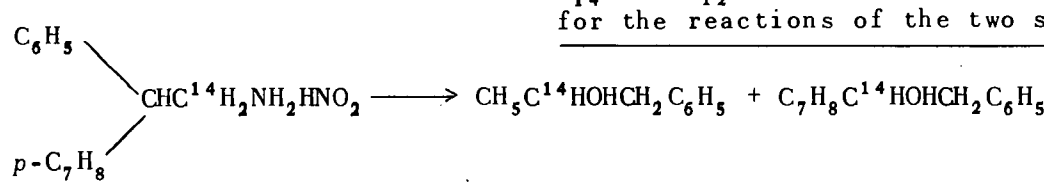


Fig. 4. Thermal Decomposition of 2-Phenyl-2-(*p*-tolyl)ethylammonium Nitrite at 70.0 ± 0.5°C.

quantitative yield of crystalline *p*-methylstilbene (m.p. 118 to 120°C) upon dehydration with phosphorous pentoxide in benzene



as indicated by the radiochemical assay method that showed the absence of appreciable amounts of the primary (or unrearranged) carbinol. The identity of the material was indicated by its chemical behavior and by the infra-red analysis that showed the close resemblance to benzylphenylcarbinol, including a pronounced peak at 2.98 μ, a characteristic of the hydroxyl group.

ISOTOPE-EFFECT STUDIES

Effect of *Meta*- and *Para*-Substituents on the Isotope Effect in the Saponification of Carboxyl-C^{14}-Labeled Ethyl Benzoates (V. F. Raaen, G. A. Ropp). The values of k_{14}/k_{12} at 25°C have been definitely established for five esters[3] and are given in Table 4. Each of the values reported for a given ester in the third column was measured on an individually prepared and purified sample of labeled ester. In an effort to find a cause for the trend of isotope-effect values through this series of esters, ethyl *m*-chlorobenzoate is being prepared with C^{14} in the carboxyl group, and the value of k_{14}/k_{12} is to be determined at 25°C.

Effect of Temperature on the Isotope Effect in the Saponification of Carboxyl-C^{14}-Labeled Ethyl Benzoate. Values of the isotope effect have been definitely established at three temperatures[3] and are given in Table 5. The values correspond to a 46-cal/mole difference between the Arrhenius activation energies for the two species of ethyl benzoate. The value of $E_{14} - E_{12}$ corresponds closely to equal values of the frequency factors A_{14} and A_{12} in the Arrhenius equations for the reactions of the two species. This result is contrary to the preliminary result in an earlier report.[3]

Study of the Methods Used in the Quantitative Evaluation of Isotope Effects (Z. Hearon,[4] G. A. Ropp). The interest in methods for the quantitative evaluation of isotope

(3) V. F. Raaen and G. A. Ropp, *Ibid.*, p. 43.

(4) Visiting consultant to the Mathematics Panel of ORNL from the University of Chicago.

Table 4

VALUES OF k_{14}/k_{12} AT 25°C FOR FIVE ESTERS

RING SUBSTITUENT	k_{14}/k_{12} (average)	PRECISION OF k_{14}/k_{12} VALUES FOR INDIVIDUAL RUNS
m-NO_2	0.937	0.937, 0.937
p-Cl	0.925	0.922, 0.926, 0.926
Unsubstituted	0.929	0.928, 0.930, 0.928
p-CH_3	0.928	0.929, 0.927, 0.928
p-OCH_3	0.916	0.916, 0.915

Table 5

EFFECT OF TEMPERATURE ON VALUES k_{14}/k_{12}

TEMPERATURE (°C)	k_{14}/k_{12}
78.5	0.939
25	0.929
0	0.918

effects has indicated the desirability of determining whether the methods reported by Stevens and Attree[5] and Bigeleisen[6] are applicable to reactions that are greater than first order in the reactant bearing the label. The discussion will indicate that the methods are limited to reactions that are first order in labeled reactant. The errors resulting from an attempt to apply the methods to a reaction that is really second order in labeled reactant have been estimated.

Let the reaction be

$$R + B \longrightarrow P ,$$

and let reactant R be tagged. The rate equations are then

$$\frac{dP}{dt} = k\, R^n\, B^m \quad , \qquad (1)$$

and

$$\frac{dP^*}{dZ} = k^*\, R^*\, R^{n-1}\, B^m \ . \qquad (2)$$

The ratio of Eq. 1 and Eq. 2 gives

$$\frac{dP}{kR} = \frac{dP^*}{k^*\, R^*} \ . \qquad (3)$$

If

$$R(0) = C_0 \quad ,$$

and

$$R^*(0) = C_0^* \ ,$$

then

$$R(t) = C_0 - nP \ ,$$

and

$$R^*(t) = C_0^* - P \ ,$$

[5] W. H. Stevens and R. W. Attree, *Can. J. Res.* **27B**, 807 (1949).

[6] J. Bigeleisen, *Science* **110**, 14-16 (1949).

and Eq. 3 becomes

$$\frac{dP}{k(C_0 - nP)} = \frac{dP^*}{k^*(C_0^* - P^*)} \quad . \qquad (4)$$

Define f^* and f as

$$f^* = \frac{p^*}{C_0^*} \text{ , and } f = \frac{P}{C_0} \quad , \qquad (5)$$

and r as

$$r = \frac{f^*}{f} = \frac{\frac{P^*}{P}}{\frac{C_0^*}{C_0}} \quad . \qquad (6)$$

Then Eq. 4 becomes

$$\frac{df}{k(1 - nf)} = \frac{df^*}{k^*(1 - f^*)} \quad ,$$

the integral of which, since

$$f = 0 \text{ at } t = 0 \quad ,$$

is

$$\frac{1}{nk} \ln (1 - nf) = \frac{1}{k^*} \ln (1 - f^*) \quad . \qquad (7)$$

Thus

$$\frac{k}{k^*} = \frac{n \ln (1 - f^*)}{\ln (1 - nf)}$$

$$= \frac{n \ln (1 - rf)}{\ln (1 - nf)} \quad . \qquad (8)$$

Since, from Eq. 5 and Eq. 6, r is the ratio of the fractional conversion of the tagged and ordinary molecules, r will not differ greatly from unity if k^*/k does not. From Eq. 8 it is clear that appreciable error is involved if it is assumed that $n = 1$ when in fact $n \neq 1$. For small f, however, Eq. 8 reduces to the same value regardless of the value of n:

$$\frac{k^*}{k} \cong n \frac{\left[- rf - \frac{(rf)^2}{2} - \ldots \right]}{\left[- nf - \frac{(nf)^2}{2} - \ldots \right]}$$

$$= \frac{r + \frac{r^2 f}{2} + \ldots}{1 + \frac{n^2 f}{2} + \ldots}$$

for small f,

$$\frac{k^*}{k} \cong r \quad .$$

This is the case for example in the Stevens-Attree data: they give

$$f = 0.101 \quad ,$$

$$r = 0.87 \pm 0.06 \quad .$$

The ratio k/k^* computed from Eq. 8 with $n = 1$, is 0.86 ± 0.016. The difference, $r - k^*/k = 0.01 \pm 0.024$, is not significant for $n = 2$. Stevens and Attree would have obtained $k^*/k = 0.758$. For $n = 1$, it is evident that

$$r(0) = k^*/k \quad , \qquad f(\infty) = 1 \quad ,$$

$$r(\infty) = 1.00 \quad , \qquad f^*(\infty) = 1 \quad .$$

For $n \neq 1$,

$$r(0) = k^*/k \quad , \qquad f(\infty) = 1/n \quad ,$$

$$r(\infty) = n \quad , \qquad f^*(\infty) = 1 \quad .$$

Thus for $n = 1$, r varies between k^*/k (which is usually close to 1) and 1. for $n \neq 1$, r varies between $k^*/k \cong 1$ and n. For any value of n,

$$\frac{k^*}{k} \text{ (computed assuming } n = 1)$$

$$= \frac{k^*}{k} \text{ (actual) } \frac{\ln (1 - nf)}{n \ln (1 - f)} \quad ,$$

since the actual value of ln $(1 - rf)$ is

$$\frac{k^*}{k}\,(\text{actual})\,\frac{\ln\,(1 - nf)}{n} = \ln\,(1 - rf)\ .$$

For $n = 2$,

$$\frac{k^*}{k}\,(\text{actual}) = 0.950\ .$$

Note that for small f, $k^*/k \cong r$ agrees with Eq. 13 of Bigeleisen, and $r(\infty) = n$ agrees with Eq. 14 of Bigeleisen when $k_3 = 0$. The calculated rate constants are given in Table 6.

Table 6

CALCULATED RATE CONSTANTS

f	CALCULATED k^*/k (Assuming $n = 1$)	COMPLETION OF REACTION (%)
0.02	0.973	4.0
0.05	0.978	10
0.10	1.009	20
0.20	1.089	40
0.30	1.219	60
0.40	1.496	80
0.45	1.829	90

WAGNER REARRANGEMENT STUDIES – 3-METHYLPHENANTHRENE-9,10-C_1^{14}

C. J. Collins

The surprising results obtained by Benjamin[7] in his study of the rearrangement of 1-methyl-9-fluorenyl (carbinol-C^{14}) have indicated the importance of studying the Wagner rearrangement of 3-methyl-9-fluorenyl (carbinol-C^{14}) to 3-methylphenanthrene-9,10-C_1^{14}. 3-methylfluorene-9-carboxylic acid was prepared from benzoylformic acid, toluene, and aluminum chloride. The acid was converted to 3-methylphenanthrene by the method outlined for phenanthrene-9-C_1^{14},[8] the intermediate compounds were purified, and analytical samples were prepared. The synthesis will be repeated with 3-methylfluorene-9-carboxylic-C^{14} acid.

A quantity (10 g) of 3-methylphenanthrene for use in model degradation experiments has been prepared by an independent synthesis through the route phenanthrene $\longrightarrow$ 3-acetylphenanthrene[9] $\longrightarrow$ 3-phenanthrylacetic acid[10] $\longrightarrow$ 3-methylphenanthrene.[10]

STUDIES OF THE REACTOR-RADIATION STABILITIES OF ORGANIC COMPOUNDS

D. N. Hess R. W. Johnson
C. W. Collins

Reactor Irradiation of Biphenyl. Carefully purified biphenyl, twice crystallized from ethanol and then sublimed, was sealed in evacuated quartz ampoules and placed in Hole 12 of the ORNL graphite reactor for periods of 16 hr to one week. The sample size varied from 20 to 400 mg. The criteria of amount of radiation damage were the melting point depression, the hydrogen evolution, and the color change.

None of the irradiated samples evidenced a melting-point depression greater than 1°C, and the hydrogen evolution was never greater than 0.8%

(7) B. M. Benjamin and C. J. Collins, *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1951*, ORNL-1260, p. 62.

(8) C. J. Collins, *J. Am. Chem. Soc.* **70**, 2418 (1948).

(9) E. Mosettig and J. Van de Kamp, *J. Am. Chem. Soc.* **52**, 3704-20 (1930).

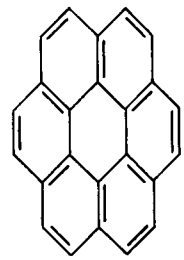
(10) W. E. Bachmann and G. D. Cortes, *J. Am. Chem. Soc.* **65**, 1332 (1943).

of the total hydrogen present in the biphenyl sample. Overnight irradiations produced no color change from the characteristic white, crystalline appearance of biphenyl, although samples that were subjected to one week's irradiation were slightly yellow in color.

In order to achieve a higher flux of both slow and fast neutrons a similar biphenyl sample was left in the LITR for one week. The hole used had an approximate shielding of 6 in. of beryllium. The melting point of the biphenyl after irradiation was depressed about 1°C, the hydrogen evolution was less than 0.8% of the total hydrogen, and the color was a light tan.

The preliminary experiments indicate that all the samples of biphenyl irradiated suffered less than 1% decomposition.

Coronene. A synthesis of coronene by the method of Newman,[11] who generously supplied 60 g of the dienic starting material compound II, is under way. It is anticipated that



Coronene

because of the symmetrical structure of coronene it should be resistant to temperatures in excess of 500°C and relatively stable when subjected to high-flux slow or fast neutrons.

(11) M. S. Newman, *J. Am. Chem. Soc.* **62**, 1683 (1940).

CHEMISTRY OF SEPARATION PROCESSES

ISOPIESTIC MEASUREMENTS AND THE OSMOTIC FREE ENERGY OF CATION EXCHANGERS

G. E. Boyd B. A. Soldano

A specially designed isopiestic apparatus (Fig. 5) has been used for some time to determine moisture-uptake isotherms for the hydrogen, lithium, sodium, potassium, ammonium, cesium, and zinc salt forms of variously cross-linked Dowex-50 type of cation exchangers. Typical data taken with a nominally 8%-DVB-content preparation are given in Fig. 6, in which moles of water per equivalent are plotted with the relative pressure. The usual sigmoid shape observed in the absorption of water vapor by many substances (cotton, silk, wool, proteins, polymers, etc.) was found. Interestingly, the "knee" of the isotherm (at $p/p_0 \approx 0.05$) corresponds to the uptake of about one water

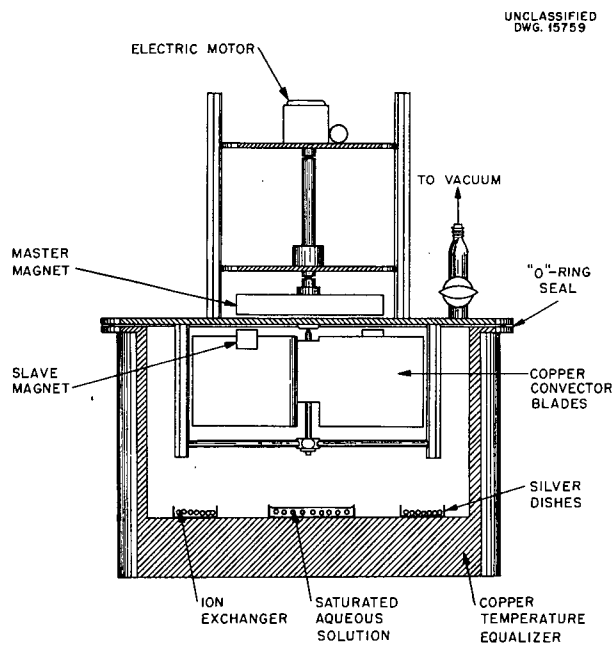


Fig. 5. Isopiestic Apparatus for Moisture-Uptake Isotherms.

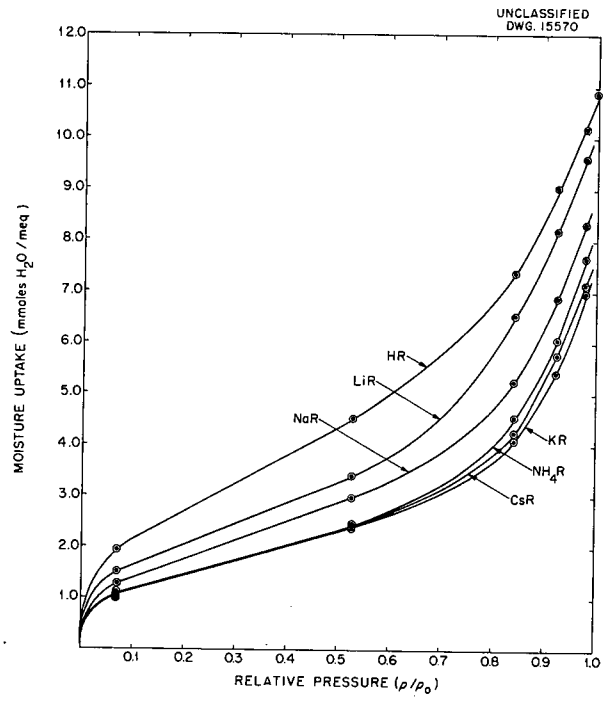


Fig. 6. Swelling-Water Isotherms for Alkali Metal Salt Forms of Nominal 8% DVB-Dowex-50 Exchanger.

molecule per exchange group. The isotherm shows an approximately linear portion between p/p_0 = 0.1 and 0.7 and finally rises sharply at relative pressures above 0.8. However, the uptake at saturation pressure does not become indefinitely large, as with plane-solid surfaces or in porous solids, but tends to a definite, finite value characteristic of the homoionic salt form.

Several thermodynamic treatments may be applied to the isotherm data. First, it will be of interest to compute mean molal osmotic coefficients, ϕ, for the variously hydrated resin salts assuming that the cations are dissolved in the water of gelation to give an electrolyte solution:

$$\nu\phi = -\frac{55.51}{m^r} \log \frac{p}{p_0} \quad . \qquad (1)$$

In Eq. 1 ν is the number of ions into which the resin salt may be assumed to dissociate, and m^r is the stoichiometric concentration in moles per 1000 g of water. A $(\nu\phi, m^r)$ plot is given in Fig. 7 in which the points at the lower concentrations were obtained with a weakly cross-linked (0.5% DVB) preparation. Points at still lower molalities are desired because they would serve to test the indicated extrapolation to $\nu\phi$ = 1 and because the activity coefficients of the resinates might then be computed by using the relation

$$-\ln \gamma = \int_{m^r=0}^{m^r} (1 - \phi)\, d \ln m^r . \qquad (2)$$

It was found, however, that with a 0.2%-DVB preparation the rate of attainment of isopiestic equilibrium was extremely slow. Further, the same isotherm was not obtained upon decreasing as upon increasing p/p_0. The apparent approach of the values of $\nu\phi$ for the exchangers toward unity is of considerable importance, since ordinary 1:1 electrolytes give $\nu\phi \longrightarrow 2$ as $m \longrightarrow 0$. Thus, as first suggested by Gluckauf and Duncan,[1] the exchanger polyelectrolyte appears to behave as a 1:n electrolyte, where n is a large number.

It is further possible, by using the data for the 0.5- and 8%-DVB preparations, to estimate the magnitudes of the swelling pressures in the various salt forms of the more highly cross-linked exchanger. The calculation may be based on the equation:

$$\log \left(\frac{a^r_{H_2O}}{a^w_{H_2O}} \right) = -\frac{\pi \bar{v}^0_{H_2O}}{2.303\, RT} , \qquad (3)$$

which may be derived from the expressions for the chemical potentials

[1] E. Gluckauf and J. F. Duncan, *Thermodynamic Treatment of Experiments with Sulphonated Resins*, Paper presented before the 120th Annual Meeting of the American Chemical Society, New York City, September 1951.

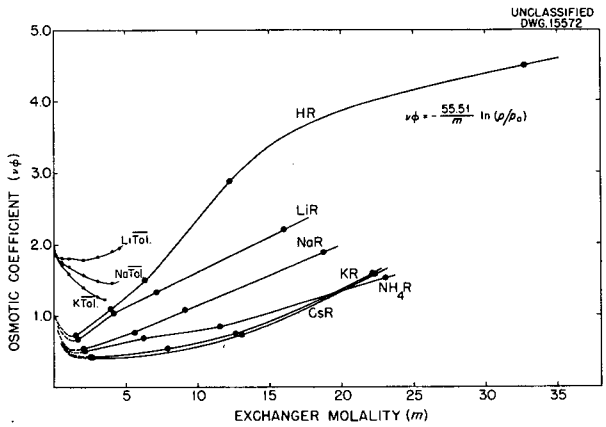


Fig. 7. Concentration Dependence of Osmotic Coefficients for Several Salt Forms of 0.5% DVB-Dowex-50 Exchanger.

of water in the exchanger, r, and in an equilibrium aqueous-solution phase, w. Subtracting two such equations as Eq. 3 for the 8%- and 0.5%-DVB preparations, respectively, gives

$$\log a_{H_2O}^{8\%} - \log a_{H_2O}^{0.5\%} = \frac{\pi \bar{v}_{H_2O}^{0}}{2.303\,RT}, \quad (4)$$

where π is the swelling pressure in the 8%-DVB exchanger, and $\bar{v}_{H_2O}^{0}$ is the molar volume of pure water, assuming that the value of π for the 0.5%-DVB preparation is negligibly small. The left-hand member of Eq. 4 is evaluated by comparing the water activities in the same salt forms of the two exchangers at the same molality. As may be seen from Fig. 8, swelling pressures, π, as large as 160 atm may occur in the 8%-DVB preparation. The equivalent volumes of the exchangers were estimated from the relation

$$V = V(\text{dry}) + V_{H_2O}$$

Thus, V(dry) for the hydrogen form was measured pycnometrically as 130 ml/eq, whereas $V_{H_2O} = 1000/m^r$, so that

$$V(HR) = 130 + \frac{1000}{m^r}.$$

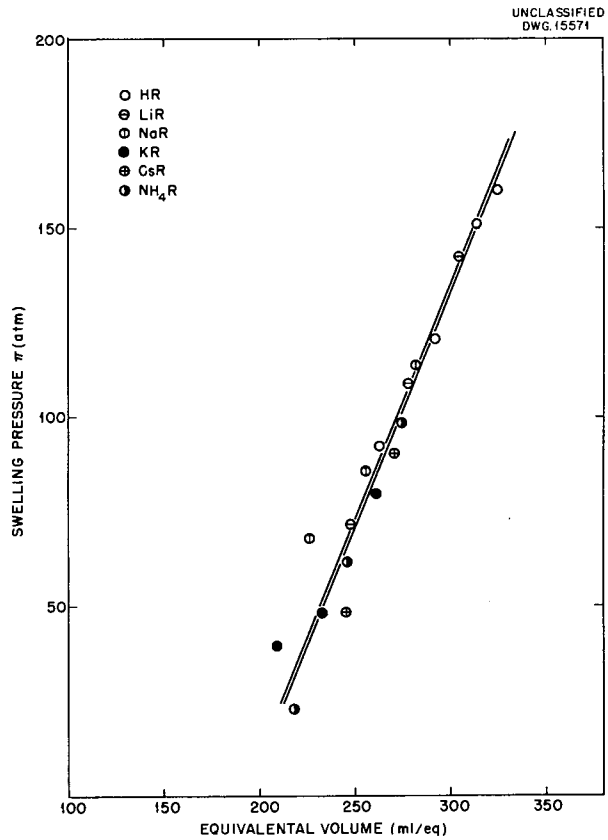


Fig. 8. Variation of Swelling Pressure with External Exchanger Volume for Several Salt Forms of 8% DVB-Dowex-50 Exchanger.

Figure 8 also shows that the swelling pressure is a function only of the external volume of the exchanger and is independent, as would be expected, of the nature of the cation it contains. The (π, V) relation appears linear in the range covered by the measurements. It is to be expected that the curves may become nonlinear and may deviate from one another at low pressures.

ELECTROCHEMICAL PROPERTIES OF ION-EXCHANGE MATERIALS

B. A. Soldano G. E. Boyd

An experimental program involving studies of the electrochemical properties of coherent ion-exchange materials

such as membranes, rods, etc. has been initiated.[2] Equipment and techniques for the accurate measurement of resin-membrane conductances, transport numbers in exchangers, equilibrium Donnan-electrolyte partition, moisture, and exchange capacity have been developed. Preliminary determinations were undertaken to confirm values reported for a commercially available homogeneous cation-exchange membrane material, CR-51. Specific conductivity, κ, measurements on the sodium-salt form of the membrane are compared in Fig. 9 that also gives the variation of κ with concentration for aqueous sodium chloride solutions.

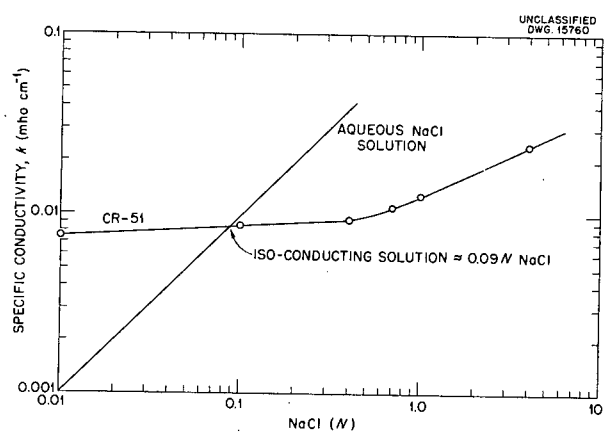


Fig. 9. Specific Conductivity of Sodium Polysulfonate Ion-Exchange Membrane.

Membrane-potential determinations were also made employing the concentration cell:

$$\mathrm{Ag;\ AgCl}(a_{\mathrm{I}})\ \|\ \mathrm{AgCl}(a_{\mathrm{II}});\ \mathrm{Ag}, \quad (1)$$

where a_{I} and a_{II} are the mean ionic activities of electrolyte (NaCl) in the two compartments separated by the membrane. The potential of the cell is given by:

$$E = \frac{2RT}{F} \int_{a_{\mathrm{II}}}^{a_{\mathrm{I}}} t_+ \, d \ln a_r \quad (2)$$

where t_+ represents the transport number of the cation (Na^+) in the membrane corresponding to the mean ionic activity, a_r, of NaCl in the membrane.

An ideally permeselective cation membrane would have $t_+ = 1$ so that in general,

$$t_+ = E/E_0 \quad (3)$$

where

$$E_0 = \frac{2RT}{F} \ln \frac{a_{\mathrm{I}}}{a_{\mathrm{II}}} \quad (4)$$

Eq. 3 will be valid, provided that the membrane is sufficiently thick so that its two faces are in equilibrium with the solutions in I and II, and the ratio $a_{\mathrm{I}}/a_{\mathrm{II}}$ is sufficiently small that the variation of t_+ with $\ln a_r$ is virtually linear.

In practice, it is necessary to flow the solutions through I and II, otherwise the ratio $a_{\mathrm{I}}/a_{\mathrm{II}}$ will not remain constant because of the diffusion of NaCl across the membrane. The cell potential was found to be independent of the flow for rates ranging from 1 to 12 cc/min. However, when flow through one compartment was stopped, changes as large as 1 mv were observed. The Ag;AgCl electrodes used in the measurements reported in Table 7 agreed with one another to within 0.06 millivolts. An assymetry potential of 0.1 mv was observed in the measurements. Table 7 shows that reasonably good confirmation of the earlier results was obtained. Further,

[2] J. H. Gross and R. E. Wacker, *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1951*, ORNL-1053, p. 90.

[3] W. Juda, N. W. Rosenberg, J. A. Marinsky, and A. A. Kasper, *J. Am. Chem. Soc.* **74**, 3736 (1952).

Table 7

EXPERIMENTAL AND THEORETICAL MEMBRANE-POTENTIALS FOR CR-51 EXCHANGER CORRESPONDING TO VARIOUS SODIUM CHLORIDE SOLUTIONS
(Twofold Difference in Concentration)

NaCl CONCENTRATION PAIR		IDEAL MEMBRANE E_0 (mv)	CELL POTENTIAL (mv)		TRANSPORT NUMBER OF Na^+
Normality I	Normality II		This Work	Juda *et al.*	
1/28	1/64	33.96	33.15	32.53	0.976
1/8	1/4	32.55	29.32	28.73	0.901
1	2	38.0	23.49	24.34	0.618

the decrease in permiselectivity with increased concentration of NaCl is reflected in the decrease in t_{Na^+}. Presumably the remaining fraction of the current is transported by the chloride ions that are able, at higher concentrations, to penetrate the membrane.

Radiation Damage Studies. The relatively high electric conductance of the CR-51-type membranes, together with their good permiselectivity up to 0.5 *N*, has stimulated much interest in their employment in the recovery, concentration, and separation of electrolytes. The value of the membranes to AEC problems, however, may very well depend upon whether or not their properties remain unaffected by nuclear radiations. Therefore, preliminary investigations were made in which the conductances, moisture contents, and exchange capacities were determined using samples of CR-51 exposed to reactor neutrons for varying periods.

Strips of Lumite-backed membrane were cut from a larger sheet and then converted into the sodium-salt form by exhaustive treatment with NaCl solution. The membrane samples were irradiated in a sealed glass tube together with sufficient water to keep them moist at all times. The same strip was used throughout for the conductance measurements in order to build up a progressively increased radiation dosage. The reactor bombardments were monitored using cobalt wires and the induced activity in the cobalt subsequently measured in a calibrated 4π-geometry, argon-filled ionization chamber. This measurement yielded an *nvt* value which was taken as a measure of the radiation dose.

After irradiation the membrane strips were again treated with NaCl solution and then rinsed until no chloride ion could be detected in the wash water. Specific conductances were measured using a simple Lucite cell accurately machined to accept the membrane strip.[3] The resistance determinations were probably accurate to within 2%, however, larger inaccuracies were introduced by uncertainties in the geometry of the strips, resulting from the tendency of the membrane to become brittle and flake under reactor irradiation.

Exchange-capacity measurements were also made throughout on another membrane strip. In this case, after

irradiation the exchanger was converted to the hydrogen form and then titrated with NaOH to determine its capacity. Care was exercised to prevent the loss of any solid because of chipping, etc.

Moisture contents were determined on a third strip of membrane. In this case, however, after each exposure a piece was cut off, weighed, and then heated to dryness over P_2O_5 in a vacuum oven and reweighed.

Table 8 summarizes the changes observed in specific conductance, exchange capacity, and moisture with exposure to reactor radiations.

It is readily seen that changes in exchange capacity afford a very poor criterion of radiation damage. At most only a roughly 5% decrease is observed after prolonged bombardment. However, both the moisture and specific conductance show a definite variation. The specific conductance remains constant or rises slightly with increased exposure at first and then decreases progressively to a final value 30% less than the initial. The moisture content appears to rise abruptly at first, then to remain roughly constant with increased irradiation and finally to decrease to a value somewhat less than that for unirradiated membrane. The changes in membrane thickness parallel the moisture variations. After prolonged bombardments a decided warping was observed as a consequence of the membrane shrinking and pulling away from its backing. The membrane material also appeared to have increased density and to be more brittle. The increased density also revealed itself in the capacity titrations where an extremely slow neutralization reaction was finally observed. The possibility of carboxyl-group formation in the membrane by reactor radiations was suggested.

ORGANIC CHEMISTRY OF SOLVENTS

W. H. Baldwin C. E. Higgins

Estimation of the Equivalent Weight of Salts. It has been indicated[4] that cation-exchange resins have been found satisfactory for the estimation

[4] W. H. Baldwin and C. E. Higgins, *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1952*, ORNL-1285, p. 57.

Table 8

VARIATION OF PROPERTIES OF A SODIUM POLYSULFONATE ION-EXCHANGE MEMBRANE WITH EXPOSURE TO THE RADIATIONS IN THE ORNL GRAPHITE REACTOR

RADIATION DOSE ($nvt \times 10^{16}$)	EXCHANGE CAPACITY (meq.)	SPECIFIC CONDUCTANCE ($ohm^{-1}\ cm^{-1}$)	MOISTURE IN WET EXCHANGER (%)	MEMBRANE THICKNESS (cm)
0	211.5	0.00782	41.4	0.08509
0.49	212	0.00770	45.3	0.09271
3.84	214	0.00818	45.5	0.09525
8.18	208	0.00783	46.0	0.09550
15.7	198	0.00698	47.5 (?)	0.09525
24.1	199	0.00536	39	0.09093

of the equivalent weight of several inorganic and organic salts. Particular interest has been shown in such materials as the barium salts of the butyl phosphate esters. Attempts to extend the method to the use of anion-exchange resins have shown the precision to be of the order of 5% as compared to less than 1% with cation-exchange resins such as Dowex-50. This lower precision seems to result from the decomposition of the anion-exchange resin (Dowex-1) by the alkali liberated during the reaction.

Attempted Synthesis of Dioctylpyrophosphoric Acid. Personal communications[5] have revealed that mixtures of P_2O_5 and octanol-2 are capable of extracting small quantities of uranium (100 ppm) from 20 to 30% *ortho*-phosphoric acid. A likely component of such a mixture (in addition to mono- and dioctylphosphoric acids) is the symmetrical dioctylpyrophosphoric acid. Difficulties in the purification of the intermediate reaction products, from thermal decomposition of the high molecular weight compounds, have limited all attempts to prepare this compound up to the present time.

[5] K. B. Brown, Materials Chemistry Division.

CHEMICAL PHYSICS

NEUTRON DIFFRACTION STUDIES

H. A. Levy S. W. Peterson
D. E. Lavalle[1]

Coherent Scattering Cross Section of Phosphorus. The thermal-neutron coherent scattering cross section of phosphorus has been determined from the neutron-diffraction pattern of aluminum phosphide, AlP. This compound was chosen because its crystal structure is simple (zinc blende type) and because the cross section of aluminum is relatively small.

Commercial aluminum phosphide proved to be contaminated with α- and γ-Al_2O_3 to an extent that made the precise measurement of the phosphorus cross section impossible. Therefore, the preparation of AlP by direct combination of the elements was undertaken. After several attempts, two samples were obtained that, after chemical analysis and x-ray examination, proved suitable for the neutron work. In both cases, considerable metallic aluminum remained, but the Al_2O_3 contamination was sufficiently low. A satisfactory balance of total aluminum would have indicated that the AlP was stoichiometric. The phosphide analysis was taken as representative of the percentage of AlP in the preparations. However, the total phosphorus analysis was higher than was accounted for by the phosphide analysis, inconsistent with the total aluminum balance, and nonconcordant between the two preparations. The total phosphorus value is believed to be unreliable. An analysis for total aluminum by the ammonia precipitation method also gave nonconcordant results. The details of the preparation and analysis have been described elsewhere.[2] The composition of the two preparations is given in Table 9.

Samples of the two preparations were ground and packed into thin-walled aluminum cylinders in a dry box containing nitrogen. Neutron-diffraction patterns were obtained to a maximum scattering angle of 80 deg,

[1] Analytical Chemistry Division.

[2] D. E. LaValle, *Analytical Chemistry Division Quarterly Progress Report for Period Ending March 26, 1952*, ORNL-1276, p. 45.

Table 9

ANALYSIS OF ALUMINUM PHOSPHIDE SAMPLES

ANALYSIS NO.	CONSTITUENT	METHOD	ANALYSIS (%)	
			Sample 1 (ignited)	Sample 2 (reprocessed)
1	Phosphide (as AlP)	PH_3 evolution	91.36, 90.01, 90.55 Average 90.64	89.83, 87.99, 87.73 Average 88.52
2	Al	H_2 evolution	8.34, 7.93 Average 8.14	8.69, 8.98, 8.62 Average 8.76
3	Al_2O_3	HCl sublimation	1.24, 1.35	4.92, 3.04
4	Total Al	Oxime after HNO_3	50.55, 50.66	51.00, 51.06
5	Total Al	Calculated from analyses 1, 2, and 3	51.0 , 51.1	52.6 , 51.6
6	Total P	MgP_2O_7 and phosphomolybdate after HNO_3	48.20, 50.85	44.56, 45.90
7	Total P	Calculated from analysis 1	41.3	40.3

in a manner described elsewhere,[3] with neutrons of wavelength 1.16 Å. When necessary, the measured intensities of the Bragg peaks were corrected for scattering caused by the aluminum present as an impurity and by the aluminum container, and for second-order scattering of neutrons of one-half the prominent wavelength in the case of (200). Values of $|F|^2$ were obtained from the intensities in the usual way and the absolute scale was established by comparison with the (111) peak of metallic nickel (σ_{Ni} = 13.4 barns).[4] The percentage of AlP in the sample was taken into account in establishing the absolute scale. Values of $|F|^2$ are listed in Table 10 and plotted logarithmically against $\sin^2\theta$ in Fig. 10. The uncertainty values listed are estimated from statistics of the counting, precision of the scale determination, estimation of the background, and resolution of adjacent reflections from each other.

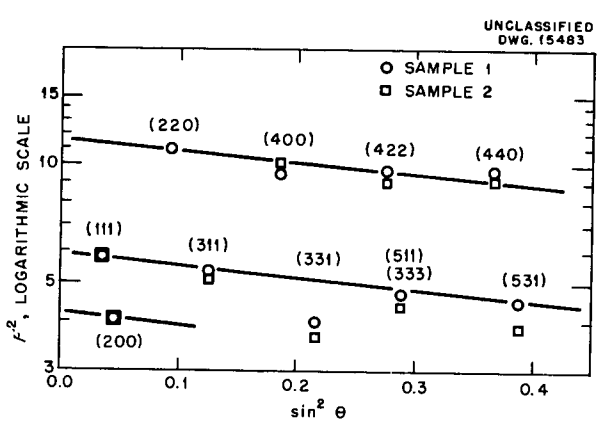


Fig. 10. Neutron Diffraction Data from AlP.

(3) H. A. Levy and S. W. Peterson, "Neutron Diffraction Determination of the Crystal Structure of Ammonium Bromide in Four Phases" (submitted for publication to *J. Am. Chem. Soc.*).

(4) C. G. Shull and E. O. Wollan, *Phys. Rev.* **81**, 27 (1951).

Table 10

NEUTRON-DIFFRACTION DATA FROM ALUMINUM PHOSPHIDE

hkl	$\|F\|^2$ (obs.)		UNCERTAINTY (%)
	Sample 1 (ignited)*	Sample 2 (reprocessed)*	
111	5.84	5.82	1.4
200	0.40	0.41	4.0
220	11.0	10.93	3.1
311	5.37	5.08	3.4
222			
400	9.49	10.06	10.5
331	4.00	3.64	10.2
420			
422	9.72	9.00	5.2
511 to 333	4.73	4.38	5.5
440	9.59	9.15	10.5
531	4.52	3.83	15.2

*For description of samples see Ref. (2).

Nonvanishing structure factors for the zinc blende structure are of three types:

1. $h + k + l = 4n$, $|F|^2 = 16(f_{Al} + f_P)^2$;
2. $h + k + l = 4n + 2$, $|F|^2 = 16(f_{Al}^2 + f_P^2)$;
3. $h + k + l = 2n + 1$, $|F|^2 = 16(f_{Al} - f_P)^2$.

The observed values fall into three families in Fig. 10 in accord with the zinc blende structure. Extrapolation of each family to zero angle yields squared structure values corrected for the temperature motion of the lattice. The extrapolations in Fig. 10 were made linearly and with a single slope, corresponding to a single Debye-Waller temperature factor. The supposition is reasonable for this crystal in view of the similarity of masses of Al and P.

The extrapolation yields the values:

1. $16(f_{Al} + f_P)^2 = 11.60 \pm 0.6$,
2. $16(f_{Al}^2 + f_P^2) = 5.97 \pm 0.2$,
3. $16(f_{Al} - f_P)^2 = 0.42 \pm 0.05$.

The data yield 0.500, 0.495, and 0.510 for f_P when the known value,[4] $f_{Al} = 0.35$, is inserted. The first value is considered the most reliable. Therefore, $f_P = 0.50 \pm 0.03 \times 10^{-12}$ cm, and $\sigma_{coh}(P) = 3.14$ barns. The phase of the scattering is positive.

RADIO-FREQUENCY SPECTROSCOPY

R. Livingston H. Zeldes
B. Benjamin

Nuclear Moments of Iodine. The microwave study of methyl iodide to determine the nuclear moments of I^{131} has been reactivated. The chemical processing system has been cleaned and repaired and is ready for operation. The microwave spectrometer has been replaced by a more sensitive instrument that is being adjusted and refined. Experiments with radioactive material should start soon.

Quadrupole Spectroscopy. A number of new techniques have been developed

to the point where the collection of quadrupole resonance data is possible. In the past, there have been a number of occasion when there has been a desire to view quadrupole lines at temperatures not available with the usual constant-temperature baths. Therefore, a cryostat has been developed that will allow measurements to be made from essentially liquid nitrogen temperature up to room temperature. Initial measurements are being made on hexachloroethane.

Some study has been devoted to the effect of pressure on the frequencies of quadrupole resonance lines. At pressures up to 2500 psi positive effects have been seen in $NaClO_3$ and $KClO_3$. One of the four lines in hexachloroethane also gave a detectable frequency shift. The shift in $KClO_3$ has been measured at three temperatures and has been found to increase progressively in going from 77 to 195 to 273°K. The shifts observed are on the order of one part in 10,000 for a pressure of 2500 psi. The construction of a simple pressure-boosting device to give pressures over 5000 psi is now nearly complete.

The studies on chlorates are continuing with consideration being given to the possibility of distortion of the chlorate ion in the crystal lattice. In order to gather information on assymmetry in the field gradient tensor, Zeeman studies on single crystals are being initiated. Suitable crystals of $NaClO_3$ have been grown. The preparation of single $KClO_3$ crystals has given considerable difficulty, however, a special crystal-growing apparatus seems to be producing satisfactory crystal growth. A preliminary Zeeman experiment has been done on $NaClO_3$ by using the chart-recording spectrometer. Apparently adequate sensitivity will be available.

2,2-Dichloropropane has been synthesized and the Cl^{35} resonance observed, thus completing a sequence of "methyl-substituted chloromethanes." The frequency was very close to the predicted value. Recent details on the alkyl chlorides will appear elsewhere.[5]

[5] R. Livingston, *J. Chem. Phys.* **20**, 1170 (1952).

CHEMISTRY OF THE SOLID STATE

HIGH-TEMPERATURE X-RAY DIFFRACTION

M. A. Bredig

An experimental coil for high-frequency induction heating has been fabricated. In addition, high-resistance carbon, a new material for electrical resistance heating, has been received and a few heating elements have been made. Both types of heaters will be tested in the near future.

REMOTELY CONTROLLED X-RAY DIFFRACTION SPECTROMETER

M. A. Bredig B. S. Borie
Metallurgy Division

G. E. Klein F. A. Sherrill
Solid State Division

The remotely controlled x-ray diffraction spectrometer that belongs to the Solid State Division has been temporarily loaned for use as a double-crystal spectrometer. It will

be used without the remote control features.

EFFECTS OF RADIATION ON CRYSTAL STRUCTURE

M. A. Bredig

There was no experimental work done on the effects of radiation on crystal structure project during this quarter.

DETERMINATION OF THE HIGH-TEMPERATURE, GLASERITE TYPE OF CRYSTAL STRUCTURE OF A_2BX_4 COMPOUNDS

R. D. Ellison M. A. Bredig

Future progress in the interpretation of the Patterson vector map in terms of atomic positions appears to depend on more reliable space-group information. Twinning seems to be the cause for discrepancies leading to the appearance of hexagonal instead of trigonal symmetry in the x-ray patterns. It is hoped that new crystal preparations will lead to a solution of the problem.

METAL-METAL HALIDE SYSTEMS

M. A. Bredig H. R. Bronstein
J. W. Johnson W. T. Smith[1]

Sodium Metal in Sodium Chloride. The experimental results discussed in the preceding progress report[2] gave strong indication that subhalides such as CaCl or BaCl do not exist in the solid state but confirmed the comparatively high solubilities of the metals in melts of their halides, up to 35 mole %. The theory proposed by Harker to Cubiciotti[3] uses the concept of vacant "octahedral holes," in what is assumed to be essentially a close packing of spherical anions, to explain the higher solubility of the metals in dihalides (for example, 25 mole % Ba in $BaCl_2$) as compared with the low solubility in monohalides (for example, mole % K in KCl). In the monohalides all the "octahedral holes" are occupied by the cations of the normal salt, but in the dihalides one-half of these "holes" are vacant and at least partially available for occupancy by metal atoms. The older data give 15 mole % sodium as soluble in molten NaCl at 850°C.[4] Therefore, a check and expansion of the older experimental work on monohalides appeared to be very desirable. A modification of the theory to include cases with which it seems to disagree in its present form, was a possibility.

Using improved experimental techniques, a number of determinations of the solubility of sodium metal in molten sodium chloride at temperatures between the melting point of sodium (near 800°C) and 1000°C were made. Fig. 11 represents the results obtained thus far. There is a comparatively rapid increase in the solubility from a small value at the melting point, to 20 mole % at 1000°C, with no indication of a reversal in the trend. This is an obvious contrast to the decrease in solubility of the alkaline earth metals in their halides observed under comparable conditions.[3] The high solubility observed for sodium in molten sodium chloride is in disagreement with the Harker-Cubiciotti theory, which requires the presence of "empty octahedral holes" in a packing of spherical anions, not available in NaCl. A possible resolution for the discrepancy may be found

[1] Consultant from the University of Tennessee.

[2] M. A. Bredig, J. W. Johnson, H. R. Bronstein, and W. T. Smith, *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1952*, ORNL-1285, p. 72.

[3] D. D. Cubiciotti and C. D. Thurmond, *J. Am. Chem. Soc.* 71, 2149 (1949).

[4] R. Lorenz and R. Winzer, *Z. anorg. allgem. Chem.* 183, 121-6 (1929).

by assuming that sodium ions are being transferred increasingly with rising temperature from "octahedral" to "tetrahedral holes," thus making the "octahedral holes" available for sodium atoms. A decrease in coordination number with increasing temperature is not unexpected and is actually known to occur in the phase transitions of numerous monohalides. The hypothesis will be tested in other metal-monohalide systems. Neutron-diffraction studies may help to explain the actual coordination of halide melts as a function of temperature. Additional information may be gained from systematic investigation of the molecular volume, both as a function of temperature and of the metal concentration. Preparations for measurements of this type are under way. The greater expansion of the monohalides over that of the dihalides,[5] when changing from the crystalline to the molten state, may be significant when interpreted in terms of possible changes in coordination on melting. Coordination changes are observed in the metals lead and bismuth.[6] By using x-ray diffraction of molten potassium chloride, Lark-Horovitz and Miller[7] have not observed a major change in the first sphere of coordination on melting (reported change: 6 ⟶ 5.8), but they have found a considerable change in the second sphere of coordination (12 ⟶ 8.3).

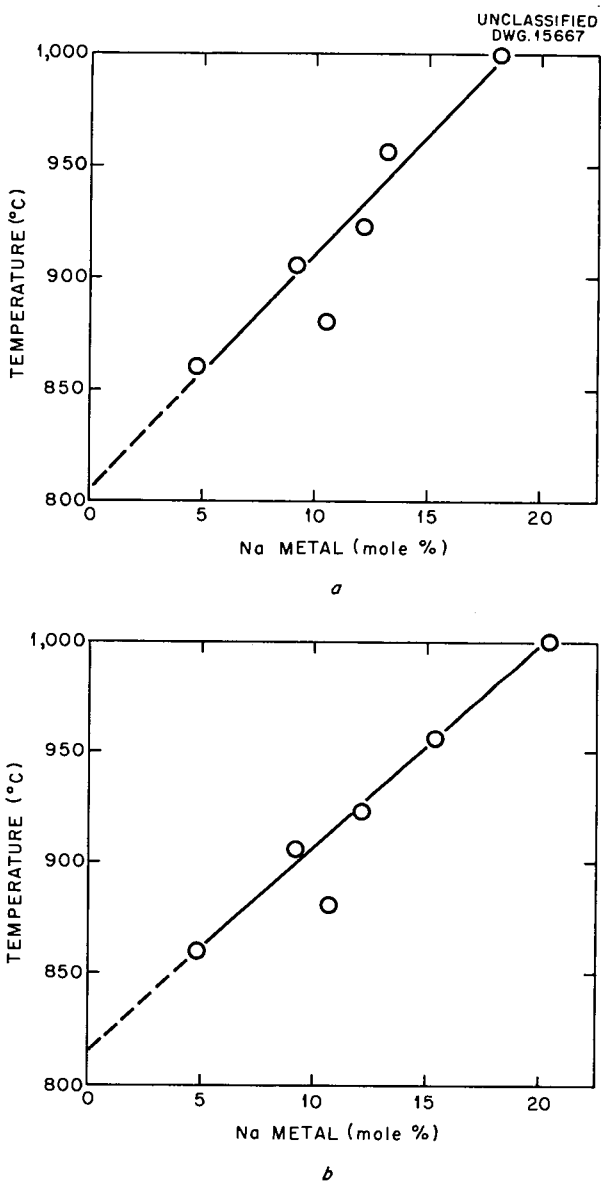


Fig. 11. (*a*) Average Values of Mole % Na in Salt Phase. (*b*) Mole % Na in Upper Layer of Salt Phase.

Potassium Metal in Fluoride Eutectics. Experiments dealing with the solubility of alkali metal in the ternary eutectic of the system LiF-NaF-KF were continued. After washing the solidified salt phase free from adhering metal with alcohol, the values obtained ranged from 1.6 to 3.0 mole %. However, the figures are believed to be too low. A large fraction of the adhering metal is assumed to have actually dissolved in the molten salt phase, but it agglomerated on cooling to a large extent and was no longer protected from the alcohol by the surrounding

(5) W. Klemm, W. Tilk, and S. Müllenheim, *Z. Elektrochem.* **34**, 523-28 (1928).

(6) G. P. Smith, W. H. Bridges, J. V. Cathcart, P. C. Sharrah, and N. C. Simpson, *Metallurgy Division Quarterly Progress Report for Period Ending July 31, 1952.* ORNL-1366 (in press).

(7) E. P. Miller and K. Lark-Horovitz, *Phys. Rev.* **51**, 61 (1937).

solid salt. More credence is now given to the results obtained directly from the alcohol washings. The values vary from 6.2, 6.8, and 8.0 mole % at 490°C to 9.7 mole % at 880°C. A theoretical discussion similar to the one for the simple sodium metal-sodium chloride system is unwarranted at present because of the complexity of the situation in the multicomponent system. There is uncertainty with regard to the reduction equilibriums between the three alkali metals. Present efforts are directed toward obtaining greater precision through further improvements in experimental techniques. Also, there is the possibility of including the reduction equilibriums in the interpretation of the experimental results.

RADIATION CHEMISTRY

OXIDATION OF URANIUM(IV) BY GAMMA RAYS

C. Hochanadel

A study is being made of the gamma-ray induced oxidation of uranium(IV) in sulfuric acid solution. Uranium(IV) solutions were prepared by reducing uranyl sulfate either by using zinc analgam in a Jones reductor or by electrolysis using platinum electrodes with the electrode compartments separated by an Alundum crucible. The progress of the reaction was followed as a function of total dose by measuring the optical absorption of uranium(IV) at 6520 Å by means of a Beckman DU spectrophotometer. Samples were degassed in a vacuum before irradiation. A Corex optical cell (either 2- or 10-cm path length) was connected to the irradiation cell and properly lead shielded during irradiation to prevent coloring of the optical window by radiation. A complete dose-concentration curve could be obtained from a single sample.

Initial experiments with 10^{-3} and 10^{-2} *M* uranium(IV) in 0.1 *M* H_2SO_4 showed that uranium(IV) is oxidized completely to uranium(VI) at a rate that decreases with increasing dose. The initial yield amounts to approximately 3.6 equivalents oxidized per 100 ev absorbed and is the same for both 10^{-2} and 10^{-3} *M* uranium(IV). An equivalent amount of hydrogen gas is produced during the oxidation.

SOME EFFECTS OF COBALT GAMMA RAYS ON AQUEOUS SOLUTIONS AS A FUNCTION OF pH

T. J. Sworski

A solvent frequently employed in radiation chemistry studies, 0.8 *N* H_2SO_4, has been reported[1] to act as a radical remover. In order to determine the effect of pH in aqueous benzene solutions, it is necessary to understand the effect of pH in water saturated with helium, oxygen, or a hydrogen-oxygen mixture. Some preliminary results are reported here. Baker and Adamson sulfuric acid was used to adjust the pH.

Helium-saturated Water. Two reactions are believed to occur simultaneously in the decomposition of water by ionizing radiations:

$$2H_2O \rightsquigarrow H_2 + H_2O_2, \ (F) \ ,$$

$$H_2O \rightsquigarrow H + OH, \ (R) \ .$$

The broken line in Fig. 12 is the reported[2] yield (molecules of H_2 or H_2O_2/100 ev absorbed in solution) of 0.46 for reaction (*F*). The yield of H_2O_2 in helium-saturated 0.8 *N* H_2SO_4 (pH ~ 0.4) previously reported[1] as

[1] T. J. Sworski, *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1952*, ORNL-1285, p. 66.

[2] C. J. Hochanadel, *J. Phys. Chem.* **56**, 587 (1952).

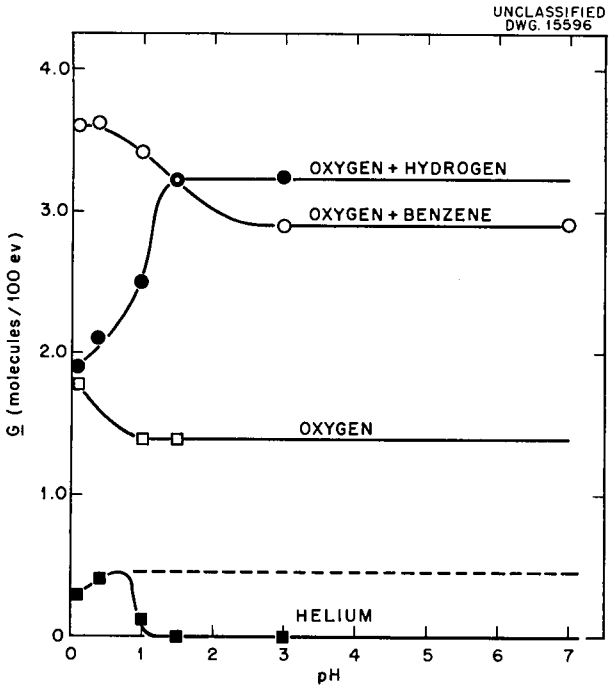


Fig. 12. Initial Yields of Hydrogen Peroxide as a Function of pH in Water Saturated with Helium, Oxygen, Oxygen + Benzene, and Oxygen + Hydrogen.

0.38 agrees with the reported[2,3] yield of H_2 from reaction (*F*) occuring in solutions of oxidizing and reducing agents in 0.8 *N* H_2SO_4. Figure 12 shows that in 1.5 *N* H_2SO_4 (pH ~ 0.1) the yield of H_2O_2 decreased to 0.29. The result may be interpreted as a further decrease of the yield of reaction (*F*) with increased acidity. The yield of 0.12 at a pH of 1.0 is interpreted as resulting from incomplete radical removal by the solvent. No H_2O_2 was observed at a pH of 1.5 or at a pH of 3.0.

Although the radical-removing action of highly acid solutions may be attributed to the presence of impurities in the acid, it is suggested that the following mechanism may be operative:

$$H + H^+ \longrightarrow H_2^+ ,$$

$$H_2^+ + OH \longrightarrow H^+ + H_2O .$$

The first reaction was proposed by Weiss[4] to explain increasing oxidation with decreasing pH in oxygen-free iron(II) solutions.

Water Saturated with a H_2 + O_2 Mixture. In water saturated with a hydrogen-oxygen mixture, an initial H_2O_2 yield of 3.20 has been reported[2] that is independent of pH in the range 2.0 to 7.0. Figure 12 shows that at a pH of less than 2.0 the initial yield decreases with decreasing pH until in 1.5 *N* H_2SO_4 (pH ~ 0.1) the enhancing effect of hydrogen, reported by Toulis,[5] is removed. On the other hand, the initial yield of H_2O_2 in oxygen-saturated solutions increases as shown in Fig. 12.

Helium-saturated Aqueous Benzene Solutions. The formation of H_2O_2 in helium-saturated aqueous benzene solutions is shown as a function of pH in Fig. 13. At a constant dose, the H_2O_2 concentration decreases with increasing pH until no H_2O_2 is detectable in unbuffered solutions. The H_2O_2 observed is attributed to reaction (*F*), with benzene acting as the radical remover, and the pH dependency is that expected from the work of Fricke and Hart.[6]

At a pH of 1.5, the initial yield of H_2O_2 is 0.58 and is not lowered by 10^{-3} *M* KBr. The conclusion is that benzene enhances the yield from reaction (*F*). The increased yield is surprising because no other solute has been reported to produce the same effect.

(3) A. O. Allen and E. Johnson, paper submitted to *J. Am. Chem. Soc.* (1952).

(4) J. Weiss, *Nature* **165**, 728 (1950).

(5) W. J. Toulis, *The Decomposition of Water by Radiation*, UCRL-583 (Feb. 10, 1950).

(6) H. Fricke and E. J. Hart, *J. Chem. Phys.* **3**, 596 (1935).

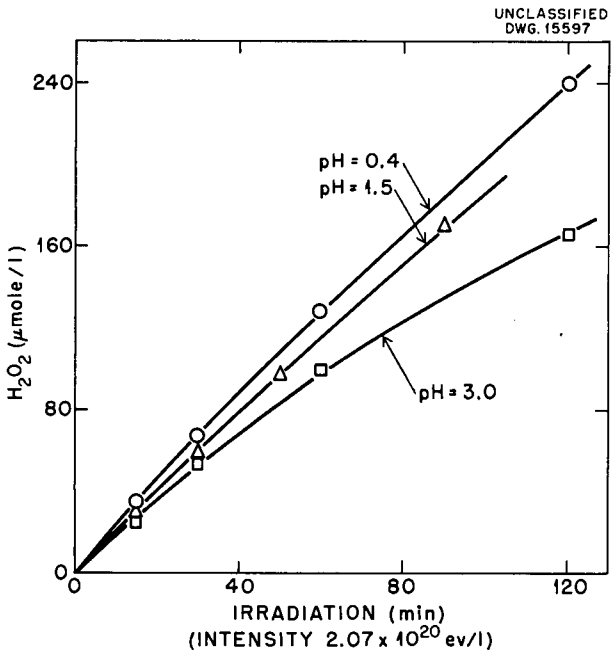


Fig. 13. Hydrogen Peroxide Formation in Helium-Saturated Aqueous Benzene Solutions.

Oxygen-saturated Aqueous Benzene Solutions. As shown in Fig. 12, the H_2O_2 yield in oxygen-saturated aqueous benzene solutions increases at low pH to a value of 3.60. The phenol yields are being investigated.

EFFECT OF IONIZING RADIATION ON ELECTRICAL CONDUCTIVITY OF ALKALI HALIDE CRYSTALS

J. A. Ghormley

The effect of reactor radiation on the electrical conductivity of lithium fluoride and the effect of x rays on the conductivity of potassium chloride have been reported.[7] The ionic conductivity of both of the alkali halides was greatly reduced by the radiation. The ionic conductivity is mainly the result of the migration of positive-ion vacancies. Ionizing radiation produces positive "holes." Some of the "holes" become localized at positive ion vacancies and make the vacancies incapable of contributing to electrical conductivity. Exposure of the irradiated potassium chloride to room light gave an increase in the ionic conductivity in addition to the expected photoconductivity. Subsequent heating of the irradiated lithium fluoride restored at least part of the initial ionic conductivity.

Experimental determinations of the electrical conductivity of some alkali halides during heating of the crystals before and after irradiation have been completed. The crystals were heated at a constant rate, 10°C/min, and the current produced by a 135-v potential between colloidal-graphite electrodes painted on opposite sides of the crystals was measured and recorded by means of a vibrating-reed electrometer and a Brown recorder.

Immediately after irradiation, the conductivity of lithium fluoride (Fig. 14) was consistently lower than that of the same sample heated a second time. The behavior of sodium chloride (Fig. 15) and potassium chloride (Fig. 16) was somewhat different. The conductivity exhibited two maximums when sodium chloride was heated the first time after irradiation. The temperatures of the maximums correspond very closely with two glow-curve peaks observed for sodium chloride. The conductivity behavior of potassium chloride was similar, although distinct peaks were not observed.

The peaks in the conductivity curve for sodium chloride and the high

[7] J. A. Ghormley and H. A. Levy, *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1949*, ORNL-607, p. 157.

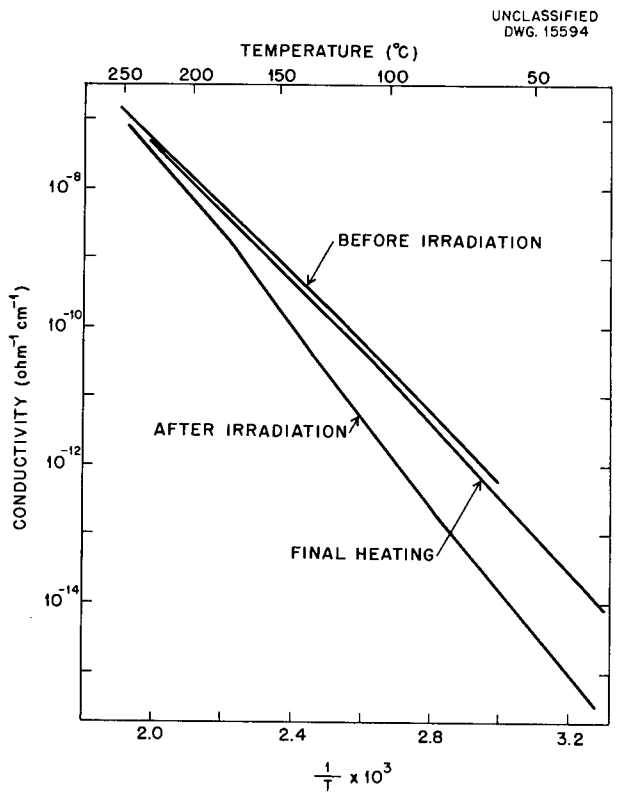


Fig. 14. Conductivity of LiF Crystal Measured During Heating at Constant Rate of 10 deg/min Before and After 4 × 10^6 - r Irradiation with Gamma Rays.

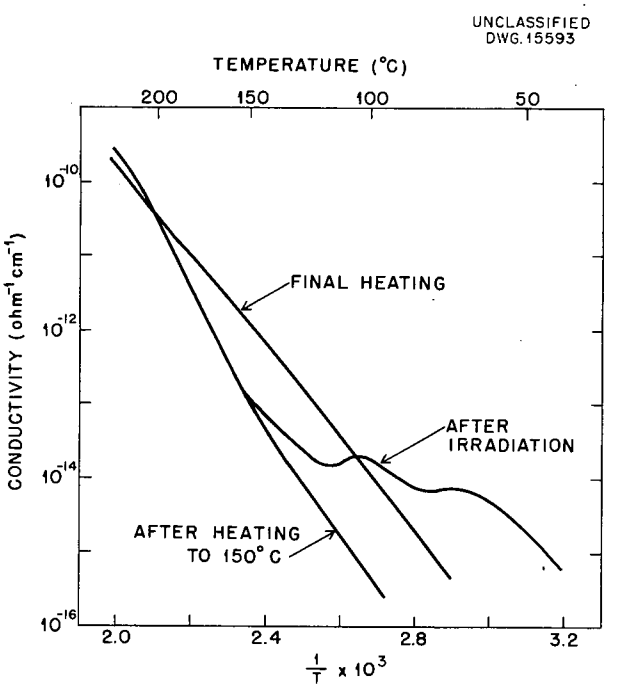


Fig. 15. Conductivity of NaCl Crystal Measured During Heating at Constant Rate of 10 deg/min After 10^6 - r Gamma Irradiation.

conductivity just above room temperature for irradiated potassium chloride are attributable to thermal release of trapped charges. Similar conductivity peaks have been reported by Dutton, Heller, and Maurer[8] for potassium chloride at lower temperatures. The increase in the conductivity of the irradiated crystals at higher temperatures may result from the thermal release of the positive "holes" trapped at positive-ion vacancies, followed by migration of the positive "holes" to trapped electrons, or it may result from the thermal release of trapped electrons that are able to migrate to the trapped "holes." Either process results in the release of trapped "holes" from positive-ion vacancies and restores the initial ionic conductivity.

[8] D. Dutton, W. Heller, and R. Maurer, *Phys. Rev.* **84**, 363 (1951).

CHEMICAL EFFECTS OF IONIZING RADIATION ON INORGANIC SOLIDS

A. C. Stewart

The investigation of the products formed in ice subjected to ionizing radiation is being continued. A gas-analysis system has been assembled and some preliminary measurements have been made on hydrogen and oxygen production in ice exposed to gamma rays. Work has been initiated on the chemical effects of radiation on sodium iodide in the dihydrate and anhydrous forms.

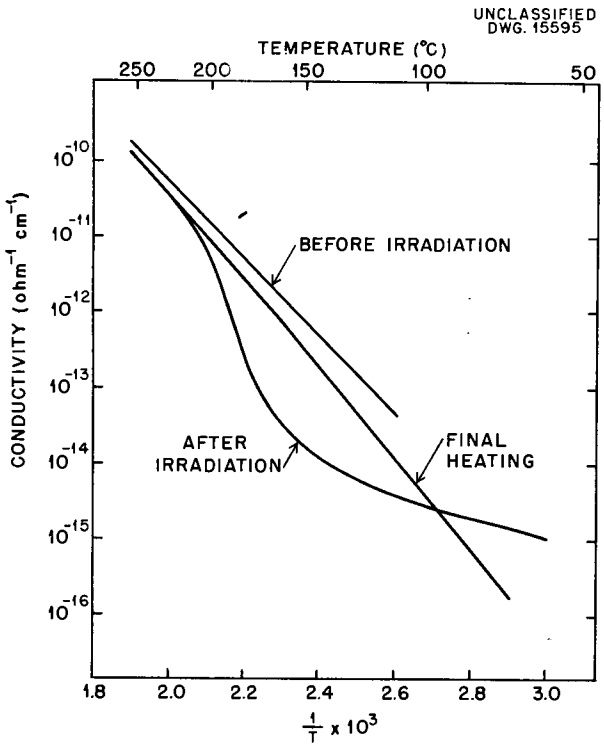


Fig. 16. Conductivity of KCl Crystal Measured During Heating at Constant Rate of 10 deg/min Before and After 4×10^6 - r Gamma Irradiation.

REACTOR CHEMISTRY

SOLUBILITY OF UO_3 IN UO_2SO_4 SOLUTIONS AT 250°C

J. S. Gill E. V. Jones
W. L. Marshall

Experimental solubility data for UO_3 above 100°C in UO_2SO_4 solutions containing 20, 30, and 40 g of uranium per liter have been given in previous reports.[1,2] The data were obtained by the synthetic method in silica tubes and indicated a solubility ratio, U to SO_4, of about 1.04 at 250°C. The data were erratic; therefore, a more complete investigation was started with initial determinations of the solubility at 25 and 100°C. The solubility of a UO_3 hydrate, that appeared to be $UO_3 \cdot \frac{1}{2}H_2O$ by analysis, in UO_2SO_4 was determined from low uranium concentrations to above 50 wt % uranium. The resulting solubility ratios were 1.40 at 25°C and 1.36 at 100°C.[3] The investigation was discontinued in favor of more immediate

(1) W. L. Marshall, J. S. Gill, and C. H. Secoy, *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950*, ORNL-685, p. 32.

(2) W. L. Marshall and J. S. Gill, *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1950*, ORNL-1036, p. 13.

(3) W. L. Marshall and J. S. Gill, *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending February 28, 1951*, ORNL-990, p. 134.

problems because only a low-concentration reactor was considered at 250°C at that time.

The change to fuel media with different uranium concentrations and the development of a filter-bomb apparatus for filtering a solution from the solid phase at the equilibrium temperature have resulted in the need for further study of the system.

The apparatus now used was originated by Zemel and Stoughton. It is composed entirely of titanium and consists of two sections separated by a sintered-platinum filter disk. The solution is brought to equilibrium in the lower end of the unit either by rocking or by a magnetic mixer, depending on the type of apparatus used. The thermostating is accomplished by aluminum heating blocks or a liquid-salt bath. The solution is filtered from the solid phase by inverting the filter-bomb unit and cooling the lower end. Analyses are then made for sulfate and uranium.

The solubility data given in Figs. 17 and 18 and in Table 11 show an excess solubility for UO_3 in UO_2SO_4 solutions at 250°C. The scatter of the data in Fig. 18 probably results from analytical difficulties at the low concentrations. The solid phase has been identified as a UO_3 hydrate. Analytical data indicated the composition was $UO_3 \cdot \frac{1}{2}H_2O$ rather than $UO_3 \cdot 1H_2O$ or $UO_3 \cdot 2H_2O$. The structure is the platelet type that was observed by Blomeke in his study of UO_3-H_2O slurries at 250°C.[4] Some of the UO_3 crystals in equilibrium with UO_3-UO_2SO_4 solutions are as large as 3 mm long and 3 mm wide, even though the original UO_3 was a fine powder.

[4] F. R. Bruce, J. O. Blomeke, L. E. Morse, and J. P. McBride, *Homogeneous Reactor Project Quarterly Progress Report for Period Ending November 15, 1951*, ORNL-1221, p. 128.

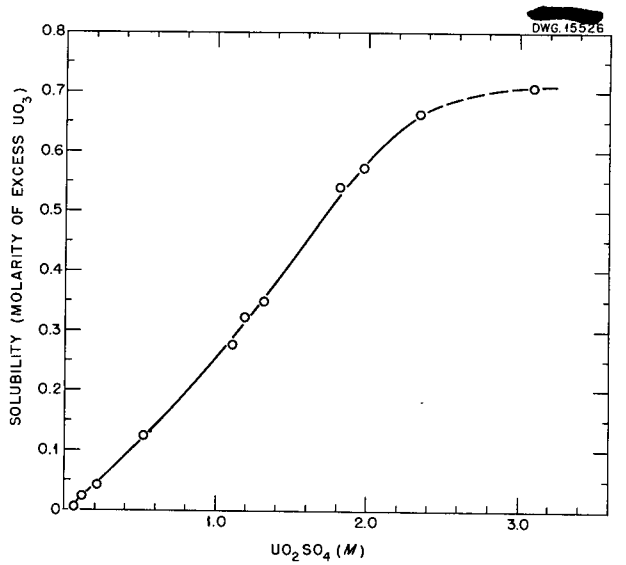


Fig. 17. Solubility of UO_3 in UO_2SO_4-H_2O at 250°C (Molarity Based on Room-Temperature Densities).

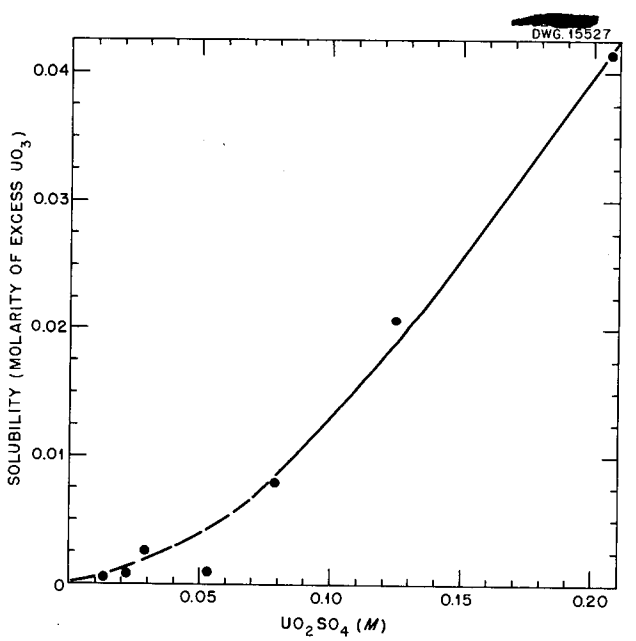


Fig. 18. Solubilities of UO_3 in UO_2SO_4-H_2O Solutions in Dilute Concentrations at 250°C.

The ratio of UO_3 to SO_4 is plotted as a function of the total uranium concentration in Fig. 19. The solubility-ratio decrease in dilute solution is apparent. At first it appeared

Table 11

SOLUBILITY AND OTHER CHARACTERISTICS OF UO_3 IN UO_2SO_4-H_2O SOLUTIONS AT 250 °C *

SAMPLE	MIXING TIME AT 250 °C (hr)	TOTAL MOLARITY OF URANIUM	MOLARITY OF SO_4	EXCESS UO_3 SOLUBILITY (*M*)	TOTAL MOLE RATIO OF UO_3 TO SO_4	SOLID PHASE	pH (at 25 °C)	TEMPERATURE OF APPEARANCE OF TWO-LIQUID PHASES (°C)
1	72	0.0134	0.0127	0.0004	1.06	UO_3 Hydrate	3.80	
2	48	0.0228	0.0220	0.0008	1.038	UO_3 Hydrate	3.40	
3	168	0.0323	0.0298	0.0025	1.08	UO_3 Hydrate	3.50	
4	75	0.0525	0.0518	0.0007	1.01	UO_3 Hydrate	3.31	
5	75	0.0869	0.079	0.0079	1.10	UO_3 Hydrate	3.52	
6	78	0.1458	0.1251	0.0207	1.17	UO_3 Hydrate	3.32	
7	48	0.2472	0.2059	0.0413	1.20	UO_3 Hydrate	3.41	292.8 (?)
8	17	0.6529	0.5317	0.1212	1.23	UO_3 Hydrate	3.20	271.5
9	78	1.381	1.106	0.275	1.25	UO_3 Hydrate	2.90	265.7
10	78	1.506	1.185	0.321	1.27	UO_3 Hydrate	2.91	
11	72	1.657	1.308	0.349	1.267	UO_3 Hydrate	2.84	
12	17	2.352	1.812	0.540	1.30	UO_3 Hydrate	2.66	267.5
13	36	2.542	1.970	0.572	1.29	UO_3 Hydrate	2.65	
14	48	3.002	2.341	0.661	1.28	UO_3 Hydrate	2.52	270.0
15	78	3.805	3.096	0.709	1.23	UO_3 Hydrate	1.91	

*Molarity based on room temperature densities.

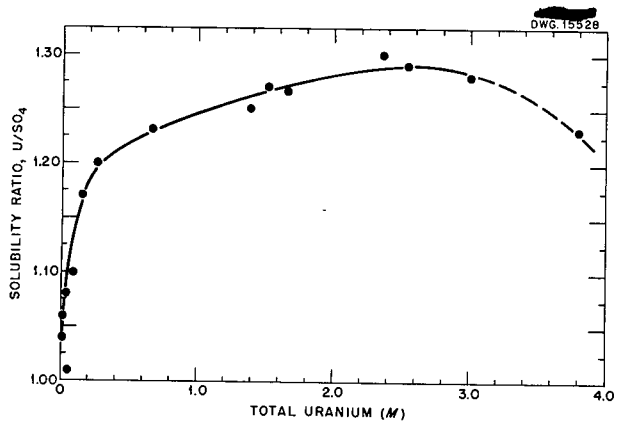


Fig. 19. Solubility Ratio, U/SO_4, in UO_3-H_2SO_4 Solutions at 250°C.

that the ratio would decrease below 1.0 at concentrations below 10 g of uranium per liter, but Fig. 18 shows that the ratio apparently remains greater than 1.0

The synthetic solutions containing the desired solubility ratios were placed in silica tubes and rocked at 250°C for 72 hours. A slight orange-yellow precipitate appeared after 24 hr and increased slowly during the remaining 48 hours. When the tubes were cooled a rather large amount of the same orange-yellow precipitate appeared. The precipitate has been identified as the uranyl silicate previously observed in the study of UO_2F_2-H_2O systems in SiO_2 tubes.[5] It is now believed that the erratic data reported for solutions containing 20, 30, and 40 g of uranium per liter resulted from the silicate that previously was not suspected to occur in the UO_2SO_4 solutions in silica tubes.

The acidity data for the saturated solutions are given in Fig. 20 and are compared to UO_2SO_4 solutions containing a stoichiometric amount of sulfate. All the acidities were

[5] W. L. Marshall and J. S. Gill, *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORNL-870, p. 25.

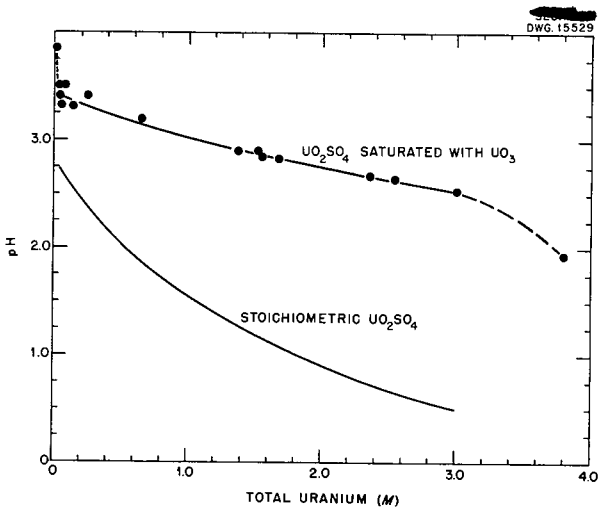


Fig. 20. Acidity of UO_2SO_4 Solutions Saturated with UO_3 at 250°C (Acidities Measured at 25°C).

determined at 25°C. Silicon dioxide is known to be more soluble in alkaline media; therefore, the higher pH of the UO_3-saturated solution may account for the increased solubility of the silica.

A similar solubility study of the sulfate system at 175°C is in progress. A similar study of the system, UO_3-UO_2F_2-H_2O at 250 and 175°C, is planned for the future. Later an attempt will be made to define completely both the UO_3-UO_2SO_4-H_2O and the fluoride systems at 250°C and at lower temperatures.

FURTHER STUDIES OF EQUILIBRIUMS BETWEEN TWO LIQUID PHASES IN UO_3-UO_2SO_4-H_2O SYSTEMS

E. V. Jones

Using the method previously described,[6] the temperatures have been determined at which solutions containing uranyl sulfate at various

[6] C. H. Secoy, *J. Am. Chem. Soc.* 72, 3343 (1950).

concentrations separate into two liquid phases. The U-to-SO_4 ratios were adjusted to 1.20 and 1.10 by adding UO_3 to the solutions.

One of the systems studied contained uranyl nitrate at a constant concentration of 0.02 *M* in addition to a U-to-SO_4 ratio of 1.20. The data are given in Tables 12, 13, and 14. The data are plotted in Fig. 21 along with the curve for the Lietzke-Griess stoichiometric solution. As had been previously observed, the addition of UO_3 lowered the temperature at which the solutions separated into two liquid phases. It is interesting to note that the curve for the U-to-SO_4 ratio of 1.10 is almost identical to the curve for the U-to-SO_4 ratio of 1.20 in 0.02 *M* $UO_2(NO_3)_2$.

Table 12

TWO-LIQUID-PHASE TEMPERATURES FOR UO_3-UO_2SO_4-H_2O SOLUTIONS WITH A U-to-SO_4 RATIO OF 1.0

TEMPERATURE (°C)	TOTAL URANIUM (wt %)
291	7.14
282	9.23
281	11.19
279	15.63
279	19.51
279	25.93
279	31.04
279	35.20
283	38.65
290	40.69

Table 13

TWO-LIQUID-PHASE TEMPERATURES FOR UO_3-UO_2SO_4-H_2O SOLUTIONS WITH A U-to-SO_4 RATIO OF 1.20

TEMPERATURE (°C)	TOTAL URANIUM (wt %)
338*	1.40
322*	2.76
290	6.55
281	12.07
277	16.78
278	24.39
277	30.28
277	34.97
279	38.80
286	41.98
290	44.03

*No transition.

Table 14

TWO-LIQUID-PHASE TEMPERATURES FOR UO_3-UO_2SO_4-H_2O SOLUTIONS CONTAINING 0.02 *M* $UO_2(NO_3)_2$ AND A U-to-SO_4 RATIO OF 1.20

TEMPERATURE (°C)	TOTAL URANIUM (wt %)
293	6.52
279	12.02
280	16.72
279	30.20
279	34.89
283	40.38
293	44.24

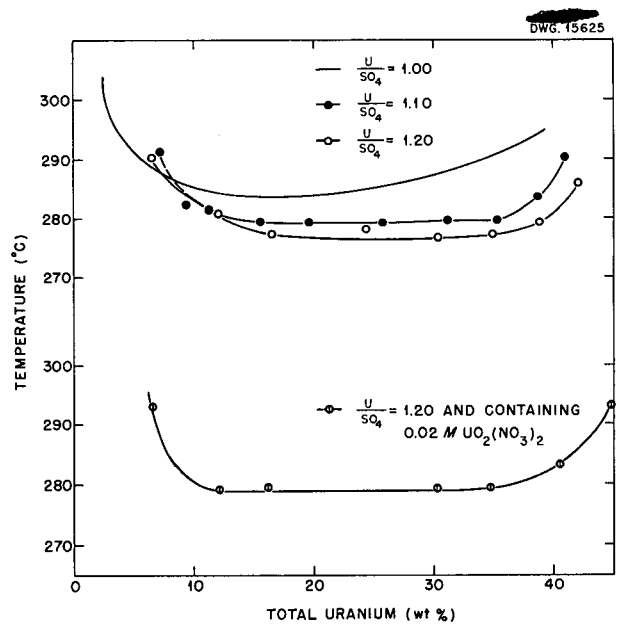


Fig. 21. Two-Liquid-Phase Temperature Curves for the System UO_3-UO_2SO_4-H_2O.

SOLUBILITY OF $BaSO_4$ IN UO_2SO_4 SOLUTIONS AT 250°C

E. V. Jones J. S. Gill

Solubility data have been determined for $BaSO_4$ in H_2O and in UO_2SO_4-H_2O solutions at 250°C by the filter-bomb method described in an earlier report.[7] Zemel has obtained similar data for $BaSO_4$ solubility in H_2O as a function of temperature.[8] The two sets of data for solubility in water at 250°C disagree by a factor of approximately 10. No explanation for the difference is available at present.

The experimental data are given in Table 15. It has been found that if the data are plotted logarithmically against the square root of the molarity of UO_2SO_4 a straight line results, as is shown by Fig. 22. This type of plot is similar to Debye-Hückel characteristics (for example, plots of the square root of the ionic strength vs. the logarithm of the solubility) in very dilute solutions. The increase in the solubility of $BaSO_4$ is rather striking. For example, $BaSO_4$ is 42 times more soluble in a 1.0 *M* UO_2SO_4 solution than in water. The large solubility increase of most of the fission products in a solution of UO_2SO_4 has been pointed out in previous quarterly reports.[9]

(7) *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending August 31, 1950.* ORNL-826, p. 78.

(8) B. Zemel, *op. cit.*, ORNL-990, p. 105.

Table 15

SOLUBILITY OF $BaSO_4$ IN UO_2SO_4 SOLUTION AT 250°C

MOLARITY OF UO_2SO_4	SOLUBILITY OF $BaSO_4$ (moles x 10^5)
0.000	0.53
0.125	1.46
0.313	3.32
0.625	8.95
0.775	10.34
1.00	17.40
1.15	22.42
1.25	37.35

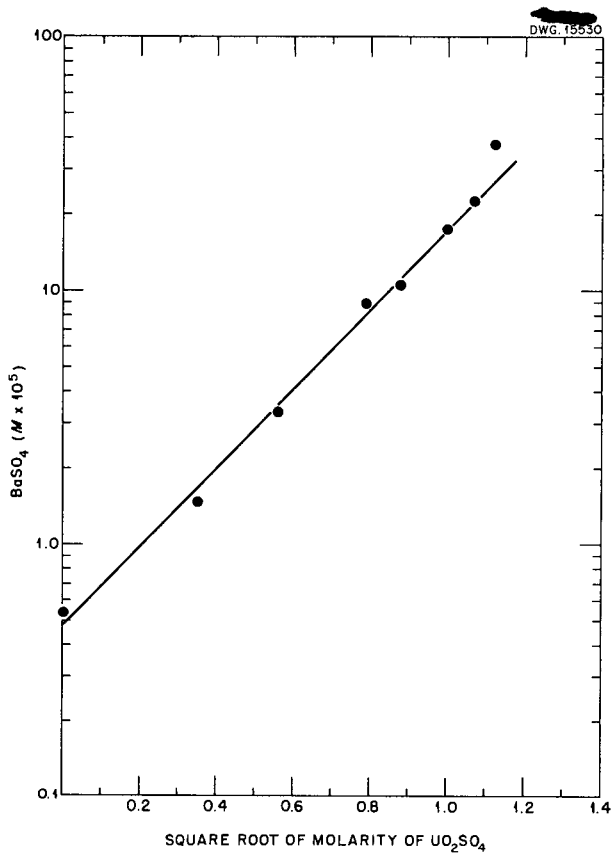


Fig. 22. Solubility of $BaSO_4$ in UO_2SO_4-H_2O at 250°C.

SOLUBILITY OF Ag_2SO_4 IN 1.26 *M* AND 0.126 *M* URANYL SULFATE

E. V. Jones

The solubility of Ag_2SO_4 in 1.26 *M* and in 0.126 *M* UO_2SO_4 has been studied by the silica-tube method previously described;[10] the temperature coefficient of solubility is positive.

(9) W. L. Marshall, R. D. Brown, H. O. Day, J. S. Gill, E. V. Jones, K. S. Warren, and H. W. Wright, *op. cit.*, ORNL-1221, p. 99.

(10) C. H. Secoy, *J. Am. Chem. Soc.* 72, 3343 (1950).

The study in 0.126 *M* UO_2SO_4 was limited to temperatures below 140°C because a reversible reaction occurred at about that temperature and yielded a reddish solid phase that is being investigated.

The data are given in Table 16 and are plotted in Fig. 23 along with the data of Seidell and Zemel[11] for the solubility of Ag_2SO_4 in water. If the logarithm of solubility is plotted against 1/T (°A) the resultant slopes above 100°C give $\Delta H_{(soln)}$ of +1.1, +2.3, and +3.7 kcal/mole in water, 0.126 *M* and 1.26 *M* UO_2SO_4, respectively.

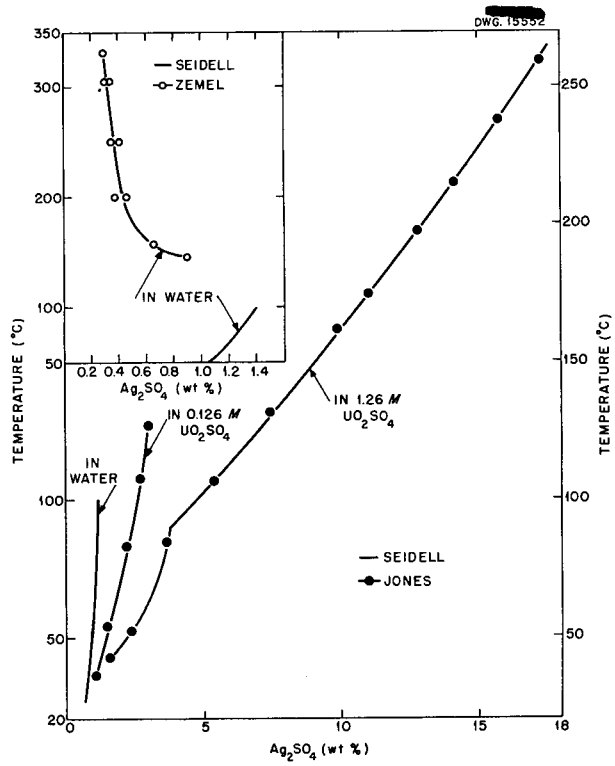


Fig. 23. Solubility of Ag_2SO_4 in 1.26 *M* and 0.126 *M* UO_2SO_4 and in Water.

INFLUENCE OF RADIATION ON THE VALENCE OF PLUTONIUM

K. S. Warren

An investigation has been started on the effect of Co^{60}-emitted gamma

[11] B. Zemel, *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending May 15, 1951*, ORNL-1057, p. 117.

Table 16

SOLUBILITY OF Ag_2SO_4 IN UO_2SO_4 SOLUTIONS

IN 1.26 *M* UO_2SO_4		IN 0.126 *M* UO_2SO_4	
Temperature (°C)	Ag_2SO_4 (wt %)	Temperature (°C)	Ag_2SO_4 (wt %)
42.5	1.54	36.0	1.04
52.0	2.36	54.0	1.46
84.6	3.63	83.3	2.18
106.5	5.38	107.8	2.72
131.4	7.43	127.4	3.01
161.6	9.89	140.0	A red product formed
174.3	11.01		
197.1	12.82		
214.9	14.14		
237.5	15.75		
259.1	17.25		

radiation and in-reactor radiation on the stability of the III and VI valence states of plutonium as sulfate. In one experiment uranyl sulfate was also present to the extent of 88.5 g per liter of solution. It was found that the tendency of plutonium(III) and plutonium(VI) to return to plutonium(IV) was greatly enhanced by the presence of the two types of radiation.

Gamma-Ray Bombardment of Plutonium Solutions. Samples of plutonium(III) and plutonium(VI) were prepared by electrolyzing plutonium(IV) sulfate in a glass cell by using platinum electrodes, without stirring, and a current density of 0.55 Ma per square centimeter of electrode surface. Portions of the electrolyte were removed from the anode and cathode compartments and sealed in 5-mm pyrex glass tubes. A Co^{60} gamma-ray source was provided in the canal of Building 3001. This source emitted about 720,000 r/hr at the particular location. After periods of exposure, which varied from 67 to 127 hr, suitable dilution of the samples was made, and plutonium determinations were carried out by two methods that permitted a comparison of the oxidized and reduced states of plutonium. Similar determinations were also made simultaneously on control samples, that is, portions of the original solution that had not been irradiated. The results are given in Table 17.

These data indicate that Co^{60}-emitted radiation (roughly 1.2 Mev) speeds up considerably the reactions in neutral solutions that result in bringing the VI or III valence states of plutonium back to the more stable IV state (on standing and without other added reagent). This is also true in the presence of uranyl ion.

In-Reactor Irradiation of Plutonium Solutions. A sample of plutonium solution was removed from the desired compartment of the electrolysis cell and suitably diluted, and 3.0 ml of the diluted solution was transferred

Table 17

VALENCE CHANGES IN GAMMA-IRRADIATED SOLUTIONS

TIME OF IRRADIATION (hr)	ORIGINAL STATE OF PLUTONIUM	METHOD OF ANALYSIS	VALENCE CHANGE AFTER IRRADIATION	
			Control sample*	Irradiated sample
67	Oxidized (VI)	Beckman Spectrophotometer	Considerable Pu(VI) retained	Pu(VI) completely removed
127	Oxidized (VI)	Beckman Spectrophotometer	Considerable Pu(VI) retained	Pu(VI) completely removed
68	Oxidized** (VI)	LaF_3 coprecipitation	50% Pu(VI) present	0% Pu(VI) present
116	Oxidized** (VI)	LaF_3 coprecipitation	35% Pu(VI) present	0% Pu(VI) present
67	Reduced (III)	Beckman Spectrophotometer	Pu(III) retained	Pu(III) removed
127	Reduced (III)	Beckman Spectrophotometer	Pu(III) retained	Pu(III) removed

*Retained after standing at room conditions for the same length of time as required for irradiation of the test sample.

**264 g of uranium (as the sulfate) present per liter.

to a silica tube. The tube was evacuated after freezing the solution and then sealed. The system was surrounded by a protective aluminum jacket and placed in water-cooled Hole 12 in the ORNL graphite reactor for overnight exposure. The tube was then removed from the reactor and allowed to decay to a safe level before opening and analyzing the contents. The use of the Beckman, or other, spectrophotometer was not feasible because of the low plutonium concentrations (0.1 mg per milliliter of solution, or less) necessary because of gas-pressure hazards in a closed system. It was necessary therefore to use chemical methods in ascertaining valence states. Besides the lanthanum fluoride coprecipitation method, which is standard for distinguishing quantitatively between plutonium(VI) and the lower valence states, an anion-exchange resin (Dowex A-1) was tried. The latter would retain valencies higher than III, and this method was used satisfactorily for separating plutonium(III) from plutonium(IV). The results are given in Table 18. The data indicate that plutonium in the VI state is rapidly reduced to the tetravalent condition by in-reactor radiation, whether in the presence of uranyl ion or not. Conversely, data obtained in connection with neutron-irradiated plutonium(III) has shown that it is rapidly oxidized to the IV state by the conditions prevailing during in-reactor irradiation of aqueous solutions.

PLUTONIUM SOLUBILITY IN UO_3-H_3PO_4-H_2O SOLUTIONS

H. W. Wright

The ratio of PO_4 to U necessary to maintain a phase-stable system of UO_3-H_3PO_4-H_2O at 250°C is about 5.2 for a 1.26 *M* uranium concentration.[12] The solubility ratio of PO_4 to U increases both as a function of temperature between 100 and 300°C and as an inverse function of uranium concentration.[13,14] The purpose of this work was to determine the effect of excess H_3PO_4 on the stabilization of plutonium in solution. Plutonium(IV) has been shown to undergo hydrolytic precipitation above 100°C in both

(12) J. S. Gill, W. L. Marshall, and H. W. Wright, *Homogeneous Reactor Project Quarterly Progress Report for Period Ending August 15, 1951*, ORNL-1121, p. 120.

(13) J. S. Gill and H. W. Wright, *op. cit.*, ORNL-1057, p. 112.

(14) R. M. Bidwell and B. J. Thamer, *The UO_3-H_3PO_4-H_2O System above 100°*. Paper presented at Second Fluid Fuels Conference, Oak Ridge, 1952.

Table 18

VALENCE CHANGES IN IN-REACTOR IRRADIATED SOLUTIONS

ORIGINAL STATE OF PLUTONIUM	TIME OF IRRADIATION (hr)	METHOD OF ANALYSIS	VALENCE CHANGE AFTER IRRADIATION	
			Control Solution	Irradiated Solution
Oxidized	16	LaF_3 coprecipitation	Pu(VI): 0.08 mg/ml	0.009 mg/ml
Oxidized*	8	LaF_3 coprecipitation	Pu(VI): 0.10 mg/ml	0.000 mg/ml
Reduced	18	Dowex A-1 ion exchange	Pu(III): 0.018 mg/ml	0.000065 mg/ml

*89 g of uranium (as the sulfate) present per liter of solution.

UO_2SO_4-H_2O and UO_2F_2-H_2O systems.[15,16] The first experiment in a silica tube was carried out at 140°C for 140 hr with a 1.05 *M* U-12.1 *M* H_3PO_4 solution containing 2 g of plutonium(IV) per liter. No precipitation of plutonium occurred. The next experiment was made with a 0.454 *M* U-3.1 *M* H_3PO_4 solution containing 2 g of plutonium(IV) per liter. After 7 hr at 200°C the entire solution formed a gel that reliquefied only after remaining at 25°C for several days. Similar results were obtained with experiments at 175°C.

Enough phosphate can be added to stabilize plutonium in a uranyl phosphate solution. However, this amount of phosphate will, in all probability, be more with respect to cross section to achieve the same objective than is necessary for a UO_2SO_4-H_2O system containing a slight excess H_2SO_4.[16]

CONDUCTIVITY OF URANYL SULFATE IN AQUEOUS SOLUTION

R. D. Brown

A previous Homogeneous Reactor Quarterly Project Report[17] contained data on the conductivity of uranyl sulfate and uranyl fluoride in aqueous solution over wide concentration ranges and at various specific temperatures in the range 0 to 125°C.

Recent efforts have been directed toward the measurement of the conductivity of uranyl sulfate in aqueous solutions at 200 and 250°C. This work has been hampered by difficulties encountered in constructing a conductivity cell that will withstand the high pressures encountered at these temperatures and by the fact that uranyl sulfate solution shows a corrosive action on the materials used for the cells. Some of the cells designed and constructed are described in the following.

A bomb type of cell, made of type 347 stainless steel, contained a silica conductivity chamber with a pyrex cover through which the electrode leads were passed. The leads and electrodes were of platinum, and entry into the bomb was made through pressure fittings with soapstone glands. This cell gave erratic results because of leakage across the lead wires, which were in contact with water vapor inside the cell.

A second bomb was constructed to hold a small pressure cell made of heavy-wall pyrex tubing. The solution was sealed inside the cell and the cell placed inside the bomb. A nitrogen pressure approximating the vapor pressure of water at the operating temperature was then admitted to the bomb. Electrical connection to the outside was made through conventional pressure fittings with soapstone glands. This cell gave fairly reliable results at 200°C in the more concentrated (>0.001 *N*) solutions. The data in Table 19 were obtained with this cell and are considered reliable to ±5%.

Table 19

CONDUCTIVITY OF URANYL SULFATE SOLUTIONS AT 200°C

CONCENTRATION (eq./l)	EQUIVALENT CONDUCTANCE ($ohms^{-1} \cdot cm^2$)
2.52	20.60
1.00	33.38
0.50	39.82
0.10	55.0
0.05	66.09
0.01	105.4
0.005	124.8

(15) K. S. Warren and H. W. Wright, *Homogeneous Reactor Project Quarterly Progress Report for Period Ending March 15, 1952*, ORNL-1280, p. 173.

(16) F. R. Bruce, D. E. Ferguson, D. D. Rauch, I. R. Higgins, and W. Tomlin, *op. cit.*, ORNL-1121, p. 178.

(17) R. D. Brown, *op. cit.*, ORNL-1280, p. 183.

It was shown, however, that considerable solution of the pyrex glass took place at this temperature. This was done in two ways—the conductivity of a solution was measured at room temperature before and after use in the conductivity cell. A sample so used (C = 0.001 N) had an equivalent conductivity of approximately 110 $ohms^{-1} \cdot cm^2$ at 25°C. After being held in the cell for 2 hr at 200°C it was removed, cooled to 25°C, and the conductivity again measured. The conductivity was then found to be approximately 130 $ohms^{-1} \cdot cm^2$. A sample of 0.1 N UO_2SO_4 was held in the bath for a period of 16 to 18 hr and then removed, and a spectrographic determination of boron was obtained. The solution was found to contain 8.2 μg of boron per milliliter, which showed considerable solution of the pyrex glass.

The first bomb cell was then modified. The platinum leads were painted with Teflon paint baked on at 250°C. This bomb cell could be fitted with either a silica or pyrex lining and tests were made with each. These cells also gave erratic results either because of vapor contact with the type 347 stainless steel or because of the solution of the silica or pyrex in the uranyl sulfate solution. Again this bomb was modified. A Teflon rod (4 cm in diameter) was hollowed out to form a cell with a tight-fitting Teflon cap through which the electrode leads were passed. These leads were coated with Teflon paint and access from the exterior was made through conventional fittings. This cell gave reasonably good data with concentrations above 0.1N, but the conductivity of dilute solutions increased rapidly when held in this cell for an appreciable length of time. This cell was also tested with pure water. It was filled at 25°C where k_{H_2O} was known to be 5×10^{-6}, and after 2 hr in the bath at 250°C the bomb was removed and allowed to cool to room temperature. The value of k_{H_2O} was then found to be about 8×10^{-5}.

Conductometric Titration. Information was desired concerning the variation in conductivity of uranyl sulfate solutions containing an excess of uranium as UO_3. Solid UO_3 was added to a stock solution of 1.25 M UO_2SO_4 to give a solution with a U-to-$SO_4^{=}$ ratio of 1.2:1. The solution thus prepared was 1.5 M in U and 1.25 M in $SO_4^{=}$, neglecting the slight volume increase due to the addition of UO_3. From this solution, others of the concentrations given in Table 20 were prepared. The conductivities of these

Table 20

SOLUTIONS PREPARED FOR CONDUCTIVITY MEASUREMENTS

SOLUTION NO.	URANIUM CONCENTRATION (M)	SULFATE CONCENTRATION (M)
1 (stock)	1.5	1.25
2	0.7	0.625
3	0.30	0.25
4	0.15	0.125
5	0.075	0.0625
6	0.0075	0.00625

solutions were measured at 25°C, and standard sulfuric acid was added in measured amounts until the sulfate concentration was greater than that of the uranium. Clearly defined endpoints were obtained in all cases by plotting the conductivity (reciprocal of the bridge reading, $1/R$) vs. milliliters of standard acid added. These plots are shown in Figs. 24 and 25.

A tabulation of the data is given in Table 21. The equivalent conductivity in each case is in good agreement with that obtained in previous work.

It is concluded that uranyl oxide (UO_3) behaves as a weak base in aqueous solution and shows a strong buffering action, as indicated by the small change in conductivity upon addition

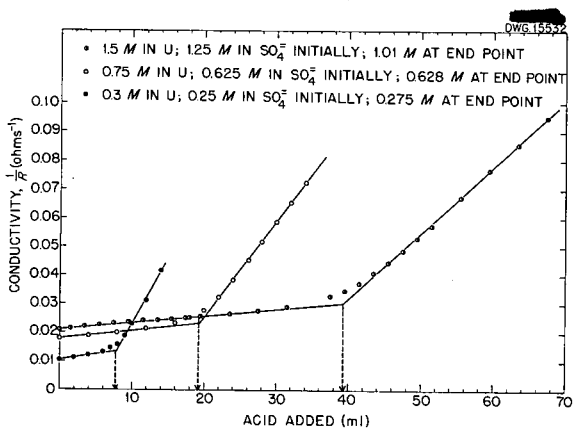


Fig. 24. Conductometric Titration of UO_3 in UO_2SO_4 Solution with 1.281 *N* Acid.

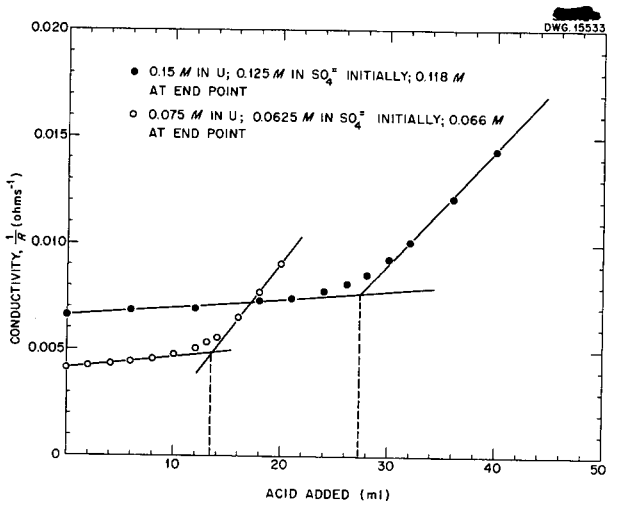


Fig. 25. Conductometric Titration of UO_3 in UO_2SO_4 Solution with 0.180 *N* H_2SO_4.

Table 21

CONDUCTOMETRIC TITRATION OF UO_2SO_4 SOLUTION CONTAINING EXCESS UO_3

SOLUTION NO.	URANIUM (eq./l)	URANIUM AT END POINT (eq./l)	$1/R$	K*	EQIVALENT CONDUCTANCE ($ohm^{-1} \cdot cm^2$)
1	3.0	2.02	0.0345	0.0173	8.5
2	1.5	1.26	0.0267	0.0134	10.6
3	0.6	0.556	0.0155	0.00775	13.9
4	0.3	0.236	0.0084	0.0042	17.8
5	0.15	0.132	0.0054	0.0027	20.4
6	0.015	0.0110	0.0012	0.0006	56.8

*Cell Constant = 0.501.

of sulfuric acid until the stoichiometric end point is reached. This is of interest in consideration of corrosion. It appears probable that since there is little difference in conductivity between the 1.2:1 and the 1:1 U-to-SO_4 solutions the corrosion effect of the two should be approximately the same.

VAPOR PRESSURES OF AQUEOUS URANYL SULFATE SOLUTIONS

H. O. Day, Jr.

The vapor pressures of saturated uranyl sulfate solutions were determined by using a compound manometer apparatus. The temperature range covered was 50 to 100°C. About 15 readings were taken at each temperature and the results were averaged.

The solid phase of uranyl sulfate froze the stirrer in the pressure vessel shortly after the determinations were started, and as a result equilibrium was attained very slowly. Any errors in the measurements can most likely be attributed to this factor. Table 22 presents the experimental data. The values at 50 and 60°C are apparently in error, probably because equilibrium was not attained. It is planned to repeat the measurements at some future date.

In order to obtain more accurate data at temperatures below 100°C, a differential vapor pressure apparatus has been built. It is hoped that the data will prove accurate enough to enable precise activity coefficients to be calculated.

This apparatus consisted of two glass vessels of about 50-ml capacity connected by separate glass tubing to a glass U-tube. The glass vessels connect to the tubing by means of standard-taper ground-glass joints. The glass U-tube was filled with dibutylphthalate as a manometer fluid, and the entire U-tube was thermostated at 103.38 ± 0.09°C. Dibutylphthalate has a vapor pressure of about 0.061 mm Hg at this temperature and an experimentally determined density of 0.9792 g/cm^3. The sensitivity of the vapor pressure measurements is therefore

Table 22

VAPOR PRESSURES OF SATURATED URANYL SULFATE SOLUTIONS

TEMPERATURE (°C)	MOLALITY OF UO_2SO_4 AT SATURATION*	VAPOR PRESSURE DEPRESSION (mm Hg)	RELATIVE MOLAL VAPOR PRESSURE LOWERING $(P_0 - P)/P_0\ m$
50	4.333	14.10 ± 0.10	0.0351_7
60	4.457	23.69 ± 0.05	0.0355_7
70	4.602	34.65 ± 0.05	0.0322_2
80	4.769	51.68 ± 0.15	0.0305_1
90	4.963	73.09 ± 0.32	0.0280_0
100	5.187	106.20 ± 0.13	0.0269_4

*C. H. Secoy, *J. Am. Chem. Soc.* **70**, 3450 (1948).

increased by a factor of over 13.5 as compared with mercury manometer measurements. The dibutylphthalate was loaded into the manometer under vacuum to remove air. Stopcocks are provided in the glass lines to close off the manometer from the rest of the system. The two glass lines leading from the pressure vessels to the manometer have stopcock connections leading to a high-vacuum line and also a reservoir of water that has been freed from air by sublimation of ice at low temperature under a vacuum. The sublimation was repeated about a dozen times. The reservoir also has a stopcock for isolating it from the high-vacuum line.

The connecting tubing from the pressure vessels to the manometer is wound with nichrome wire to allow heating to prevent condensation of water in the tubing which would otherwise be at room temperature when the pressure vessels were above room temperature. The pressure vessels were thermostated in a vigorously stirred bath of glycerol-water. The temperature of this bath was measured with a platinum resistance thermometer and controlled by means of a nickel resistance element in conjunction with a Leeds and Northrup duration-adjustment type of control. This control was excellent except at 90 and 100°C, at which temperatures the thermometer showed variations of ±0.02°C. (Temperatures of 25 to 30°C were attained by use of a water-cooled, copper, cooling coil.)

Each pressure vessel contained a small, glass-enclosed, iron magnet. By moving another magnet nearby, the contents of the vessels were amply stirred to allow equilibrium to be more quickly attained.

The technique used in a determination of vapor pressure was to weigh accurately finely powdered uranyl sulfate into one of the pressure vessels. The vessel was attached to the system and evacuated. Air-free water was distilled onto the solid uranyl sulfate and the uranyl sulfate dissolved. The solution was then frozen and the vessel again evacuated. The contents of the vessel were then allowed to thaw under a vacuum. This process of alternately freezing and melting under vacuum was repeated several times to ensure complete removal of air. Pure air-free water was distilled into the second vessel. The vessels were then immersed in the thermostat by raising the thermostat bath. The thermostat was then heated to the desired temperature and the difference in vapor pressure of the solution and of the pure water was observed on the manometer.

After completion of the pressure measurements the thermostat bath was lowered and the uranyl sulfate solution frozen by means of a dry ice-acetone bath. The pressure vessel was then removed from the line and quickly capped. The contents were then allowed to thaw. After reaching room temperature the vessel and its contents were accurately weighed. Since this weighing allowed the total mass of water to be known, the concentration of the uranyl sulfate solution could then be calculated at each temperature. Correction for the mass of water present as vapor in the connecting lines and manometer was made. So far, measurements have been made from 25 to 100°C for concentrations of about 0.6 and 2.1 *m* UO_2SO_4.

After the vapor pressures of the 2.1 *m* UO_2SO_4 solution were measured, it was noticed that the uranyl sulfate appeared discolored and had an odor similar to butyl alcohol (the odor was probably due to this substance). The conclusion reached was that the dibutylphthalate had very slowly hydrolyzed. Whether the mechanism of

this hydrolysis was a vapor-phase hydrolysis in the manometer or whether a small amount of the ester distilled into the pressure vessel and there hydrolyzed is not known. This hydrolysis would be bound to affect both the pressure measurements and the concentration measurements. The exact extent of this effect is unknown. The hydrolysis process could be minimized by making measurements more quickly and by keeping the stopcocks in the line closed except during measurements. However it was felt that finding a more suitable manometer fluid would be the best solution.

Two possible manometer fluids are *m*-diphenylbenzene and tri-*p*-cresyl phosphate. Experimental determination of their densities at 103.38 ± 0.09°C gave 1.03157 ± 0.00010 g/cm^3 for *m*-diphenylbenzene and 1.1087 ± 0.00005 g/cm^3 for tri-*p*-cresyl phosphate. The diphenylbenzene would therefore make a slightly more sensitive manometer fluid. However, the vapor pressure of this substance is roughly four times that of dibutylphthalate whereas the vapor pressure of tri-*p*-cresyl phosphate in 0.3 of a micron at 103.38°C. From this aspect the tri-*p*-cresyl phosphate would be better. The tri-*p*-cresyl phosphate is, however, an ester and might possibly hydrolyze as did the dibutylphthalate. This possibility would not exist if *m*-diphenylbenzene were used as the fluid. Therefore *m*-diphenylbenzene was chosen as the manometer fluid for the present. Measurements of the vapor pressure of uranyl sulfate solutions will determine whether this substance is satisfactory.

Results of the measurements already made with dibutylphthalate as the manometer fluid are given in Tables 23 and 24. The solid uranyl sulfate that was used to make up the solution had

Table 23

VAPOR PRESSURES OF 0.592 *m* UO_2SO_4-H_2O SOLUTIONS

TEMPERATURE (°C)	MOLALITY OF UO_2SO_4	MOLE FRACTION OF UO_2SO_4	ΔP (mm Hg)
25	0.59172	0.010548_0	0.233
30	0.59173_6	0.010548_3	0.300
35	0.59175	0.010548_5	0.392
40	0.59176_4	0.010548_8	0.511
45	0.59178	0.010549_0	0.675
50	0.59180_1	0.010549_4	0.884
60	0.59188_4	0.010550_9	1.443
70	0.59198_2	0.010552_6	2.164
80	0.59211_7	0.010555	3.107
90	0.59230	0.010558_2	4.166
100	0.59253_1	0.010562_3	5.699

Table 24
VAPOR PRESSURES OF 2.09 *m* UO_2SO_4-H_2O SOLUTIONS

TEMPERATURE (°C)	MOLALITY OF UO_2SO_4	MOLE FRACTION OF UO_2SO_4	ΔP (mm Hg)
25	2.08967	0.0362816	0.749
30	2.08972	0.0362824	1.051
35	2.08977	0.0362833	1.377
40	2.08984	0.0362844	1.830
45	2.08993	0.0362859	2.384
50	2.09003	0.0362876	3.068
60	2.09032	0.0362925	4.916
70	2.09071	0.0362990	7.591
80	2.09122	0.0363075	11.909
90	2.09189	0.0363187	16.900
100	2.09273	0.0363328	23.587

been analyzed for uranyl sulfate content (difference is water of hydration). The value taken was the mean of the analyses. This means that there is a definite uncertainty in the concentrations of uranyl sulfate as reported. The concentrations of the solutions vary from temperature to temperature because of the loss of varying amounts of water to the vapor phase. To show this variation in concentration, the actual concentrations recorded are carried to more significant figures than the accuracy of the analysis warrants. In Table 23 the uncertainty due to analysis errors is ±0.0002 in molality and $\pm 0.000003_5$ in mole fraction. In Table 24 the uncertainty due to analysis errors is ±0.0010 in molality and $\pm 0.00001_7$ in mole fraction. This refers to errors of analysis of the original uranyl sulfate and does not take into account errors due to hydrolysis of dibutylphthalate.

GAS PRODUCTION FROM URANIUM SOLUTIONS

J. W. Boyle W. F. Kieffer
H. F. McDuffie

Uranyl Nitrate. *G* values for gas production from uranyl nitrate solutions have been determined under conditions similar to those used for the studies of uranyl sulfate[18] and uranyl fluoride.[19] The data indicate that at low uranium concentrations *G* for H_2 gas production is the same as that for comparable sulfate or fluoride solutions. At higher uranium concentrations, nitrate solutions have lower $G(H_2)$ values than either of the other uranyl solutions. The results are compared in Table 25.

[18] J. W. Boyle, J. A. Ghormley, T. H. Handley, C. J. Hochanadel, W. F. Kieffer, A. C. Stewart, and T. J. Sworski, *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1951*, ORNL-1260, p. 89.

[19] H. F. McDuffie, J. W. Boyle, and W. F. Kieffer, *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1952*, ORNL-1285 (in press).

The ratio of hydrogen to oxygen present in the ampoules containing irradiated solutions of high concentration $UO_2(NO_3)_2$ suggests that the nitrate may be decomposed by reactor radiations (Table 26). The gas analysis data for the more dilute solutions of $UO_2(NO_3)_2$ are similar to those found in all analyses of irradiated uranyl sulfate and fluoride solutions. The small amount of N_2 (appearing as inert gas by the combustion technique used for gas analysis) is undoubtedly due to residual air, which is very difficult to outgas from ampoules and solutions before irradiation. The data for the more concentrated nitrate solutions show marked contrast to the results for solutions of comparable concentration containing other anions. The oxygen present is far in excess of the O_2-to-H_2 ratio of 1:2 to be expected if only water were decomposed. The identity of the large amounts of N_2 was confirmed by spectroscopic examination.

Uranous Sulfate. A solution of uranous sulfate containing 40 mg of

Table 25

G VALUES FOR H_2 PRODUCTION FROM AQUEOUS URANYL SOLUTIONS IRRADIATED IN THE ORNL GRAPHITE REACTOR AT 120°C

TOTAL U (mg/ml)	U^{235} (mg/ml)	RATIO OF FISSION ENERGY TO TOTAL ENERGY	G (moles H_2/100 ev)		
			$UO_2(NO_3)_2$	UO_2SO_4	UO_2F_2
4.24	3.95	0.959	1.63	1.63	1.66
42.3	39.4	0.995	1.50	1.51	1.58
318.1	2.29	0.932	0.6*	0.8**	1.0**
420.1	36.9	0.994	0.55	0.78	1.00

*Value calculated from data of an exploratory study by J. W. Boyle and T. H. Handley, June 1951.

**Values estimated graphically from data for other concentrations and enrichments.

Table 26

GASES PRODUCED ON REACTOR IRRADIATION OF URANYL NITRATE

CONCENTRATION OF $UO_2(NO_3)_2$ SOLUTION		COMPOSITION OF GASES PRODUCED BY REACTOR IRRADIATION		
Total U (mg/ml)	U^{235} (mg/ml)	H_2 (%)	O_2 (%)	N_2 (%)
4.2	3.95	71	25	4
42.3	39.4	68	30	2
318.1	2.3	25	27	48
420	36.9	38	34	28

uranium (93% enrichment) per milliliter was prepared from the corresponding solution of uranyl sulfate. The calculated amount of concentrated sulfuric acid to supply the additional sulfate ions needed was added to the uranyl sulfate solution and the mixture treated with zinc amalgam. Air was bubbled through the decanted solution for 5 min to ensure the oxidation of any uranium(III) formed by the reduction process. The resulting solution showed almost no precipitation of uranium(IV) as the hydroxide at room temperature, and it oxidized slowly. Most of the samples were irradiated when the uranium(IV)-to-uranium(VI) ratio was about 4.0. No attempt was made to remove the zinc sulfate present in the solutions as a product of the uranyl reduction. Silica ampoules were prepared and degassed by the same method as that used for the uranyl solution studies.[18] A temperature not exceeding 30°C was maintained during irradiation by placing the ampoules in water-filled plastic tubes and by holding the temperature of the Hole 12 cooling water to 30°C. After the ampoules were opened and the gas analyzed in the usual manner, samples of the solution were submitted for uranium analysis. From the resulting uranium(IV)-to-uranium(VI) ratio, the amount of oxidation of uranium(IV) to uranium(VI) during irradiation could be calculated. The data are presented in Fig. 26. It can be seen that the oxygen gas yields are very low but that the amount of uranium(IV) converted to uranium(VI) accounts very satisfactorily for these low yields.

The *G* value for hydrogen gas production in this system is 1.50. This is in excellent agreement with the value for uranyl sulfate and indicates that the process by which H_2 molecules are formed in a fissioning solution is not affected by the presence of the easily oxidized uranium(IV) ions.

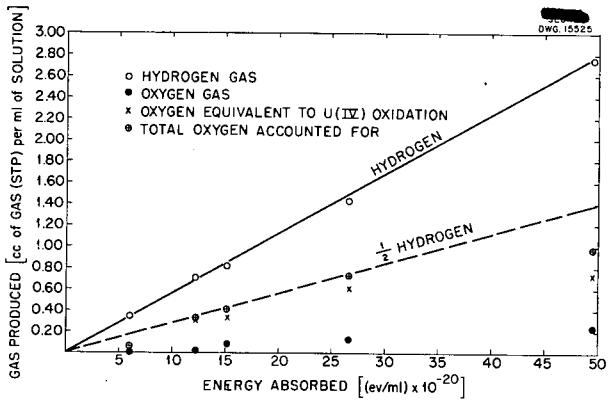


Fig. 26. Gas Production in $U(SO_4)_2$ Solutions by Pile Irradiation at 30°C.

The low oxygen yield suggests that either the dissolved oxygen or some substance intermediate in its formation reacts with the available uranium(IV) in solution. The fact that some oxygen gas is formed, even in the presence of sufficient uranium(IV) to completely remove it, probably can be explained by the escape of some of the oxygen into the gas phase before it has an opportunity to react. This hypothesis was tested by irradiating two ampoules completely filled with solution so that there was no gas space. The data indicate that when the ampoules were filled to leave a gas volume-to-liquid volume ratio of approximately 1.0, the gaseous oxygen found in the products was 17.2% of the stoichiometric amount. In ampoules where the gas-volume to liquid-volume ratio was nearly zero, the oxygen gas found was only 2.2% of the calculated total amount. Analysis of the resulting solutions indicated that uranium(IV) oxidation had occurred to account for the remaining 97.8% of the oxygen.

Investigations of the effect of increased uranium concentrations on the gas yields for uranous sulfate solutions are under way. Preliminary results indicate that a lowering of $G(H_2)$ occurs, as has been reported for uranyl solutions.

KINETICS OF THE DECOMPOSITION OF HYDROGEN PEROXIDE IN URANYL SULFATE SOLUTIONS

M. D. Silverman J. F. Manneschmidt
G. M. Watson H. F. McDuffie

Studies of the thermal decomposition of hydrogen peroxide in aqueous solutions have been undertaken because the power level for operating a homogeneous reactor at low temperatures appears to be largely limited by the formation of hydrogen peroxide and consequent precipitation of uranium peroxide.

The differential equation

$$\frac{dC_{H_2O_2}}{dt} = K - k_1 C$$

may be used to express the peroxide concentration at any time in an aqueous homogeneous reactor, where (1) K is the rate of formation of peroxide, which is assumed to be directly proportional to the power density in the reactor – it appears to be independent of temperature at 250°C or below and may be calculated from the experimental G value (molecules of H_2 per 100 ev); (2) k_1 is the specific reaction rate constant for the decomposition of hydrogen peroxide and is strongly dependent on temperature; and (3) C is the concentration of hydrogen peroxide in the solution at any time. The effects of different levels of the above variables should be known for designing and operating homogeneous reactors. As will be shown in the following sections, K can be approximated experimentally in the laboratory by controlling the rate of addition of hydrogen peroxide solutions to a system under study; k_1 can be determined by standard kinetic techniques using either dynamic or equilibrium methods; and C may be determined by equilibrium methods and by observing the concentrations associated with incipient precipitation.

Determination of Decomposition Rates. Values for k_1 obtained in 0.0045 to 0.17 M uranyl sulfate solutions at 78°C have been reported previously.[20] The rate was observed to be first order with respect to peroxide concentration in the range 4×10^{-4} to 5×10^{-3} M and apparently independent of the uranyl sulfate concentration from 0.0175 to 0.176 M. The pH of these solutions varied from 2.4 to 3.3. There was an apparent slight drop in the rate constant from 4.8×10^{-4} sec^{-1} to 4.2×10^{-4} sec^{-1} as the concentration of uranyl sulfate was lowered from 0.0175 to 0.0045 M. Confirmation of the 4.80×10^{-4} sec^{-1} value of k_1 has since been obtained at a much higher concentration of uranyl sulfate 0.75 M. Values of k_1 recently obtained at two other temperatures, 53 and 101°C, are reported in the fourth column of Table 27. It should be noted that different rate constants have been obtained for three different uranyl sulfate solutions. The third group of solutions, which had been run in the HRE loop for one week at 250°C, doubtless possessed impurities that could be expected to give a higher rate constant for the decomposition of hydrogen peroxide. All rate constants in Table 27 have been calculated by using the equation

$$\frac{dC_{H_2O_2}}{dt} = -k_1(C_{H_2O_2}) \quad .$$

The straight line plots of log k_1 vs. $1/T$ obtained for all three solutions are shown in Fig. 27. From these data, activation energies for

[20] H. F. McDuffie, J. W. Boyle, E. L. Compere, W. F. Kieffer, M. D. Silverman, and H. H. Stone, *op. cit.*, ORNL-1280, p. 158.

peroxide decomposition may be calculated from the Arrhenius rate equation,

$$k = A\ e^{-\Delta E/RT}\ .$$

Preliminary values for specific reaction rate constants, activation energies, and frequency factors, A, are summarized in Table 27. Data for other temperatures may be calculated from the following rate equations:

Solution 1

$$k = 4.49 \times 10^{12}\ e^{-25,600/RT}\ ,$$

Solution 2

$$k = 1.62 \times 10^{12}\ e^{-25,300/RT}\ ,$$

Solution 3

$$k = 1.52 \times 10^{12}\ e^{-23,700/RT}\ .$$

At the present stage of this investigation it is not known whether the relatively small difference between the activation energies of the first two solutions might not be due to experimental errors. The lower activation energy for solution 3 is in line with the larger amounts of impurities contained in this solution.

When definite values for K are simulated in the laboratory (by the addition of hydrogen peroxide at known rates to a solution of uranyl sulfate), the kinetic equation $dC/dt = K - k_1C$ may be used to obtain values for k_1. If the time dependence of C at constant K is known adequately, a plot of dC/dt vs. C will furnish a straight line with slope of $-k_1$. Alternatively, if the value of K is known and maintained constant throughout an experiment, the concentration of peroxide will approach a steady-state value (C_{ss}) at which point $dC/dt = 0$ and hence $K - k_1C_{ss} = 0$. From this it is seen that $k_1 = K/C_{ss}$. Another method for finding k_1 involves plotting the value, $C_{ss} - C_t$ (the distance away from the steady state), against time on conventional semilogarithmic paper and determining the

Table 27

SPECIFIC REACTION RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE DECOMPOSITION OF HYDROGEN PEROXIDE IN URANYL SULFATE SOLUTIONS

SOLUTION	TEMPERATURE (°C)	$k_1 \times 10^4$ (sec^{-1})	ΔE (cal)	$A \times 10^{-12}$
1*	53	0.326		
	78	4.80	25,600	4.49
	101	52.4		
2**	53	0.191		
	78	2.80	25,300	1.62
	101	28.7		
3***	53	1.93		
	78	24.1	23,700	1.52
	101	214		

*Uranyl sulfate solution prepared by the Y-12 production group.

**Uranyl sulfate solution (purer than Solution 1) prepared in the Chemistry Division of ORNL by Lietzke and Griess.

***Natural uranium fuel that had been run in the HRE loop for one week at 250°C.

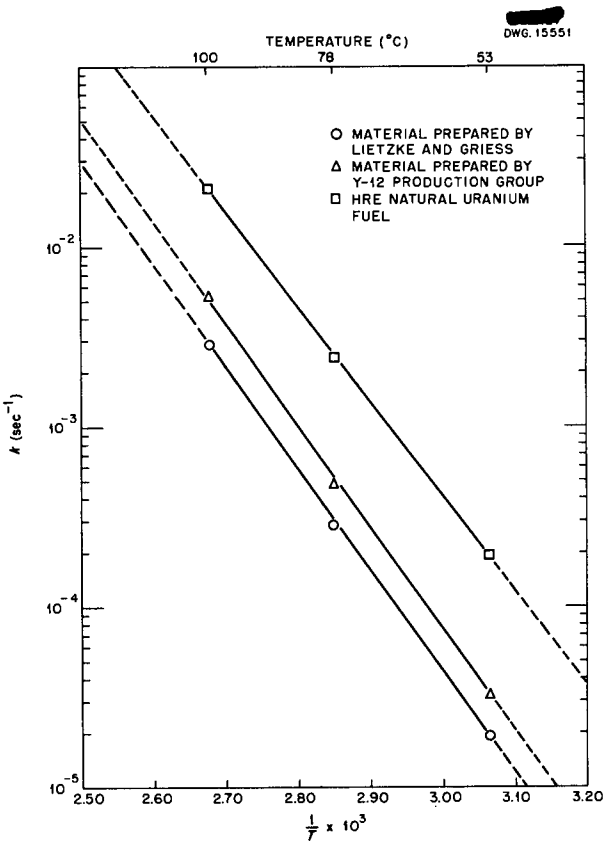


Fig. 27. Specific Reaction Rate Constants for the Decomposition of Hydrogen Peroxide in Uranyl Sulfate Solutions.

constant as for any first-order reaction.

Determinations of k_1 have been made for a variety of uranyl sulfate solutions at the boiling point by using the steady-state method. The results of these tests are presented as Table 28. Large differences in values of k_1 are noted. The Y-12 solution was made up from a relatively impure batch of uranyl sulfate and showed a fairly large value of k_1. By contrast, the Lietzke-Griess material was characterized by low values of k_1. The deterioration of this solution in successive runs is seen by comparing the k_1 values for runs 8, 9, and 10. Undoubtedly some impurities were introduced which assisted in catalyzing the decomposition of peroxide. If the behavior of the HRE 5A-6A material, which was samples of unenriched fuel that had been run in the HRE loop for one week at 250°C, can be taken as characteristic of that expected from enriched fuel in the reactor, peroxide decomposition will be very rapid. The agreement between the values of k_1 obtained by the two methods (ordinary plot of log C vs. t vs. steady-state method) is apparently excellent, especially in view of the speed of the reactions involved.

Solubility of Uranyl Peroxide. The maximum allowable hydrogen peroxide concentration in solution is limited by the solubility of uranyl peroxide formed according to the equation

$$UO_2^{++} + H_2O_2 \rightleftharpoons UO_4(s) + 2H^+ .$$

The pH of a dilute solution of uranyl sulfate (0.17 M) is noticeably affected by the addition of hydrogen peroxide. In the case of a concentrated solution (0.85 M), however, very little effect is observed because the solution acts as a buffer. Some equilibrium data, measured at 25°C, are available for this reaction;[21] however, there are no data at higher temperatures, nor are there data for the solubility of uranyl peroxide as a function of temperature, especially in uranyl sulfate solutions.

Attempts to obtain solubility data at higher temperatures have met with some measure of success even though changes in peroxide concentration and hydrogen ion concentration become quite rapid. Solubility experiments have been conducted at room temperature (30°C), 78, and 101°C. Analyses for total peroxide at the point of

[21] P. F. Grieger and J. W. Gates, Jr., *Uranium Peroxide. Part III. Discussion of the Solubility of Uranium Peroxide in Sulphate Solutions Based on the Uranyl Sulphate Association Hypothesis*, CD-4023 (May 28, 1945).

Table 28

DECOMPOSITION OF PEROXIDE IN URANYL SULFATE SOLUTIONS AT 100°C

RUN NO.	SOLUTION SOURCE	URANIUM CONCENTRATION (g/l)	K(moles/l/min)	C_{ss} (moles/l)	k_1(min^{-1})	PRECIPITATE	$T_{1/2}$(min)	COMMENTS
1	Y-12	8	0.000725 t* 0.00067 c**	0.00122	0.55	no	1.25	
2	Y-12	8	0.00151 t 0.00139 c	0.0022	0.63	yes	1.1	
5	Y-12	40	0.00145 t 0.00096 c	0.00173	0.56	no	1.25	Flask contained type 347 stainless steel turnings
6 *a* *b* *c*	Y-12	40	0.00164 0.00347 0.0057	0.00218 0.00414 0.0068	0.735 0.84 0.8	no yes? yes	0.944 0.825 0.867	Measurements of C_{ss} and K taken at different values of K, with sufficient time allowed for steady state to be reached in each case
8	Lietzke-Griess	40			0.23	no	3.0	Conventional plot of log c vs. t after one addition of peroxide
9 *a* *b* *c* *d*	Lietzke-Griess	40	0.000298 0.000312 0.000351 0.000387	0.00081 0.00092 0.00097 0.00110	0.37 0.34 0.36 0.365			Measurements of C_{ss} and K taken at different values of K, with sufficient time allowed for steady state to be reached in each case
10 *a* *b* *c* *d* *e*	Lietzke-Griess	40	0.000303 0.000445 0.000396 0.000471 0.000705	0.00069 0.00113 0.00077 0.00106 0.00131	0.5 0.395 0.515 0.445 0.54	 yes yes		Same as above A few crystals of uranium peroxide seen in microscopic examination of samples of the solution
11	HRE	5A-6A	0.0022	0.00126	1.74	no	39 sec	This solution had been used in the HRE for runs at 250°C and hence had accumulated impurities that raised the value for k_1

*t = titrated.

**c = calculated.

incipient precipitation of uranyl peroxide were made by titration with ceric sulfate. Hydrogen ion was measured using the Beckman high-temperature electrode with the Model G instrument, with appropriate corrections for the temperature factor. The point of precipitation was determined by visual observation. The data obtained at both low and high concentrations of uranium have been summarized in Table 29.

The main sources of error in these experiments were: (1) detection of formation of the precipitate since it forms very slowly in solution – hence, peroxide concentrations would always be a little high; (2) determination of the hydrogen ion concentration by means of the high-temperature glass electrode. The citrate buffer used for standardization is claimed to have a negligible temperature coefficient up to 70°C; it has been assumed to be negligible in these experiments up to 100°C. Furthermore, no data are available on the performance of this type of electrode at the temperatures employed. It is estimated that pH values at 78 and 100°C could very easily be in error by 0.1 pH unit.

In spite of the rough experimental measurements, some measure of the solubility of uranyl peroxide as a function of temperature has been obtained.

By using the steady-state method in which *K* is maintained constant, it becomes possible to maintain a given peroxide concentration for periods of time long enough to permit sensitive determination of the formation or absence of precipitated $UO_4 \cdot 2H_2O$. Preliminary experiments utilizing this technique led to a value of 0.002 to 0.004 mole per liter for the peroxide concentration at saturation in uranyl sulfate solution containing 40 g of uranium per liter at 100°C (based on experiments 6*a* and 6*b* in Table 28). This is believed to be a conservative value. The very small amounts of crystalline uranium peroxide observed in experiments 10*d* and 10*e* may have been formed

Table 29

SOLUBILITY OF URANYL PEROXIDE IN URANYL SULFATE SOLUTIONS

TEMPERATURE (°C)	UO_2SO_4 CONCENTRATION (*M*)	TOTAL PEROXIDE CONCENTRATION (*M*)	pH
30	0.16	0.00311	2.32
	0.65	0.00791	1.64
78	0.15	0.00375	2.14
	0.57	0.00685	1.66
	0.71	0.00678	1.59
100	0.112	0.00636	2.09
	0.60	0.0082	1.58
	0.54	0.00914	1.66

as a result of local supersaturation when the entering peroxide was being mixed with the boiling uranyl sulfate solution. Longer steady-state runs with carefully controlled concentrations will be required for more accurate determination of the tolerable level of peroxide.

Reactor Operation as Governed by Peroxide Decomposition. The production of hydrogen peroxide in a reactor is considered to be a function of the G value and the energy input (power density) as expressed by the formula $K = 0.0052 \times G \times PD$, where the power density is expressed in kilowatts per liter. For fuel containing 40 g of uranium per liter, G is approximately 1.5 and the peroxide formation is $K = 0.0078\ PD$ mole per liter per minute. The tolerable peroxide concentration and the tolerable power density are related by the expression:

$$PD = \frac{C_{ss}}{0.0078}\ k_1 .$$

By using a value of 1.75 for k_1 (from run 11) and an allowable steady-state peroxide concentration of 0.0039 M, the allowable power density for the HRE at 100°C is calculated to be 0.825 kw/liter and the total power of the reactor to be 41.25 kw. The accumulation or addition of catalytic materials such as corrosion products or recombination catalysts, the effects of radiation in the presence of dissolved hydrogen, and the conservative values for allowable peroxide will all tend to permit actual reactor operation at higher power levels.

Plans for Future Work. Of immediate practical importance is the question of allowable power level for low temperature operation of the HRE. To this end, actual determinations of k_1 for enriched HRE fuel will be carried out following the 250°C critical experiments but prior to operations at substantial power. Additional determinations may be carried out after runs at a low power level to determine whether impurities have been introduced which will allow operation at higher power levels.

Active exploration of remote instrumental methods for determining the peroxide level in uranyl sulfate solutions is already under way. Preliminary work using conductance methods appears encouraging. It is hoped that it will become possible to conduct studies of peroxide decomposition without having to take samples of solution from the system—this is almost a necessity for solutions in which the peroxide is decomposing at very rapid rates.

Extension of peroxide decomposition studies to temperatures in the range 100 to 150°C is contemplated. This will depend primarily on the development of rapid instrumental methods of analysis.