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CHEMISTRY DIVISION

QUARTERLY PROGRESS REPORT

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FOR PERIOD ENDING JUNE 30, 1951

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CHEMISTRY DIVISION

S. C. Lind, Acting Director
G. E. Boyd, M. A. Bredig, Associate Directors

QUARTERLY PROGRESS REPORT

for Period Ending June 30, 1951

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ABSTRACT

CHEMISTRY OF SOURCE, FISSIONABLE, AND STRUCTURAL ELEMENTS

A completion report will be issued in the next quarter on the study of the aqueous thorium thenoyltrifluoroacetone (TTA system) and on the nature of solid thorium perchlorate used to prepare aqueous solutions of thorium.

Freezing point and conductivity studies of uranyl fluoride in aqueous solution show that dissociation is slight in solutions 0.01 to 5 *m*, and that most of the uranium compound is in the form of a dimer at concentrations above 0.5 *m*.

The negative complexing of anion-exchange resins with chloride ions was determined by studying resin adsorption of cations. In 7 *M* and 12 *M* HCl the following ions were not adsorbed and formed no negatively charged complexes: Li^+, K^+, Na^+, Rb^+, Cs^+, NH_4^+, Be^{++}, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Al^{3+}, Sc^{3+}, Y^{3+}, La^{3+}, and Yb^{3+}. The elements which show strong adsorption [Co(II), Cu(II), Zn(II), Cd(II), Hg(II), Zr(IV), Hf(IV), Cb(V), etc.] are readily separable from those that do not. Fe(III) and Ga(III) adsorb about equally strongly in concentrated HCl. The complex ions are probably $FeCl_4^-$ and $GaCl_4^-$.

Investigation of the hydrolytic behavior of metallic ions has been extended to Th^{4+}, Zr^{4+}, and Hf^{4+}.

Discrepancies in the distribution of Zr between TTA-benzene solution and aqueous chloride have been found to be due to low concentrations of some oxidizing agent (probably ClO_3^-) in the $NaClO_4$ used to maintain constant ionic strength. Using pure $NaClO_4$ prepared from Na_2CO_3, the formation constant of $ZrCl_3^+$ at ionic strength 3 was found to be 1, which is believed to be a better value than the formerly accepted 1.3.

The high-level separations of technetium from solvent-extraction raffinates has proceeded to the point where over 10 g of the element is now contained in extensively decontaminated crude product fractions. Some of these fractions have been refined, and 600 mg of pure technetium metal has been produced. Solubilities of the potassium and tetraphenylarsonium pertechnetates were measured and found to be greater than those of the corresponding compounds of rhenium. The light yellow crystalline oxide formed on heating technetium metal in dry oxygen at 400 to 600°C was demonstrated to be Tc_2O_7. The intense ultraviolet absorption of pertechnetate ion in aqueous solutions was found suitable for analytical estimations down to 0.01 μg of the element.

The gamma-ray spectrum of Tc^{100} produced by $Mo^{100}(d,2n)$ was observed for the first time. No evidence for the radiations of Tc^{98} formed by a prolonged deuteron irradiation of enriched Mo^{98} has been found, suggesting a very long half-life. Decay schemes for the 2.7-day Au^{198} and for 8.0-day I^{131} have been worked out because of the importance of these isotopes as radioactive standards and as therapeutic agents, respectively. The new gamma transitions at 680 and 1090 kev in Au^{198} and their coincident

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beta-ray group of 290 ± 15 kev maximum energy were shown to be present in roughly 1% of the disintegrations, so that errors of only a few percent have been involved in previous measurements in which Au^{198} was used as a standard. The details of the complex decay scheme of I^{131} were also elucidated using a magnetic-lens beta spectrometer together with a scintillation-counter spectrometer in a coincidence-circuit arrangement.

NUCLEAR CHEMISTRY

The nuclear spin and quadrupole moment of 4.4×10^5 year Cl^{36} have been determined by microwave measurements on the hyperfine structure of CH_3Cl^{36}. The spin value $I = 2$, reported earlier by Townes and Aamodt, was confirmed, and a somewhat more accurate value of -0.0168×10^{-24} cm^2 for the quadrupole moment was found. Further measurements on the quadrupole spectra of various polyhalogen substituted methanes have indicated anomalous effects resulting from the substitution of fluorine. These effects are explained by the assumption that the introduction of fluorine into the molecule induces a small amount of double-bond character in the C-Cl (or C-Br) linkage.

An important improvement in neutron diffraction techniques for low symmetry structure determinations may result from recent studies of the single crystal method. Empirical tests with a 7.3 cu mm volume NaCl crystal using a metal-crystal monochromator have been decidedly encouraging, theoretical predictions to the contrary, and, if this case proves to be typical, the single-crystal method will be quite practical.

The kinetics of the Br_2-BrO_3^- isotopic exchange reaction in acid solutions have been examined. The anticipated exponential rate law was not well obeyed, possibly owing to the slow formation of equilibrium amounts of HBrO which undergoes a rapid exchange with Br_2.

RADIO-ORGANIC CHEMISTRY

Radiation Chemistry. The effects of gamma radiation from a 300-curie Co^{60} source upon aqueous solutions of C^{14}-labeled benzoic and acetic acids have been studied.

Fifty-two separate irradiations of aqueous carboxyl-labeled benzoic acid have given data relating the extent of decarboxylation to time of irradiation. The inhibitory actions of sodium chloride and sodium bromide for the decarboxylation of aqueous benzoic acid have been determined for irradiation times up to 30 min. The nonvolatile products of irradiation have been isolated by paper chromatography and isotope dilution methods. The formation of *m*-hydroxybenzoic, *p*-hydroxybenzoic, and salicylic acids has been demonstrated.

In five irradiations of aqueous solutions of acetic-1-C^{14} acid and acetic-2-C^{14} acid the formation of carbon dioxide, carbon monoxide, succinic acid, and glycolic acid has been demonstrated. Another compound of undetermined structure has been isolated.

Analytical Chemistry. A double ion-chamber apparatus has been developed and utilized for the determination of radioactivity concentrations in paper chromatograms of mixtures of

labeled compounds. This technique is much simpler than radioautographic techniques and allows more rapid analysis of results when applied to one-dimensional paper chromatograms.

Preparative Chemistry. The following low- and intermediate-molecular-weight compounds have been prepared: methanol-C^{14}, 600 mc; sodium acetate-2-C^{14}, 573 mc; acetic-2-C^{14} acid, 380 mc; chloroacetic-2-C^{14}, 380 mc; and malonic-2-C^{14}, 92 mc.

Synthesis of High-Molecular-Weight Compounds Containing C^{14}. Experiments are in progress which should establish the position of C^{14} labeling in the 1-methylphenanthrene which was prepared previously through a Wagner rearrangement of 1-methyl-9-fluorenyl(carbinol-C^{14}). Degradation products of the 1-methylphenanthrene which have been isolated are 1-methylphenanthraquinone and 3-methyldiphenic acid.

Mechanism Studies of Organic Reactions. The reversibility of the Friedel-Crafts acylation reaction is under study. Of the ketones studied no reversible reaction has as yet been found.

The alkaline rearrangement of α,α-dibromo(propio-1-C^{14})-phenone has been shown to proceed with phenyl group migration.

The alkaline rearrangement of *p*-methoxybenzil has been shown to proceed with 35% migration of the anisyl group and 65% migration of the phenyl group.

The migratory aptitudes of several substituted aryl groups are under study through the acid-catalyzed rearrangement of α,α-disubstituted ethanols.

During the study of the displacement of formyl groups from aldehydes by alkaline formaldehyde solution, it has been shown that phenylacetaldehyde and anthrone cannot be directly formylated by the usual techniques.

The rearrangement of (ethyl-2-C^{14})-benzene in the presence of aluminum chloride is under investigation.

Group Publication for Quarter in the Open Literature. A paper by C. J. Collins and O. K. Neville, "C^{14} Tracer Studies in the Rearrangement of Unsymmetrical α-Diketones. II. The Alkaline Rearrangement of Benzylideneacetophenone Oxide," was published in *J. Am. Chem. Soc.* **73**, 2471-3 (1951).

CHEMISTRY OF SEPARATION PROCESSES

Work is in progress on the removal of Pa^{233} from neutron-irradiated ThF_4. Experimental procedures are being considered to determine the solubility of the fluorides of uranium and of fission products in anhydrous HF. The phase study of the system UO_2F_2-HF-H_2O, now complete up to 42% HF at 25°C, will be carried to higher concentrations of HF, and the solubility of UO_2F in anhydrous HF as a function of temperature will be studied.

The kerosene diluent currently used in the Purex process reacts with 5 *M* HNO_3 above 100°C to give nitration products and carboxylic acids. These products could adversely affect the process if elevated temperatures were used.

A counting technique for solutions containing P^{32} has speeded the estimation of the organic phosphates being studied.

CHEMISTRY DIVISION QUARTERLY PROGRESS REPORT

The solubility of tributyl phosphate is low in most of the aqueous solutions tested, but the apparent solubility may appear higher because of emulsification by processes that are not yet controlled.

The rate of hydrolysis of TBP is slow at 25°C but is much faster at 75°C. Hydrochloric acid hydrolyzed TBP faster than nitric acid at 75°C.

Work on separation by electromigration through Dowex-50 has been suspended.

CHEMICAL PHYSICS

In the first experiments with the high-temperature X-ray-diffraction apparatus the patterns of the cubic and tetragonal high-temperature crystal modifications of the compounds zirconium and hafnium dioxide were recorded at 1540°C.

The metastable yellow high-temperature crystal modification of lead oxide, PbO, was found to be partially transformed in a Chalk River pile irradiation into the stable, red, low-temperature form. The simultaneous failure of the red form to convert to the yellow may be considered as an argument against the so-called "thermal spike" theory of radiation damage.

Experimental work is being started on fused salt--metal systems, such as $Ca + CaCl_2$ or $Na + NaF$, containing either subhalides or solvated metal atoms, which are expected to exhibit interesting properties in regard to corrosion and thermal conductivity.

The results of thermodynamic computations on reactions of metals with sodium hydroxide have been tabulated.

REACTOR CHEMISTRY

Emphasis on vapor pressure measurements of aqueous solutions of UO_2SO_4, $UO_2(NO_3)_2$, and UO_2F_2 has been shifted from the lower range to temperatures from 150 to 300°C.

Conductivity measurements of aqueous solutions of uranium salts will be made between 100 and 300°C. The study of the solubility of fission products in uranyl sulfate solutions will be extended above 100°C.

Studies of corrosion and solution stability have been continued both in and out of the pile. The presence of free oxygen is necessary to maintain the passivity of 347 stainless steel at 250°C. The maintenance for several weeks of pressure well above steam pressure in solutions of enriched UO_2SO_4 in stainless steel bombs exposed to the full flux of the X-10 pile indicates the stability of the solution under these conditions.

The solubilities of $La_2(SO_4)_3$ and of $Ce_2(SO_4)_3$ in water have been determined up to 350°C and will be reported in the HRE quarterly report. The electrochemical study of corrosion of stainless steel and of other metals has been continued. Discovery of contamination of UO_2SO_4 by organic materials raises a question as to interpretation of results. Experiments will be repeated using purified salts. Specimens of stainless steel freshly passivated in HNO_3 or CrO_3 solution show a positive potential of more than 700 mv toward a calomel electrode. Addition of chloride ion destroys passivation apparently by disrupting the passive film by removal of oxygen. Anodic treatment was also detrimental to the passive film.

Further experiments with anodic treatment in HNO_3 and cathodic treatment in CrO_3 solution are being made.

RADIATION CHEMISTRY

The value $G = 15.5 \pm 0.3$ Fe^{++} oxidized per 100 ev has been confirmed by new measurements, using new calorimetric measurements of gamma-ray energy at intensities of 1500, 4500, and 15,000 r/min. The yield was also confirmed by use of an ion chamber of polystyrene.

The yield for reduction of Ce^{4+} in air-saturated 0.4 *M* H_2SO_4 is 2.46 Ce^{4+} reduced per 100 ev. The ratio of yields, 15.5 Fe^{++}/2.46 Ce^{4+} = 6.4, agrees with Hardwick's 20.8/3.3, thus indicating that the discrepancy lies in the energy measurement. A program was begun to determine the steady state of gases evolved by gamma radiation of solutions of Na_2SO_4, H_3PO_4, NaOH, KBr, and UO_2SO_4.

A new method has been used for the determination of phenol in dilute aqueous solution which is not interfered with by benzene or H_2O_2. The method depends on the change in the ultraviolet absorption spectrum upon making the solution alkaline. In an oxygen-saturated solution of benzene the initial yield of phenol is 2.80 per 100 ev. From the work of Hochanadel and of Hart in the available free radicals of OH, it thus appears that each results in the formation of one molecule of phenol. In addition, a yield of 2.91 H_2O_3 per electron volt was found. The reaction mechanisms are discussed.

A definite test of the reality of the effect of gamma radiation in diminishing the catalytic activity of ZnO is expected soon.

INSTRUMENTATION

Several important efforts directed toward improving the electronic instrumentation for nuclear chemical research are being conducted:

1. A very useful mercury-relay pulse generator for checking pulse amplifiers was designed and tested.

2. A previously described single-channel differential discriminator circuit has been improved so as to give adequate performance at very high counting rates. A tube aging program is being initiated with the view of bettering the long time stability of this circuit.

3. Two new pulse-height analyzers are being readied. One of these will be a general purpose 20-channel energy analyzer, and the other will be based on the recently developed DuMont 10-channel gating tube (K 1059).

4. High-voltage power supplies capable of giving stable operation with scintillation and with proportional counters over long periods of time are being studied.

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CHEMISTRY DIVISION QUARTERLY PROGRESS REPORT

1. CHEMISTRY OF SOURCE, FISSIONABLE, AND STRUCTURAL ELEMENTS

AQUEOUS BENZENE—TTA EXTRACTION METHOD FOR AQUEOUS THORIUM STUDIES

W. C. Waggener and R. W. Stoughton

Study of the aqueous thorium thenoyltrifluoroacetone (TTA) system is continuing as outlined in the preceding quarterly report.[1]

The nature of the solid thorium perchlorate used to prepare aqueous solutions of thorium is also being investigated. It is planned to issue a completion report within the next quarter covering this work.

UNDISSOCIATED SPECIES AND DIMERIZATION IN AQUEOUS SOLUTIONS OF URANYL FLUORIDE

J. S. Johnson and K. A. Kraus

C. H. Secoy[2] has measured the freezing point depressions, θ, of aqueous solutions of uranyl fluoride, and from these data has calculated the mean formal activity coefficients $\gamma_{\pm f}$ by the standard equation[3]

$$\ln \gamma_{\pm f} = -j - \int_0^m \frac{j}{m}\, dm + \frac{c}{\nu} \int_0^m \frac{\theta}{m}\, d\theta \qquad (1)$$

where $j = 1 - \theta/\lambda\nu m$, m is the molality, c is a constant dependent on the solvent, ν is the number of moles of particles per mole of solute, and λ is the freezing point depression constant (1.860). Complete dissociation into UO_2^{++} and $2F^-$ was assumed; i.e., ν, the number of moles of particles per mole of solute, was taken as 3. Extremely small values of $\gamma_{\pm f}$ were found (see Fig. 1.1), indicating that only a small fraction of the solute is completely dissociated.

This fraction α can readily be estimated from the equation[4]

$$\gamma_{\pm f} = \alpha\gamma_{\pm} \qquad (2)$$

where $\gamma_{\pm}$ is the mean activity coefficient of the ions. Since, by comparison with strong 2:1 electrolytes, $\gamma_{\pm}$ almost certainly is larger than 0.5, α may be estimated from the data of Fig. 1.1 to be less than 0.26, 0.05, 0.009, and 0.0032 in 0.01, 0.1, 1.0, and 5.0 m solutions, respectively. Therefore incompletely dissociated and possibly polymeric species must predominate at these concentrations. Since the conductivity of uranyl fluoride solutions is very low,[5,6] it appears advantageous to calculate formal activity coefficients γ_f from the freezing point

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[1] W. C. Waggener and R. W. Stoughton, "Aqueous-Benzene-TTA Extraction Method," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1951*, ORNL-1053, p. 18 (Oct. 5, 1951).

[2] C. H. Secoy, "The Mean Activity Coefficients of Uranyl Fluoride in Water Solutions at 25°C," *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, ORNL-795, p. 28 (Oct. 3, 1950).

[3] G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, p. 347, McGraw-Hill, New York, 1923.

[4] H. S. Harned and B. B. Owen, *Physical Chemistry of Electrolytic Solutions*, 2d ed, p. 146, Reinhold, New York, 1950.

[5] G. R. Dean, *Properties of Uranyl Fluoride*, Metallurgical Laboratory Report CC-2092 (Sept. 11, 1944).

[6] F. W. Tober and C. E. Larson, *Application of Conductivity Measurements to a Study of (a) Complex Formation Between TO_2 and F^- and Al and F^-; (b) Titration of F^- Ion with H Ion*, TEC Y-12 report 0.375.2 (Sept. 25, 1945).

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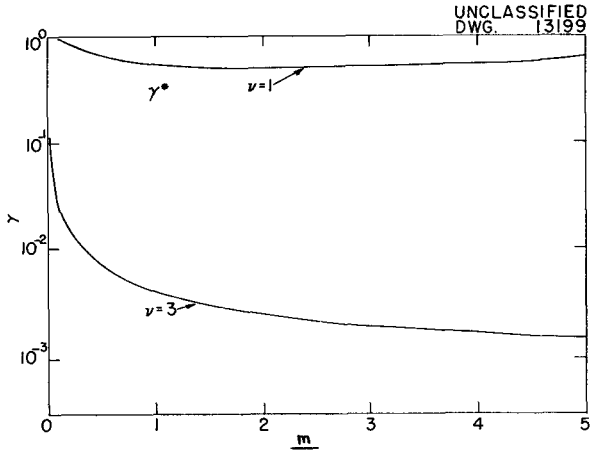

Fig. 1.1 - Activity Coefficients of UO_2F_2.

data on the assumption that uranyl fluoride is undissociated, i.e., using $\nu = 1$ in Eq. (1). In this case, j/m after passing a maximum reaches very negative values at low concentrations, indicating that ν was chosen too small (Fig. 1.2).

Although this choice of ν makes

$$\int_0^m j/m \, dm$$

of Eq. (1) unbounded, useful results can be obtained assuming that $\nu = 1$ pertains even at infinite dilution and setting

$$\int_0^{m^*} j/m \, dm = -\ln \beta$$

where β is a constant and m^* is some arbitrary molality of UO_2F_2 (in this case $m^* = 0.2$) at which dissociation is small. From the experimental data for $m > m^*$ and Eq. (1), values of γ_f^* can then be calculated which are related to γ_f by the equation

$$\ln \gamma_f = \ln \gamma_f^* - \int_0^m j/m \, dm = \ln \beta\gamma_f^* \quad (3)$$

The calculated values of log γ_f^* for UO_2F_2 are shown in Fig. 1.1. They first decrease rapidly with m, have a minimum near $m = 2$, and then slowly increase. The curve of log γ_f^* vs. m thus differs greatly from the linear plot expected for an uncharged species.[7] The initial decrease of γ_f^* suggests that ν is less than 1 and that dimerization (or further polymerization) of the solute therefore occurs. The increase in γ_f^* at high m would then be due to changes in the activity coefficients of the various species.

It will be assumed that only dimerization occurs and that the activity coefficients γ_1 and γ_2 of the undissociated monomer and dimer are given by the equations

$$\log \gamma_1 = b_1 m \quad (4)$$

$$\log \gamma_2 = b_2 m \quad (5)$$

where b_1 and b_2 are constants and m is the formal solute molality.[7,8] Further, it appears reasonable that

$$2b_1 = b_2 \quad (6)$$

by analogy with nonelectrostatic interaction terms in equations developed by Scatchard and Epstein.[8]

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[7] Harned and Owen, *op. cit.*, p. 209.

[8] G. Scatchard and L. F. Epstein, "The Calculation of the Thermodynamic Properties and the Association of Electrolytic Solutions," *Chem. Revs.* 30, 211 (1942).

[redacted]

The monomer-dimer equilibrium constant, K_d, for the reaction $2UO_2F_2 \rightleftharpoons (UO_2F_2)_2$ will then be

$$K_d = m_2\gamma_2/m_1^2\gamma_1^2 = m_2/m_1^2 \qquad (7)$$

The activity of the monomer a_1 can be expressed by the equation

$$a_1 = a_f = m\gamma_f = \beta m\gamma_f^* = m_1\gamma_1 \qquad (8)$$

where a_f is the formal activity calculated on the basis that all solute is in the form of the undissociated monomer.

Since

$$m = m_1 + 2m_2 \qquad (9)$$

and hence, from Eq. (7),

$$m_1 = \frac{-1 + \sqrt{8K_d m + 1}}{4K_d}, \qquad (10)$$

combination of Eqs. (4) and (8) yields

$$\log a_f^* - \log \frac{(\sqrt{8K_d m + 1} - 1)}{4K_d} = b_1 m - \log \beta \qquad (11)$$

There should thus be a value of K_d which would yield a straight line with slope b_1 and intercept $-\log \beta$ if the left side of Eq. (11) were plotted against m. Linearity (within experimental error) is obtained over a large range of values of K_d (for $2 < K_d < 9$), although in all cases the slope gives a value for b_1 of 0.09 ± 0.01. Hence, although the exact extent of dimerization is not established, most of the uranium is in the form of a dimer at concentrations above 0.5 m, and the logarithms of the activity coefficients follow the suggested linear laws [Eqs. (4), (5), and (6)].

Dissociation of the UO_2F_2 into two particles has been ignored in this treatment.[9] From the negative values of j/m at low concentrations and the previous estimates of dissociation into three particles, this process might be expected to be appreciable. It will now be considered in calculation of the j/m vs. m curve. For various values of K_d, values for the dissociation constant

$$K' = \frac{m'^2 (\gamma_\pm')^2}{m_1\gamma_1} \qquad (12)$$

(where m', is the molality of UO_2F_2 dissociated with $\nu = 2$, and $\gamma_\pm$, the mean activity coefficient of dissociated species) were selected such that the calculated freezing point depression is equal to the experimental value at some molality at which both dissociation and dimerization are appreciable. It is assumed that $\log \gamma_\pm' = b'm = (b_1/2)m$ and that the activity coefficients of the individual species (γ_i) can be expressed by the equation

$$\ln \gamma_i = -j_i - \int_0^{m_i} (j_i/m_i)\, dm_i = 2.303\, b_i m \qquad (13)$$

[9] UO_2F_2 solutions are known to be acidic, pH 3.7 to 1.5, in the range 0.07 to 5.4 m. (W. L. Marshall, J. S. Gill, and C. H. Secoy, "The Uranyl Fluoride—Water System," ORNL-795, *op. cit.*, p. 22). The pH values are lower than would be expected (about 7) if dissociation were solely to UO_2F^+ and F^- and higher than would be expected if the reaction were only hydrolysis to UO_2OHF and HF. Probably both reactions occur.

Differentiation yields

$$-dj_i/dm_i - j_i/m_i = 2.303b_i\ dm/dm_i$$
$$= -(1/m_i)\ d(j_i m_i)/dm_i \qquad (14)$$

or

$$j_i m_i = (1 - \theta_i/\lambda\ m_i)m_i$$
$$= -2.303 \int_0^{m_i} b_i m_i\ dm \qquad (15)$$

The right hand side of Eq. (15) may be integrated for each species by substituting for dm its value in terms of m_i, K', and K_d. The equation can then be solved for θ_i. The total calculated freezing point depression (hence the j) for any concentration is given by the sum of the θ_i's.

The calculated j/m vs. m plot for $K_d = 7$ and $K' = 1.9 \times 10^{-3}$ is shown in Fig. 1.2. The agreement with experiment is satisfactory,* indicating again that although both dimerization and dissociation need to be considered at low concentrations, neutral species predominate at a higher concentration.

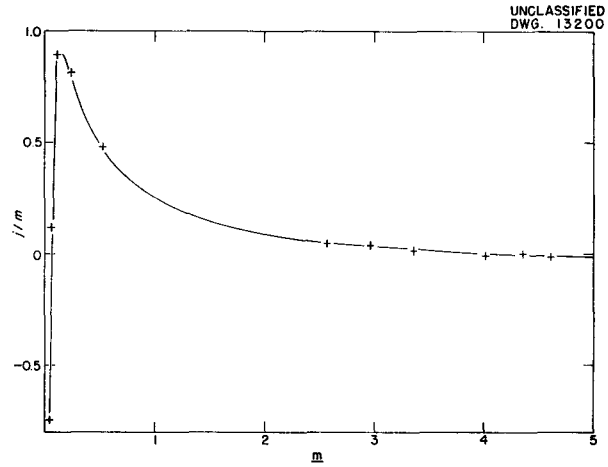

Fig. 1.2 - Values of j/m for UO_2F_2. Curve is calculated for $K_d = 7$, $K' = 1.9 \times 10^{-3}$. + = experimental points ($\nu = 1$).

ANION-EXCHANGE STUDIES IN HYDROCHLORIC ACID SOLUTIONS

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

Some Elements of the First, Second, and Third Groups. Most of the elements of these groups in the periodic table are not expected to form negatively charged complexes with chloride ions and hence should show negligible adsorption by anion-exchange resins. To test this prediction the anion-exchange behavior of the ions Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+; Be^{++}, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}; and Al^{3+}, Sc^{3+}, Y^{3+}, La^{3+}, Yb^{3+} was studied in 7 M and 12 M HCl. The elution constants E were measured with about 40-cm columns (about 0.04 cm^2 cross-sectional area A) by determining the volume V of solution necessary to move a band of the ion in question off the column. The eluents were analyzed by various spot testing techniques.

E was calculated from the equation[10]

$$E = dA/V$$

where d in this case is the length of ion-exchange column.

*It must be pointed out that the constants given are very approximate since, within the precision of the data, moderate changes in K_d can be compensated with changes in K'.

[10] K. A. Kraus and G. E. Moore, "Anion Exchange Studies. I. Separation of Zirconium and Niobium in HCl-HF Mixtures," *J. Am. Chem. Soc.* 73, 9 (1951).

TABLE 1.1

Elution Constants of Various Ions

ION	IN 7 *M* HCl	IN 12 *M* HCl	ION	IN 5 *M* HCl	IN 7 *M* HCl	IN 12 *M* HCl
Li^{+}	2.2	2.3	Ca^{++}		2.5	2.5
Na^{+}	2.6	2.7	Sr^{++}		2.4	2.6
K^{+}	2.4	2.5	Ba^{++}	2.4		
Rb^{+}	2.5	2.4	Al^{3+}			2.6
Cs^{+}	2.4	2.6	Sc^{3+}		1.5	0.7
NH_4^{+}	2.2	2.5	Y^{3+}		2.3	2.5
Be^{++}	2.0	2.2	La^{3+}		2.4	2.6
Mg^{++}	2.3	2.6	Yb^{3+}		2.5	2.6

The results of the experiments are summarized in Table 1.1.

It may be noticed that the elution constants of most of these elements are approximately 2.5, which is probably the maximum value when no adsorption takes place. Since

$$E = 1/(i + D)$$

where i is the fractional interstitial space and D the distribution coefficient (amount per cubic centimeter of bed ÷ amount per cubic centimeter of solution), it can be seen that for $D = 0$, $E = 1/i$ is its maximum value for any column. With these columns, therefore, $i = 1/\sim 2.5 = 0.4$.

With these elements definite adsorption (and hence formation of a negatively charged ion) was observed only for Sc(III), although even for this element adsorption is small ($D = 1/E - i = 0.26$ and 1.0 for 7 *M* and 12 *M* HCl solutions, respectively). Some very slight adsorption, barely outside experimental error, seems indicated for Li(I) and Be(II).

By extrapolation to the last row of the periodic table, the value of $E = 2.5$ is expected for Fa^{+}, Ra^{++}, and Ac^{3+}. Since neither lanthanum nor gadolinium, practically the extremes of the rare earth series, showed any adsorption, the prediction can be made that no rare earth would be adsorbed.

From the large values of the elution constants the conclusion may be reached that these elements are readily separable from those which show strong adsorption, e.g., Fe(III), Co(II), Cu(II), Zn(II), Cd(II), Hg(II), Zr(IV), Hf(IV), Cb(V), etc.

Iron(III). Further studies[11,12] of the adsorption of iron(III) from chloride solutions by Dowex-1 have

[11] G. E. Moore and K. A. Kraus, "Adsorption of Iron by Anion Exchange Resins from Hydrochloric Acid Solutions," *J. Am. Chem. Soc.* 72, 5792 (1950).

[12] K. A. Kraus, G. E. Moore, and F. Nelson, "Anion-Exchange Studies of Metal Complexes," ORNL-1053, *op. cit.*, p. 19.

been carried out, emphasis centering primarily on identification of the adsorbed iron species.

From capacity measurements and comparison of adsorbabilities in sodium chloride, lithium chloride, and hydrochloric acid solutions, it can be concluded that $FeCl_4^-$ is the adsorbed iron species.

Final analysis of the data is now in progress, particularly with respect to evaluation of the stability constants of various iron chloride complexes. A summary report is being prepared.

Gallium(III). Gallium is known to be extractable by ethers from aqueous hydrochloric acid solutions in a manner analogous to iron(III).[13-15] In particular the existence of negatively charged species appeared probable in view of the fact that $HGaCl_4$ was identified[12] as the extracted compound. Since iron, for which $HFeCl_4$ had been identified in the ether phase, had been found to be strongly adsorbed by anion-exchange resins[11] (probably as $FeCl_4^-$), similarly strong adsorption was to be expected for gallium (as $GaCl_4^-$).

In a series of shaking experiments using gallium solutions containing tracer Ga^{72}, the expected great similarity in anion-exchange behavior between Fe(III) and Ga(III) was established as shown in Fig. 1.3. Except in concentrated HCl, gallium is even more strongly adsorbed than iron, and many separations involving gallium (e.g., from aluminum; see above) should be excellent. It is interesting that iron and gallium are adsorbed about equally in concentrated hydrochloric acid, in which the fraction of iron and gallium as MCl_4^- is probably unity, further confirming the previous

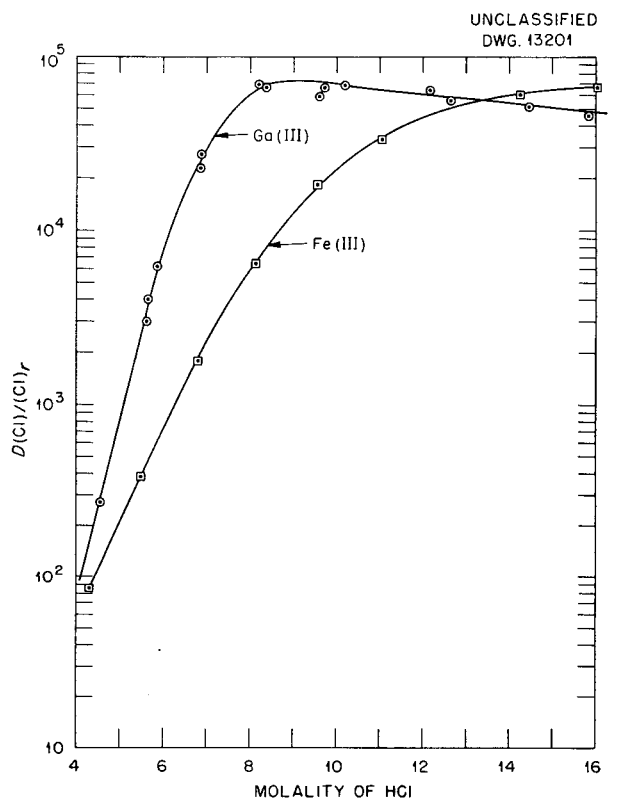

Fig. 1.3 - Adsorption of Ga(III) and Fe(II) on Dowex-1. 40% loading with respect to M(III); D = observed distribution coefficient, resin/solution; (Cl) = chloride concentration of solution; $(Cl)_r$ = chloride concentration of resin (from capacity).

(13) E. H. Swift, "A New Method for the Separation of Gallium from Other Elements," *J. Am. Chem. Soc.* 46, 2375 (1924).

(14) D. C. Grahame and G. T. Seaborg, "The Distribution of Minute Amounts of Material Between Liquid Phases," *J. Am. Chem. Soc.* 60, 2524 (1938).

(15) N. H. Nachtrieb and R. E. Fryxell, "The Extraction of Gallium Chloride by Isopropyl Ether," *J. Am. Chem. Soc.* 71, 4035 (1949).

belief that negatively charged complexes of the same charge are adsorbed about equally.[16]

HYDROLYTIC BEHAVIOR OF METAL IONS

K. A. Kraus and R. W. Holmberg

Thorium(IV). The hydrolysis of thorium(IV) in perchlorate solutions has been re-examined, and further data have been obtained at low thorium concentrations, making the range covered 2.5×10^{-4} to 1.5×10^{-2} *M* Th(IV).

Although, as previously reported, the main hydrolysis reactions (for hydroxyl numbers $n < 0.5$) are

$$Th^{4+} + 4H_2O \longrightarrow Th(OH)_2^{++} + 2H_3O^+ \qquad (K_{12})$$

and

$$2Th^{4+} + 3H_2O \longrightarrow Th_2O^{6+} + 2H_3O^+ \qquad (K_{22})$$

it was found necessary also to use the reactions

$$Th^{4+} + 2H_2O \longrightarrow ThOH^{3+} + H_3O^+ \qquad (K_{11})$$

and

$$2Th^{4+} + 3H_2O \longrightarrow Th_2OOH^{5+} + 3H_3O^+ \qquad (K_{23})$$

for best fit of the data.

Neglecting possible small complexing by chloride ions in the perchlorate solutions (prepared by dissolving $ThCl_4$ in 1 *M* ClO_4^-), the following values of the constants were obtained:

$K_{11} = 5 \times 10^{-5}$ $\qquad$ $K_{12} = 1.5 \times 10^{-8}$

$K_{22} = 1.5 \times 10^{-5}$ $\qquad$ $K_{23} = 9 \times 10^{-9}$

Zirconium(IV) and Hafnium(IV). Earlier work on the hydrolysis of zirconium[17] in chloride solutions is being extended to perchlorate solutions of ionic strength $\mu = 1.0$. A similar investigation of the hydrolysis of hafnium(IV) is underway. No results can be reported at this time.

ZIRCONIUM IN AQUEOUS HCl-$HClO_4$

J. P. McBride and R. W. Stoughton

Recent experiments designed to determine the aqueous complexes formed between Zr^{4+} and Cl^- by measuring the partition of Zr^{95} tracer between TTA-benzene solutions and aqueous chloride solutions (at ionic strength 3.00 and 1.00 *M* H^+) have yielded inconsistent distribution values.[18-20] It has been demonstrated recently that low concentrations of oxidizing impurities in the $NaClO_4$ used in maintaining the ionic strength constant have been the source of the trouble.

Comparison of $NaClO_4$ Preparations. Most of the experiments were performed

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[16] K. A. Kraus and G. E. Moore, "Anion Exchange Studies. III. Protactinium in Some HCl-HF Mixtures: Separation on Niobium, Tantalum, and Protactinium," *J. Am. Chem. Soc.* 73, 2900 (1951).

[17] S. Y. Tyree, Jr., and K. A. Kraus, "Some Observations on the Hydrolytic Behavior of Zirconium," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1949*, ORNL-499, p. 26 (Dec. 6, 1949).

[18] J. P. McBride and R. W. Stoughton, "Zirconium in Aqueous HCl-$HClO_4$," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORNL-870, p. 88 (March 1, 1951).

[19] J. P. McBride and R. W. Stoughton, "Zirconium in Aqueous HCl-$HClO_4$," *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1950*, ORNL-1036, p. 21 (Sept. 10, 1951).

[20] J. P. McBride and R. W. Stoughton, "Zirconium in Aqueous HCl-$HClO_4$," ORNL-1053, *op. cit.*, p. 88.

with solutions prepared using G. Frederick Smith's (G.F.S.) $NaClO_4$ reagent. These experiments were characterized by (1) aqueous-over-benzene distribution values which were self-consistent and consistent with previously determined values attained after 1 day of shaking, and (2) marked increases with time in the aqueous-over-benzene extraction coefficients for systems containing Cl^- when the shaking time was extended over 2- to 22-day periods.

Sodium perchlorate solutions prepared by the neutralization of double-vacuum-distilled G.F.S. $HClO_4$ with Baker's c.p. NaOH gave distribution values which were somewhat higher than expected from previous work but which did not change with time. The higher values may have been due to an impurity in the NaOH or to an impurity leached from the walls of the neutralization vessel.

A $NaClO_4$ preparation using the same acid and Baker's c.p. Na_2CO_3 gave values in line with those expected; when this $NaClO_4$ was used, the distribution ratios did not show a change with extended shaking up to 14 days. Equilibrium was apparently obtained in less than 20 hr under the following conditions: ionic strength (i.e., *M* $HClO_4$ + *M* $NaClO_4$ + *M* NaCl) = 3.00; (H^+) = 1.00 *M*; (Cl^-) = 0 to 2.00 *M*; $Zr(TTA)_4$ (in benzene at start of equilibration) = 10^{-5} *M*; (TTA) = 0.00667 *M* in benzene; equal volumes in both phases; 25°C.

Concerning G.F.S. $NaClO_4$ and Pertinent Extraction Data. Iodometric analysis of a 3 *M* solution of the G.F.S. $NaClO_4$ revealed it to be 0.026 *N* in oxidizing power, as demonstrated by the formation of iodine in a concentrated HCl solution of I^-. Since no iodine was produced by the same salt in dilute acid (1 *N* H_2SO_4), the absence of ClO^-, ClO_2^-, and ClO_2 is demonstrated. Hence the oxidizing agent is believed to be ClO_3^- (No such oxidizing impurity was found in the $NaClO_4$ made from double-vacuum-distilled G.F.S. $HClO_4$ and Baker's c.p. Na_2CO_3.) The mechanism by which the distribution ratio is changed with time as a result of the presence of the oxidizing impurity is not known. However, it is known that both chloride ion and the impurity (in the G.F.S. $NaClO_4$) must be present in order for the effect to be observed and that the effect is largely due to destruction of the TTA. These factors will now be discussed.

Using the impure $NaClO_4$, at 1 *M* $HClO_4$ and 2 *M* $NaClO_4$ (i.e., no NaCl) no change with time after 1 day was observed. Likewise, at 1 *M* $HClO_4$ and 2 *M* NaCl (i.e., no $NaClO_4$) no change with time was observed after about 1 day. In the range of 0 to 2 *M* NaCl the observed change (at any one time) showed a maximum at a little below 1 *M* chloride ion and approached zero at the limits. The maximum was very near 1 *M* Cl^- at shorter times (2 to 4 days) and shifted to lower chloride as the whole effect increased with time. This observation is consistent with the rates depending on the first power of Cl^- and of the impurity (probably ClO_3^-), and with the decrease of the impurity concentration as the reaction proceeds. (As the Cl^- varies from 0 to 2 *M* the initial concentration of the oxidizing impurity varies from 0.0173 to 0 *N*.)

Some benzene-TTA solutions after prolonged contact with aqueous solutions containing Cl^- and G.F.S. $NaClO_4$

were analyzed for TTA content spectrophotometrically. Under the conditions employed the change in distribution ratio was equivalent to a 33% decrease in TTA concentration; the observed TTA decrease was about 30%, showing that the change is at least largely due to destruction of TTA.

The aqueous phases used in the experiments just discussed were subsequently shaken with different benzene solutions containing the original concentration of TTA (i.e., 0.00667 *M*) and showed a distribution ratio (aqueous/benzene) somewhat larger than expected on the basis that the above mentioned change with time was due solely to decrease in TTA concentration. This indicates that simultaneously with the destruction of the TTA, a complexing agent is produced which tends to keep the zirconium in the aqueous phase. Assuming one molecule of such a complexing agent to be produced per molecule of TTA destroyed, a formation constant for the complex formed with Zr(IV) of the order of 1000 is indicated.

Chloride Complexing at Ionic Strength (*M* $HClO_4$ + *M* $NaClO_4$ + *M* NaCl) = 3.00 *M*. Extraction experiments performed with the pure $NaClO_4$ (prepared from Na_2CO_3) gave a value of 1.0 for the formation constant of $ZrCl^{3+}$ at ionic strength 3. This compares favorably with the value of 1.07 found at (H^+) = 3.00 *M*; ionic strength = 3.00. It is 30% lower than the value of 1.3 previously found[18] for the above conditions, i.e., (H^+) = 1.00 *M*. The difference cannot be explained, but the more recent value is supported by a great many more experiments and is believed to be the better value. It should be pointed out that the older value was obtained using $NaClO_4$ prepared from NaOH, and the distribution values obtained for presumably identical conditions were uniformly higher.

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2. NUCLEAR CHEMISTRY

CALORIMETRY OF RADIOACTIVITY

G. H. Jenks

As mentioned in the previous quarterly report,[1] this group has undertaken to determine the C^{14} abundance in a sample of $C^{14}O_2$-$C^{12}O_2$ by means of a gas-density balance, the determination to be made in connection with our study of the decay characteristics of C^{14}. The apparatus required for the measurements has been assembled and perfected, and measurements on the sample will be started soon.

RADIOFREQUENCY SPECTROSCOPY

R. Livingston

Nuclear Spin and Quadrupole Moment of Cl^{36}. The hyperfine structure of the $J = 1 \rightarrow 2$ rotational transition of the molecule $Cl^{36}CN$ has been reported by Townes and Aamodt.[2] In their study the hyperfine structure was only partly resolved but they deduced a spin of 2 and quadrupole moment of -0.0172×10^{-24} cm^2 for the Cl^{36} nucleus. The spin of 2 has caused considerable difficulty in an interpretation of the β decay characteristics of Cl^{36}. This has made it desirable to check the Cl^{36} spin using a different molecule. Such a study has been completed in collaboration with C. Johnson and W. Gordy of the Duke University Physics Department. The $J = 0 \rightarrow 1$ transition hyperfine structure in CH_3Cl^{36} has been completely resolved and measured. The spin has been confirmed as 2, and a somewhat more accurate quadrupole moment value of -0.0168×10^{-24} cm^2 has been determined. This new value is in satisfactory agreement with the value of Townes and Aamodt. The work will be reported in *Physical Review* as a Letter to the Editor.

The method for synthesizing CH_3Cl^{36} was worked on at this laboratory; the measurements were made with the aid of a microwave spectrometer transported and assembled here by the Duke University group. Initial observations were also made here, but, because of spectrometer limitations, the work was transferred to Duke University for final observations.

Three methods for synthesizing methyl chloride were tried. The reaction of methyl *p*-toluenesulfonate on sodium chloride and dimethyl sulfate on sodium chloride were not satisfactory. The final method made use of the reaction of sodium chloride with methyl alcohol and concentrated sulfuric acid in the following manner: A solution of about 16 mg of chlorine as sodium chloride was pumped on and baked to dryness in the 25-ml ampoule shown in Fig. 2.1. The reagent was prepared by mixing 4.5 ml of CH_3OH with 3 ml of concentrated H_2SO_4. The ampoule was removed from the vacuum system and cooled in liquid nitrogen, and 0.075 ml of the reagent was added with a micropipet. The ampoule was then quickly evacuated and sealed at the 8-mm tubing while still cooled in liquid nitrogen. The sealed ampoule was heated in an oven at 175°C for

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[1] G. H. Jenks and F. H. Sweeton, "Calorimetry of Radioactivity," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1951*, ORNL-1053, p. 112 (Oct. 5, 1951).

[2] C. H. Townes and L. C. Aamodt, "Nuclear Spin and Quadrupole Moment of Cl^{36*}," *Phys. Rev.* 76, 691 (1949).

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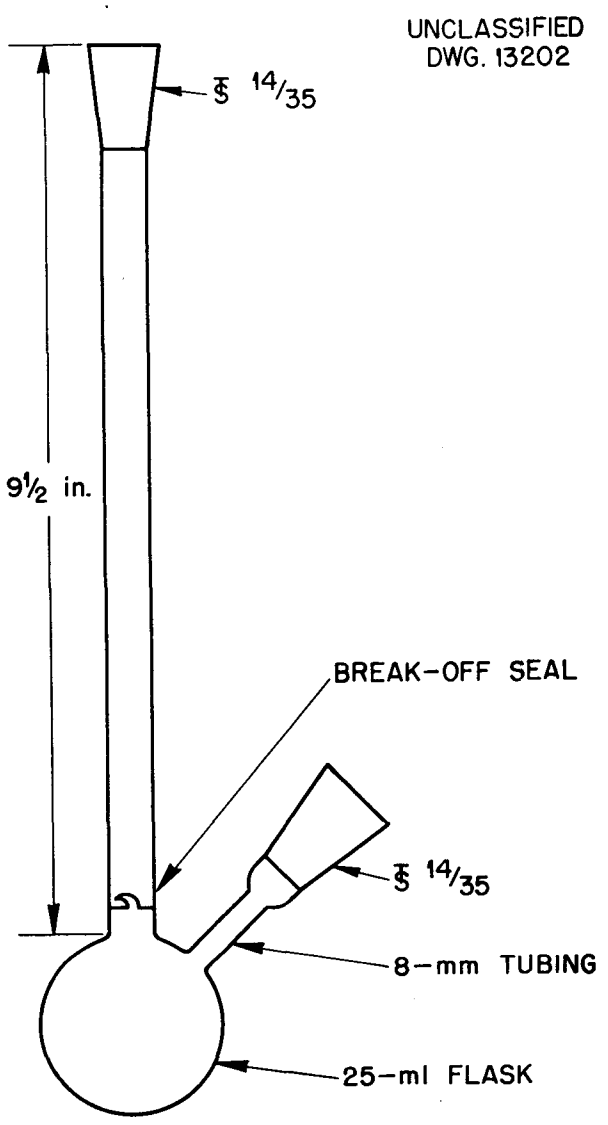

Fig. 2.1 - Ampoule for Synthesis of CH_3Cl^{36}.

1 hr. The ampoule was installed on the spectrometer vacuum line, and it was opened at the break-off seal while cooled in liquid nitrogen, evacuated to remove residual gases and methyl chloride, and then transferred directly to the spectrometer cell at dry ice temperature.

The Half-life of Cl^{36}. The half-life of Cl^{36} can be determined by measuring the disintegration rate of a weighed sample whose isotopic composition is known. The microwave studies on CH_3Cl^{36} reported above offer an excellent opportunity to make an isotopic analysis. The $J = 0 \rightarrow 1$ rotational lines of the CH_3Cl^{35} molecule in an excited vibrational state lie very close to the CH_3Cl^{36} lines. The intensity of the vibrational state lines of CH_3Cl^{35} can be calculated with considerable accuracy and can also be conveniently compared with the CH_3Cl^{36} lines. A preliminary estimate indicates a Cl^{36} abundance of about 0.5%. S. Reynolds of this Laboratory is collaborating by carrying out the disintegration rate measurement.

Pure Quadrupole Spectra of Chlorine Compounds. In the last quarterly report[3] quadrupole coupling values were given for Cl^{35} in various substituted methanes. These are summarized schematically below, in which the values are in megacycles:

CH_2Cl_2 ———— 71.98 megacycles

$CHFCl_2$ ———— 72.99

CF_2Cl_2 ———— 76.90

$CHCl_3$ ———— 76.56

$CFCl_3$ ———— 78.92

CCl_4 ———— 81.18

All chlorine couplings should have a negative sign. Only the magnitude is considered here. The coupling increases by 4.58 megacycles in replacing a hydrogen by chlorine in

[3] R. Livingston, "Radiofrequency Spectroscopy," ORNL-1053, *op. cit.*, p. 106, esp. p. 109.

CH_2Cl_2 and increases by 4.62 megacycles in a similar substitution in $CHCl_3$. The average effect of replacing hydrogen by chlorine is a coupling increase of 4.6 megacycles. Similarly, the average effect of replacing hydrogen by fluorine is a coupling increase of 2.4 megacycles. As explained in the last quarterly report,[4] the coupling change in replacing hydrogen by more highly electronegative chlorine or fluorine is in the expected direction owing to a polarization effect which makes the carbon-chlorine bond less ionic. However, a larger effect would be expected with fluorine since it is more highly electronegative than chlorine. In order to help explain the anomaly, an effort was made to observe chlorine resonances in various bromine-substituted chloromethanes so that the bromine effect could be compared with the chlorine and fluorine effects. Resonances could not be found in the six chlorobromomethanes (CH_2ClBr, $CHCl_2Br$, CCl_3Br, etc.); however, observations were successful on CF_2BrCl. It has one absorption line for Cl^{35} at 38.3418 megacycles, giving a coupling of 76.68 megacycles. The resonance has also been observed in CF_3Cl for Cl^{35} which has one line at 38.0886 megacycles and a corresponding coupling of 76.18 megacycles. If the couplings for the three molecules CF_3Cl, CF_2Cl_2, and CF_2BrCl are compared, it appears that the changes in coupling due to bromine and chlorine substitutions are consistent while those due to fluorine are anomalous. The anomaly can be completely explained by assuming that the introduction of fluorine in the molecule causes some double-bond character in the carbon-chlorine linkage. Double-bond character causes a drop in coupling which compensates for some of the increase due to the fluorine polarization effect. It has been found by electron diffraction that the carbon-chlorine bond distances in chloromethanes shortens when fluorine is introduced in the molecule. Pauling[5] indicates that this is due to a $F^{-}C{=}Cl^{+}$ resonant structure giving rise to about 5% double-bond character.

The CF_3Cl coupling reported above has also been determined by Coles and Hughes[6] by microwave observations on the gas. The coupling in the solid is only 2.4% lower than the gas value.

The quadrupole spectrum of CH_3Cl has not yet been observed, but an extrapolated value for it may be obtained in two ways. Using the 4.6-megacycle value for a chlorine substitution with the CH_2Cl_2 coupling gives a predicted value of 67.4 megacycles while extrapolating from the CF_3Cl value using 2.4 megacycles per fluorine atom gives 69.0 megacycles. These values are in reasonable agreement, but they fall too far below the microwave value[7] for gaseous CH_3Cl of 75.13 megacycles. Several reasons for this discrepancy have been considered without success. Crystalline field effects would not be expected to perturb the values this much. If crystalline fields produced such large random variations in coupling constants the mass of data on the substituted methanes should not have

(4) *Ibid.*, esp. pp. 110, 111.

(5) L. Pauling, *The Nature of the Chemical Bond*, 2d ed., p. 236, Cornell University Press, Ithaca, N. Y. (1944).

(6) D. K. Coles and R. H. Hughes, "Microwave Spectrum of CF_3Cl," *Phys. Rev.* 76, 858 (1949).

(7) W. Gordy, J. W. Simmons, and A. G. Smith, "Microwave Determination of the Molecular Structures and Nuclear Couplings of the Methyl Halides," *Phys. Rev.* 74, 243 (1948).

correlated so well. If a systematic effect resulted from the solid the CF_3Cl value would not have compared so favorably with the gas value. It is noted that an explanation that would allow a systematic change in the couplings upon going to molecules with more and more hydrogen might be desirable. Hydrogen bonding has been discounted. The effect of interactions between the chlorine spin system and lattice vibrations has been considered. Dehmelt and Krüger[8] have observed that the chlorine resonance frequency in solid trans-dichloroethylene increases with decreasing temperature. The effect has been ascribed by them to an interaction between the spin system and torsional lattice vibrations. It has been decided to remeasure the couplings mentioned above at lower temperatures. One such measurement, on CH_2Cl_2, has been completed at liquid hydrogen temperature, and the observed frequency increased from 35.9912 to 36.2325 megacycles, corresponding to a coupling increase from 71.98 to 72.47 megacycles. Although the increase is in the right direction it is too early to predict if it enough. It will be necessary first to complete measurements on the other compounds at liquid hydrogen temperature and possibly at liquid helium temperature. It is interesting to note that if the CF_3Cl coupling increases at lower temperatures it may be in even better agreement with the gaseous value.

The observed coupling for solid chlorine, 108.5 megacycles, and its comparison with the atomic beam value mentioned in the last quarterly report[9] has been published.[10]

The quadrupole spectrum apparatus has been rebuilt so that measurements can be more easily made at liquid hydrogen and helium temperatures. The improvement in sensitivity, owing to a more favorable Boltzmann distribution of energy levels, may make it possible to observe resonances at much lower frequencies than is now possible. The new possibilities include nitrogen and boron compounds.

NEUTRON DIFFRACTION STUDIES

H. A. Levy and S. W. Peterson

Single-Crystal Neutron Crystallography. *Introduction.* Neutron crystallography to date has employed the powder method for collection of data. In this method the sample takes the form of a packed mass of microscopic crystallites in random orientations. With available neutron flux, the collection of data is severely limited by low intensity of diffracted neutrons and by poor resolution of one diffracted line from another; the latter is associated with compromises in the design of the spectrometer necessary to make optimum use of the limited neutron flux available. In practice these limitations have restricted feasible crystal structure problems to crystals of high symmetry (tetragonal or higher), small cell dimensions, and few parameters.

These limitations largely disappear in an experimental method in which the sample is a single crystal.

[8] H. G. Dehmelt and H. Krüger, "Quadrupol-Resonanzfrequenzen von Cl- und Br-Kernen in Kristallinem Dichloräthylen und Methylbromid," *Z. Physik.* 129, 401 (1951).

[9] R. Livingston, *op. cit.*, esp. p. 110.

[10] R. Livingston, "The Pure Quadrupole Spectrum of Solid Chlorine," *J. Chem. Phys.* 19, 803 (1951).

Greatly increased resolution without intensity loss arises from the fact that observation of a reflection depends on adjustment of three parameters—two angles of orientation for the crystal specimen and one for the detecting counter—rather than only the latter as in the powder method. The following further advantages of single crystal methods may be listed:

Reduced Sample Size. In the powder method only that fraction, of the order of 1%, of the random array of crystallites which are correctly oriented contribute to observation of a given reflection. In a single crystal method the entire sample, when correctly oriented, contributes to the reflection. Sample sizes might thus be reduced 100-fold.

Reduced Diffuse Background. When incoherent scattering contributes a heavy diffuse background to a diffraction pattern, this background would be reduced in proportion to the mass of the sample, that is, of the order of 100-fold. The necessity for deuteration of hydrogen-containing materials might well be eliminated.

Individual Reflections Observable. As in X-ray crystallography, all reflections can be individually observed in most single crystal methods, whereas, with powders, reflections occurring at the same Bragg angle are never resolvable.

In spite of the foregoing advantages, single-crystal neutron crystallography has been neglected in favor of the powder method because of the existence of serious uncertainty in the interpretation of single crystal intensity data. This uncertainty arises from the phenomenon known as extinction. Briefly, this phenomenon enters as follows: For a sufficiently small crystal rotated in a beam of radiation (X-ray or neutron) with angular velocity ω the integrated power in a Bragg reflection E is given by

$$E = I_0 QV/\omega \qquad (1)$$

where I_0 is the incident intensity, V the volume of the crystal, and Q a quantity calculable from the structure of the crystal and the experimental arrangement. The determination of Q is the object of the measurement. In this expression it is assumed that a negligible fraction of the incident intensity is reflected, so that all parts of the crystal are uniformly irradiated, a valid assumption if V is small enough. If this is not true, two types of deviations may occur, both of which decrease the value of E. In perfect crystals, in which there is phase coherence of radiation impinging on different parts of the crystal, this decrease is called *primary extinction*; in mosaic crystals, in which phase coherence is lacking, the phenomenon is called secondary extinction. In real crystals, both phenomena occur, although the latter is usually predominant. When either type of extinction is important, the exact calculation of E is a complex matter, depending on the crystal size and shape, and, in the case of mosaic crystals, state of perfection or mosaic spread.

A theoretical examination of the importance of extinction in neutron crystallography has been made by Bacon and Lowde.[11] These workers extended the usual formulas of X-ray

[11] G. E. Bacon and R. D. Lowde, "Secondary Extinction and Neutron Crystallography," *Acta Crystallographica* 1, 303 (1948).

diffraction to apply to nonabsorbing or slightly absorbing crystals (the situation applicable to the neutron case) and applied their results to numerical computation for the strong reflections of magnesium oxide to obtain the deviation of E from the simple QV expression. They concluded that in crystals sufficiently large to use for neutron crystallography (i.e., large enough to permit the observation of many reflections with a single specimen) secondary extinction would be of overriding importance and would preclude the possibility of determining the quantity Q from experimental data. They further estimated that crystals small enough to permit determination of Q could be no larger than 0.1 mm in thickness, much too small for use with monochromatic neutron beams then available.

A single crystal method of limited applicability was later proposed by Lowde.[12] This procedure employed a polychromatic neutron beam directly from a nuclear reactor. The elimination of the monochromating step permitted sufficient increase in intensity (largely by relaxing the severe beam collimation achieved by Bragg reflection) to permit observation of strong reflections from a single crystal of volume as small as 1 mm^3. This use of a polychromatic beam, however, introduces the serious disadvantage of making it impossible to observe individually the various orders of a reflection, a feature which would seriously limit applicability of the method.

We have been led to question the validity of the severe size restriction put forth by Bacon and Lowde by the following considerations:

1. Their consideration was based on the strongest reflection from magnesium oxide. The severity of secondary extinction is steeply dependent on the reflecting power of the crystal plane in question, so that for more weakly reflecting planes the extinction corrections would be much smaller and correspondingly the size limitations less severe.

2. It is often possible in X-ray crystallography to make approximate corrections for extinction by use of a simple formula involving one empirically determined parameter for the crystal specimen used. The same procedure should be applicable, at least in some instances, in the neutron case.

3. The introduction of metal crystal monochromators has made available monochromatic neutron beams more intense by a factor of about 8 than those considered by Bacon and Lowde, making possible the use of smaller crystals than was formerly thought feasible.

We have made an empirical test of the feasibility of utilizing single-crystal neutron intensity for crystal structure studies by measuring reflections from several specimens of a crystal of known structure, NaCl. The results, given in Table 2.1 and 2.2 have been decidedly encouraging. Relative observed intensities were predictable to ±10% without extinction corrections with a specimen volume as large as 7.3 mm^3, and this

[12] R. D. Lowde, *A Technique for Single Crystal, Neutron Diffraction Analysis*, Report No. A.E.R.E. G/R 577, Harwell, England (1950).

TABLE 2.1

Experimental and Theoretical Intensities from a Single Sodium Chloride Crystal

Size of specimen: 0.0105 g, approximately 1.5 x 1.7 x 2.4 mm parallel to cube axes

Rotation axis: [011], in plane of the two larger dimensions

INDICES	CALCULATED $(E\omega/I_0\lambda^3 m) \times 10^{-4}$	OBSERVED $(E/m) \times 10^{-4}$	$(I_0\lambda^3/m) \times 10^{16}$
111	2.58	30.2	11.7
200	9.45	105.2	11.2
220	6.29	73.2	11.6
311	1.20	15.3	12.7
222	4.85	61.3	12.6
400	4.02	47.5	11.8
331	0.828	9.90	12.0
422	2.77	35.6	12.8
333	0.630	8.04	12.8
511	0.630	8.65	13.7
440	2.34	28.8	12.3
600	2.10	24.9	11.8
442	2.10	26.8	12.7
533	0.416	6.07	14.6
622	1.75	21.9	12.5
444	1.61	21.1	13.1
711	0.358	4.52	12.6
551	0.358	4.56	12.7
553	0.312	4.44	14.2

agreement is somewhat improved with a small extinction correction. If this case proves to be typical, the single crystal method will be quite practical for crystal structure studies by neutron diffraction.

Experimental. Three specimens of NaCl of different sizes, cleaved from a single synthetic large crystal, were mounted with wax on the end of a glass fiber set in a goniometer head in a manner quite similar to standard X-ray crystallographic practice. The desired crystal zone axes were brought parallel to the rotation axis of the spectrometer by maximizing the intensity of several neutron reflections as a function of the rocking adjustments of the goniometer head. The procedure for measuring reflection intensities was as follows: The correct counter setting for a particular reflection was computed from the neutron wavelength and the known interplanar spacing and the counter angle so adjusted. The crystal was then rotated about the chosen zone axis until the reflection reached maximum counting rate. The crystal and counter were then geared together and the entire reflection was scanned, the crystal usually rotating at the rate of 8°/hr and the counter synchronously at 16°/hr. The total number of counts in the reflection was recorded by means of a scaler and register, and the background rate, with crystal and counter just out of the reflecting position, was similarly recorded. Simultaneously the shape of the reflection was automatically recorded by means of a count-rate meter and strip-chart recorder. After the correct correlation of crystal and counter had been found for one reflection in a zone, that for all the remaining reflections in that zone could be computed; these computed settings were found to be correct experimentally.

Results. Table 2.3 presents the results of the measurements for one specimen, the smallest, for which extinction corrections should be least important. For comparison with theory, the appropriate expression,

TABLE 2.2

Comparison of Intensities from Three Sodium Chloride Specimens

Rotation axis: [011] in plane of the two larger dimensions

INDICES	INTENSITY [(counts/g) x 10^{-4}]		
	SMALL SAMPLE, 10.5 mg, 1.5 x 1.7 x 2.4 mm	MEDIUM SAMPLE, 15.8 mg, 0.6 x 2.5 x 4.5 mm	LARGE SAMPLE, 72.9 mg, 1.6 x 4.0 x 4.6 mm
111	30.2	31.8	28.9
200	105.2	100.3	78.3
220	73.2	81.0	
400	47.5	47.4	
331	9.90	10.2	
422	35.6	34.1	
333	8.04	7.8	7.22
511	8.65	7.6	
440	28.8	28.7	26.0
600	24.9	25.4	17.5
533	6.07	5.0	
711	4.52	4.3	

adapted from the standard X-ray expression, is

$$E_{hkl} = \frac{I_0 \lambda^3 m N_A N F_{hkl}^2}{\omega M Z \sin 2\theta} \qquad (2)$$

in which E_{hkl} is the number of neutrons diffracted into Bragg reflection (hkl), I_0 is the incident intensity, λ the neutron wavelength, m the mass of the specimen, N_A Avogadro's number, N the number of unit cells of crystal per unit volume, F_{hkl} the structure factor for the reflection, ω the angular velocity of rotation of the crystal, M the molecular weight, Z the number of molecules per unit cell, and θ the Bragg angle. Scattering amplitudes used for Na and Cl were those given by Shull and Wollan.[13] Individual temperature factors,

$$\exp\,[-B(\sin\theta/\lambda)^2],$$

were used for Na and Cl, with the values

$$B_{Na} = 1.55 \times 10^{-16}$$

and

$$B_{Cl} = 1.25 \times 10^{-16}$$

given by Waller and James.[14] The

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

[14] I. Waller and R. W. James, "On the Temperature Factors of X-Ray Reflexion for Sodium and Chlorine in the Rock Salt Crystal," *Proc. Roy. Soc. London* A117, 214 (1927).

TABLE 2.3

Yields of Technetium from Individual Runs

RUN NO.	GROSS BETA IN CRUDE Tc PRODUCT* (mc)	TOTAL Tc PRODUCT BY ANALYSIS (mg)	TOTAL Tc PURIFIED (DISTILLED) (mg)
Chalk River			
1			118
2			209
3	35	520	471
4	38	678	
5	35	517	
6	76	688	
7	51	776	
8	95	992	
9	91	980	
10	66	791	
11	134	1,474	
12	122	815	
13	123	1,093	
14	151	1,351	
15	129	1,533	
16	54	612	
17		1,907	
18	65	1,680	
		16,407	
Hanford			
1	28	467	
2	57	436	
3		431	
4	35	782	
		2,116	
Total		18,850	

*Specific activity of $Tc^{99} \approx 10$ mc per 1000 mg.

second column of the table lists values of $E_{hkl}\omega/I_0\lambda^3 m$ calculated from Eq. (2). The third column lists measured values of E_{hkl}/m, and the fourth column the appropriate ratio giving experimental values of $I_0\lambda^3/\omega$. The constancy of these values is a test of the applicability of expression (1) and indicates that the specimen is behaving very nearly as an ideal crystal. Actually there appears to be a slight tendency for the values from strong reflections to be lower in proportion to the intensity of the reflection. This is in accord with the approximate expression for the effect of secondary extinction,[15]

$$I_{corr} = I_{obs}/[1 - gI_{obs}]$$

Evaluation of the correction by a graphical procedure gave the corrected value* of $I_0\lambda^3/\omega$ of 13.0×10^{-16}. The corresponding value* of I_0 is 3.8×10^8 counts/min/cm^2. This value is characteristics of the central, most intense portion of the neutron beam and is consistent with that obtained from measurements on nickel powder.

Table 2.2 shows the comparison of intensities obtained from the three crystal specimens. The quantities listed are E_{hkl}/m, the number of neutrons counted per gram of crystal, corrected for variations in incident beam intensity. It is seen that the strongest reflections in the larger crystal show a tendency to be low, indicating greater extinction in these specimens. The greatest effect is, however, only 25%.

Conclusion. The degree of conformity of the small crystal specimen to ideal behavior is ample for structure determination purposes. Even the

[15] Internationale Tabellen zur Bestimmung von Kristallstrukturen, rev. ed., vol. II, p. 261, Ann Arbor, Mich., 1944.

*This value is associated with a reading of the beam monitor of 3.45×10^5 counts/min.

larger specimens do not show serious departures from ideality, except for the strongest reflections. If crystals encountered in structural studies behave similarly, there is every reason to believe that single crystal methods will be feasible and will open complex structures to attack by neutron diffraction. Inasmuch as we have found crystals much larger than the limiting size of Bacon and Lowde[11] to behave nearly ideally, a critical evaluation of their theoretical treatment seems to be in order.

Work in Progress. *Ammonium bromide:* A brief description of the structural study of deuteroammonium bromide, reported in the last quarterly report,[16] has been submitted for publication as a Letter to the Editor in *Physical Review.*

Ammonium chloride: Diffraction data from deuteroammonium chloride havebeen collected and preliminary computations have been made with the help of Barbara McGill of the Mathematics Panel. Some single crystal data from ordinary ammonium chloride have also been collected.

Vitreous silica (with W. O. Milligan, Rice Institute): A radial distribution integral has been computed from neutron scattering data. Interpretation of this integral is now in progress. A complete description will probably be the subject of a special report.

Potassium bifluoride: Extensive single crystal data have been collected and their interpretation is nearly complete.

Platinum oxide and palladium oxide (with J. Waser, Rice Institute): Neutron diffraction data from powdered platinum and palladium oxides have been collected. Interpretation is underway.

Br_2 - BrO_3^- EXCHANGE USING RADIOACTIVE Br^{82}

O. E. Myers and R. W. Stoughton

The kinetics of the Br_2^* - BrO_3^- isotopic-exchange reaction are being studied by means of 36-hr Br^{82} tracer using a method described previously.[17] More than 150 runs have been followed for a maximum period of about three weeks. The expected exponential law was not followed very well; subsequent work has shown that this is a result of the slow formation of equilibrium amounts of HBrO, which undergoes rapid exchange with Br_2.

Neither the rate of formation of HBrO, which is no doubt related to the exchange rate, nor the amount present at equilibrium is sufficiently well known to permit an unambiguous interpretation of the data at the present time. Recent efforts have been directed toward an indirect determination of the HBrO concentration in the system. Skew Y tubes were constructed as shown (see Fig. 2.2) with 20 ml of standard acidified Br_2^* solution in one arm and 20 ml of a known concentration of $HBrO_3$ in the other; the tubes were frozen, evacuated, and sealed. In the vertical position either arm could be placed in front of a counter; in the horizontal position the solutions could be efficiently stirred, without being mixed, and large liquid surfaces

[16] H. A. Levy and S. W. Peterson, "Neutron Diffraction Study of the Crystal Structure of Ammonium Bromide," ORNL-1053, *op. cit.*, p. 93.

[17] S. M. McElvain and J. F. Vozza, "Piperidine Derivatives. XX," *J. Am. Chem. Soc.* 72, 897 (1950).

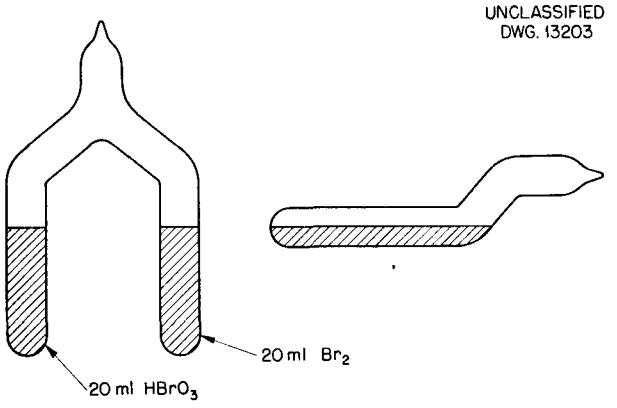

Fig. 2.2 - Y Tube for Determining Br_2-BrO_3 Exchange Using Radioactive Br^{82}.

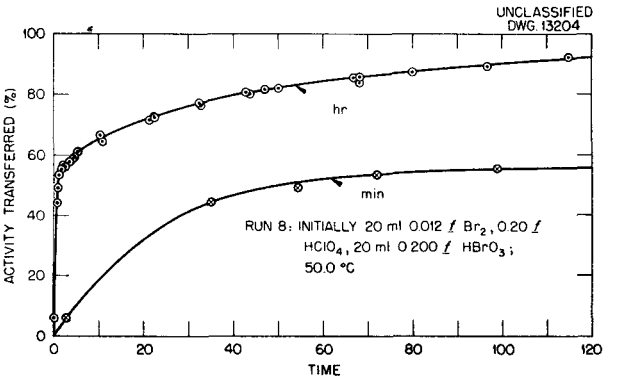

Fig. 2.3 - Rate of Appearance of Br^{82} in $HBrO_3$ Arm. (See Fig. 2.2.)

were presented. Attainment of vapor phase equilibrium was very much faster than the attainment of exchange equilibrium, so that the thermodynamic and radiochemical activities of the species Br_2 remained the same in both arms. An anthracene scintillation counter was constructed so that counting operations could be performed in the laboratory through the walls of a thermostat.

The radioactivity in the BrO_3^- arm is the sum of the known Br_2 activity and that of HBrO and $HBrO_3$. If a correction is made for bromate activity on the basis of the exponential exchange law any "excess" radioactivity must be due to $HBrO^*$, at the same specific activity as that of Br_2^*. Thus the amount of HBrO may be determined. Then, for the equation

$$HBrO_3 + 2Br_2 + 2H_2O = 5HBrO$$

the equilibrium constant can be found. All standard free energies in this equation are known except that for $HBrO_3$. The first series of Y-tube experiments yielded results (shown in Fig. 2.3) which were insufficiently sensitive for a precise determination of $\Delta F°$ ($HBrO_3$). The value is of the order of 5000 cal/mole, however, in agreement with Latimer's estimate.[18]

The calculations are most involved, and hence it has not been considered worth while to carry them out in detail in the absence of reasonably accurate knowledge of the concentrations of all the principal species involved. There is evidence that the exchange rate depends upon the first power of the concentrations of HBrO and $HBrO_3$. Empirically, the experimental rate law for an ionic strength up to 1.5 is

$$\text{Rate} = k(Br_2)^{0.27\pm0.16}\,(BrO_3^-)^{1.4\pm0.3}\,(H^+)^{1.4\pm0.2}$$

The value of k at 25°C is of the order of 0.01 hr^{-1}, and the activation energy is between 18 and 22 kcal/mole. This agrees very well with the equation reported by Betts[19] for an independent investigation at ionic strength 1.75.

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[18] W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, New York, 1938.

[19] R. H. Betts, private communication.

Construction is nearly completed on an automatic "exchange reactor" which will provide almost continuous monitoring of the Y-tube system. It is felt that it will then be possible to obtain adequately precise data so that a detailed analysis of the exchange kinetics may be made.

The counting equipment has been designed to permit studies at elevated temperatures.

RESULTS OF THE FIRST LARGE-SCALE SEPARATION OF TECHNETIUM

G. W. Parker and W. J. Martin

After more than a year a large-scale isolation program of the fission-produced synthetic elements from Chalk River metal wastes[20] has been partially completed, resulting first in a surprising yield of Tc^{99} of more than 95% of the calculated 19 g possible. Final purification is being rapidly completed, and a limited number of research problems involving the physical and chemical properties of technetium are being started.

Requests from other laboratories for moderate amounts of pure compounds are being favorably considered provided the intended research does not duplicate that already undertaken.

Technetium Characterization Program at ORNL. At present only a modest amount of research on technetium on a macro scale is planned. The radioactivity of the isotope amounts to only a mild danger since the soft betas (0.3 Mev) are completely shielded by a very thin cover such as a watch glass. On the other hand, a serious contamination hazard is present in the 10 mc/g specific activity.

Owing to the relatively high specific activity it is intended that principally problems requiring relatively larger quantities of the element will be undertaken here. A brief outline of the proposed work* is given below:

1. Methods of separation from radiochemical wastes.
2. Physical properties of the element and its principal oxides, including melting points, vapor pressures, and optical absorption spectra.
3. Physical-chemical properties, e.g., magnetic susceptibilities and kinetics of isotopic exchange reactions.
4. Nuclear properties, e.g., fission yield, capture cross-section, and nuclear magnetic moment.

Other fields of obvious interest which are not being investigated are:

1. Biological behavior and hazards.
2. Metallurgy and thermionic properties.
3. Dry chemistry and X-ray investigations.

[20] G. W. Parker, G. M. Hebert, P. M. Lantz, W. J. Martin, and G. E. Creek, " New Hot Laboratory Facilities and Flow Plan for the Recovery of Fission Products and Neptunium from ORNL Redox Pilot Plant CR Wastes, *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950, Part I, Chemical Research,* ORNL-685, p. 62 (June 16, 1950).

*Includes, besides that of the authors, work known to be in progress by G. E. Boyd, R. Livingston, C. M. Nelson, J. W. Cobble, and W. T. Smith.

Summary of the Yields of Technetium from Individual Runs. Using the precipitation method previously described[21] based on perchlorate carrying of technetium as tetraphenyl arsonium pertechnetate, all locally available high-level radiochemical wastes have now been processed with a resulting yield of about 18 g of technetium.

The estimated yield (95% of calculated) remains subject to correction since it is based only on radiochemical methods. The Radiochemical Group of the Analytical Chemistry Division has analyzed each of the sulfuric acid solutions of the tetraphenyl compounds, first by a long rhenium sulfide—carrying process suggested by the authors and also by a short chloroform extraction method[22] adapted by the analysts.[23]

The variations in the yield between runs is attributable to the temporary holdup in the large vessels. The lower yield from the Hanford source material is due partly to the higher level in the Chalk River wastes as well as to a twofold dilution of the waste.

Included in Table 2.3 are the observed gross beta activities obtained on each product fraction (usually a volume of strong sulfuric acid of 5 to 6 liters), of which the richer cuts always exhibit a green coloration. The remarkable decontamination from mixed fission products (2000 to 3000 curies) is apparent.

Few data are available on the overall yield after final purification, which is now essentially sulfuric acid distillation. Only on run 4 is a yield (approximately 93%) indicated.

Observations on the Solubility of Potassium Pertechnetate ($KTcO_4$) and Tetraphenyl Arsonium Pertechnetate [$(C_6H_5)_4AsTcO_4$]. Since it might be expected that the commercial methods[24] for the purification of limited amounts of rhenium should be adaptable to the problem of preparing pure compounds of technetium, some of the results[25] from the extensive work at the University of Tennessee Department of Chemistry on rhenium have been applied in the hope that the sparingly soluble alkali metal salts of technetium might be found useful.

A study of the solubilities of these compounds as well as of their relative value for radiochemical decontamination has been initiated and some results for the potassium salt are reported. Smith and Long have summarized the solubilities of the corresponding alkali metal salts of perrhenic acid as follows:

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(21) G. W. Parker and W. J. Martin, "Coprecipitation of Pertechnetate (TcO_4^-) and Various Anions by Tetraphenyl Arsonium Chloride," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORNL-870, p. 47 (March 1, 1951).

(22) S. Tribalat, "Extraction and Determination of Traces of Rhenium, Especially in Molybdenites," *Anal. Chim. Acta* 3, 113 (1949).

(23) E. I. Wyatt, "Radioisotope Analysis," *Analytical Chemistry Division Quarterly Progress Report for Period Ending June 26, 1951*, ORNL-1113, p. 52 (Nov. 27, 1951).

(24) B. S. Hopkins, *Chapters in the Chemistry of the Less Familiar Elements*, vol. II, Chap. 20, Stipes Publishing Co., Champaign, Ill., 1939.

(25) A. S. Goldin, *A Radioactive Tracer Investigation of Rhenium Chemistry*, Thesis, University of Tennessee, March, 1951.

SALT	SOLUBILITY AT 30°C (moles/100 grams H_2O x 10^2)
$LiReO_4$	140
$NaReO_4$	53.2
NH_4ReO_4	3.25
$KReO_4$	0.508
$CsReO_4$	0.287

The insolubility of the cesium salt reported[26] is exceeded among all the metal salts of perrhenic acid only by silver and thallium(I).

In Fig. 2.4 the results of the solubility study of potassium pertechnetate are compared with those of a similar study of the perrhenate ion by Goldin.[25] The solubility product constants obtained at 27°C (0.44) and at 7°C (0.14) show the expected decrease and thereby the advantage of crystallizing the salt at lower temperatures. Incidentally, in one crystallization of $KTcO_4$ a decontamination from Ru^{106} by a factor of 40 was obtained. The potassium salt is observed to crystallize in a blunt white tetragonal form, probably isostructural as usual with $KReO_4$. The next step in this solubility study will be made with the cesium salt.

Tetraphenylarsonium perrhenate, unquestionably a satisfactory gravimetric form for the determination of rhenium, has been used by the authors[27] in a quantitative measurement of the specific activity of technetium. Under the conditions of the precipitation, with excess reagent, the unprecipitated portion is quite small (Fig. 2.5); nevertheless, the solubility of the technetium compound is relatively greater and was the object of a further investigation. In Fig. 2.5 the temperature coefficient of solubility for both the rhenium and technetium compounds is found to be negligible up to 50°C with an exponential rise to 100°C. On a semilog scale a straight-line extrapolation was used to give the missing point on the technetium curve at 100°C. A significant temperature coefficient[28] has been found in complex solutions such as the redox wastes and in solutions containing acetate ion. An increased solubility in the presence of acetate ion is also reported by Goldin.[25]

[26] W. T. Smith, Jr., and S. H. Long, "The Salts of Perrhenic Acid. I. The Alkali Metals and Ammonium," *J. Am. Chem. Soc.* 70, 354 (1948).

[27] G. W. Parker, "A Re-evaluation of the Half-life of Tc^{99}," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORNL-870, p. 45 (March 1, 1951).

[28] R. W. Atteberry, private communication.

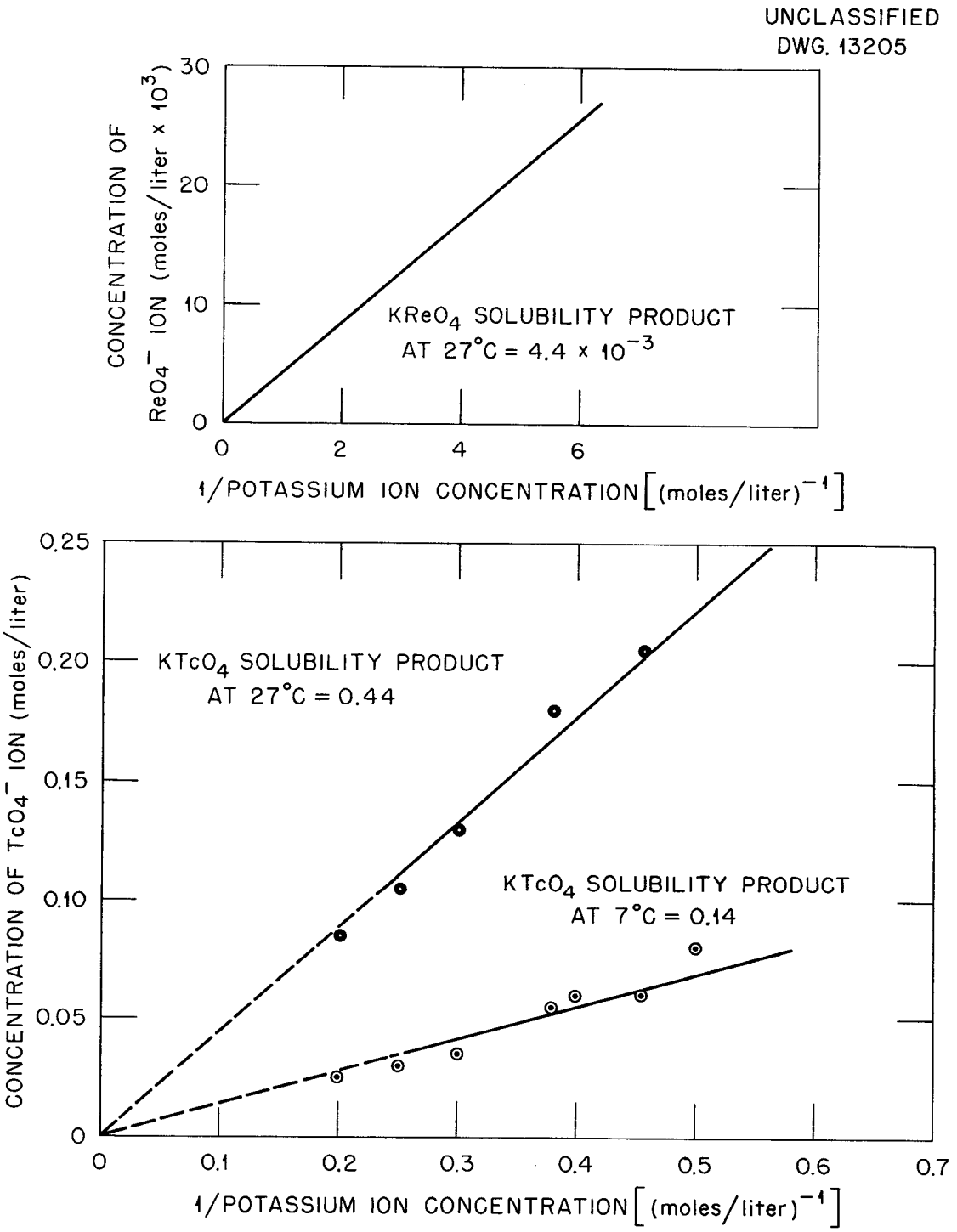

Fig. 2.4 - Solubility Products. Top, Goldin's data for perrhenate ion; bottom, our data for pertechnetate ion.

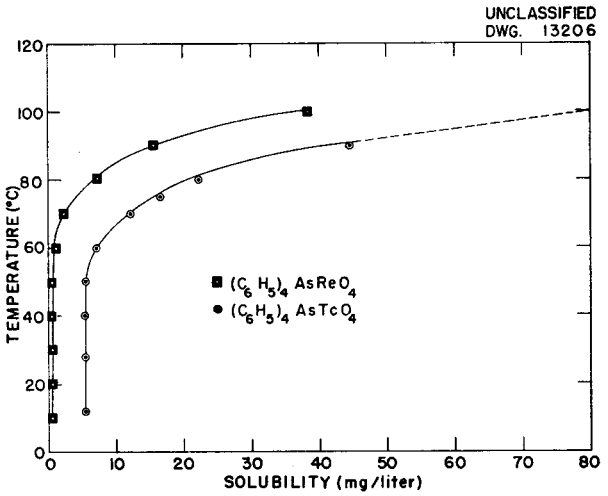

Fig. 2.5 - Relative Depressed Solubilities of the Compounds $(C_6H_5)_4AsTcO_4$ and $(C_6H_5)_4AsReO_4$. Molar ratio of $(C_6H_5)_4AsCl$ to ReO_4^- or TcO_4^- = 17.

CHEMISTRY OF TECHNETIUM: PREPARATION OF PURE TECHNETIUM METAL

C. M. Nelson G. E. Boyd
J. W. Cobble W. T. Smith, Jr.*

The availability of milligram quantities of technetium has led to the initiation of further studies on the chemistry of technetium in addition to those previously reported.[29] The object of a second study will be the characterization of the valence states of technetium compounds in aqueous solution by measurement of their oxidation-reduction potentials. Such a thermodynamic study is a necessary prerequisite to understanding the solution chemistry of this element.

During the past quarter some effort has been devoted to the preparation of pure technetium metal to be used as a starting material for compound preparation. Approximately 600 mg of pure metal has been prepared.

The technetium was received[30] in 8 to 10 liters of process crude consisting of a mixture of tetraphenyl arsonium pertechnetate plus tetraphenyl arsonium perchlorate in concentrated sulfuric acid.[31] No successful way has yet been found to obtain the technetium directly from this solution. Sulfide precipitation, for example, was feasible only in dilute (2 to 3 *N*) sulfuric acid solutions, but, unfortunately, the tetraphenyl compounds in the starting mixture precipitate at this dilution. Destructive distillation of the tetraphenyl compounds by refluxing the concentrated sulfuric acid solution was found to be laborious and time-consuming.

Thus far the most successful method for separating technetium from the process crude has been that of electrolytic reduction in the original sulfuric acid solutions. Roughly liter volumes were electrolyzed for two days with platinum electrodes at a potential of about 3 volts using a current density of about 10 ma/cm^2. A jet black material was formed in

*Professor of Chemistry, University of Tennessee; ORNL Consultant.

[29] C. M. Nelson, G. E. Boyd, and W. T. Smith, "Chemistry of Technetium: Measurement of Magnetic Susceptibilities," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1951*, ORNL-1053, p. 51 (Oct. 5, 1951).

[30] We are indebted to G. W. Parker and his group for supplying the starting tetraphenyl arsonium solutions containing about 1 g of technetium.

[31] G. W. Parker and W. J. Martin, "Coprecipitation of Pertechnetate Ion (TcO_4^-) and Various Ions by Tetraphenyl Arsonium Chloride," ORNL-870, *op. cit.*, p. 47.

suspension. This material, which can be separated by filtering through a fine sintered glass disk, probably consists of a mixture of technetium metal, technetium oxide, carbon, and absorbed organic material. The technetium can then be distilled from the gross electrodeposit by transferring the latter to a distilling flask, cautiously adding nitric, perchloric, and sulfuric acids and then heating gently.* After the precipitate goes into solution the temperature can be raised to distil over first the perchloric and then the sulfuric acid. The distillation was carried to near dryness. It is best to collect the distillate in ammonium hydroxide, since warm solutions of concentrated perchloric acid appear to lose technetium by volatilization.

The distillate was diluted and made 2 *N* in acid, bromine water was added, and H_2S was bubbled in. The precipitation of the technetium sulfide is best effected by an initial formation in cold solutions, followed by boiling on a water bath during the final stages. The insoluble sulfide was collected by centrifuging and was washed in 2 *N* sulfuric acid. Almost always small quantities of elemental sulfur were occluded which, if desired, can be removed by solvent extraction or by heating in hydrogen.

The metal can be prepared by reduction of the sulfide with hydrogen.[32] However, we have found this to be slow and generally unsatisfactory. Since both the sulfide and metal are black, there is no easy way to determine when the reduction is complete.

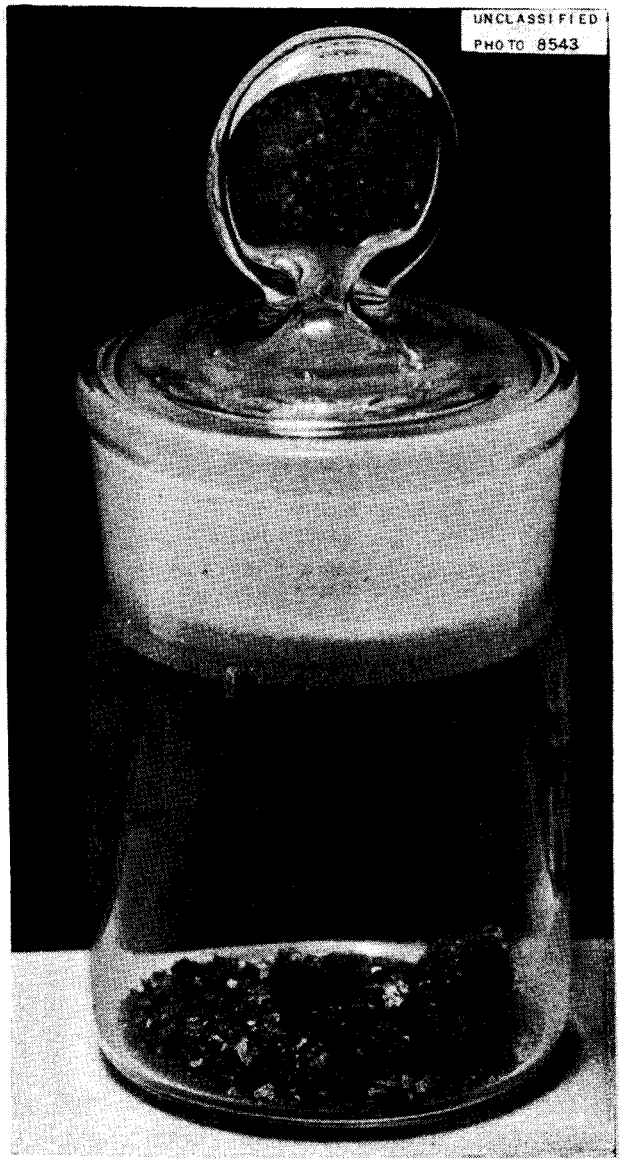

Fig. 2.6 - Pure Technetium Metal, 554 mg.

Technetium metal can be prepared readily from ammonium pertechnetate by reduction with hydrogen at 300 to 400°C. The moist technetium sulfide precipitate was first dissolved with ammonium hydroxide and hydrogen peroxide and the solution evaporated

*This mixture froths considerably owing to gas evolution. The reaction is exothermic; extreme caution is necessary.

[32] S. Fried and N. F. Hall, Abstracts of 116th ACS Meeting, Detroit, p. 13, April, 1950.

to dryness on a water bath. The resulting crystals of ammonium pertechnetate and ammonium sulfate together with excess sulfur were transferred to a porcelain boat which was placed in a silica combustion tube through which hydrogen was passed while the temperature was maintained at 350°C for one hr. At this temperature the sulfur distilled off and the pertechnetate was reduced rapidly to the metal. The ammonium sulfate was removed by raising the temperature to 550 to 600°C. The technetium metal so prepared was porous and mossy and initially possessed a lustrous, metallic appearance (Fig. 2.6). On exposure to air and moisture, however, it turned black rapidly. Arsenic will be removed in the foregoing procedure since volatile arsine is formed and removed by the hydrogen stream. The procedure is adequate for handling amounts up to 100 to 200 mg with simple equipment and modest shielding requirements.

Spectrochemical analysis of the technetium metal showed it to be of high purity. A radiochemical analysis, however, revealed a small amount of contaminating ruthenium activity. Further purification would be necessary if this preparation were to be used for radiochemical studies, but for chemical studies this impurity is of no consequence. A summary of the above procedure is given in a flow diagram (Fig. 2.7).

PREPARATION OF TECHNETIUM HEPTOXIDE FROM TECHNETIUM METAL; ABSORPTION SPECTRUM OF PERTECHNETATE ION

G. E. Boyd C. M. Nelson
J. W. Cobble W. T. Smith, Jr.*

In the study of the chemistry of fission-product technetium (Tc^{99}) it was desirable to establish the formula of the light yellow crystalline oxide formed on heating the metal in dry oxygen at 400 to 600°C. Fried and Hall[32,33] have referred to the compound formed with oxygen as TcO_3. Rhenium metal when burned under these conditions forms Re_2O_7.[34] We were first led to the view that the yellow oxide in reality was Tc_2O_7 by the observation that the titer of a Ce(IV) solution was not changed after adding milligram quantities of the oxide. Furthermore, the absorption spectrum (Fig. 2.8) of an aqueous solution of this compound was identical with that obtained after its treatment with alkaline H_2O_2, suggesting that the technetium was already Tc(VII).

To test this conclusion sizeable quantities of technetium metal** were burned to form the yellow oxide (m.p. 119.5 ± 0.1°C) which was then purified by repeated sublimations into the cooler portions of the reaction tube. A solution containing a known weight of technetium was prepared by sealing the yellow oxide off from the quartz reaction system, weighing, breaking, and dissolving in water, and then reweighing the quartz after complete solution. The compound was very hygroscopic and dissolved to give a pink solution whose color disappeared upon dilution. A potentiometric *p*H

*Professor of Chemistry, University of Tennessee; ORNL Consultant.

**We are indebted to G. W. Parker and his group of the Chemistry Division, ORNL, for supplying us with about 1 g of fission product technetium as tetraphenyl arsonium pertechnetate; the preparation of NH_4TcO_4 from this material will be reported in another communication.

(33) S. Fried, A. H. Jaffey, N. F. Hall, and L. E. Glendenin, "Half-Life of the Long-lived Tc^{99}," *Phys. Rev.* 81, 741 (1951).

(34) A. D. Melaven, J. N. Fowle, W. Brickell, and C. F. Hiskey, in *Inorganic Synthesis*, vol. III, p. 188, McGraw-Hill, New York, 1950.

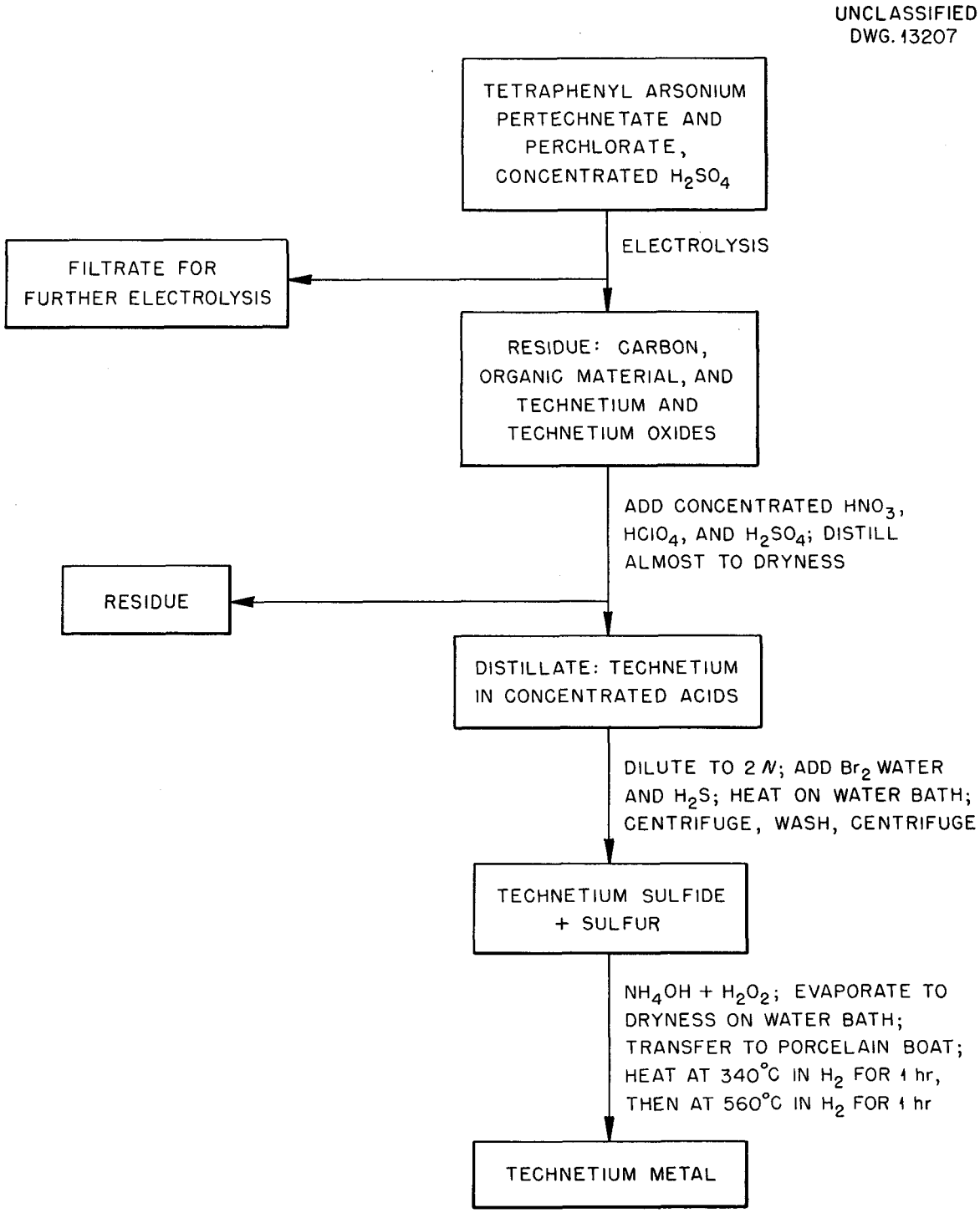

Fig. 2.7 - Flowsheet for Preparation of Technetium Metal.

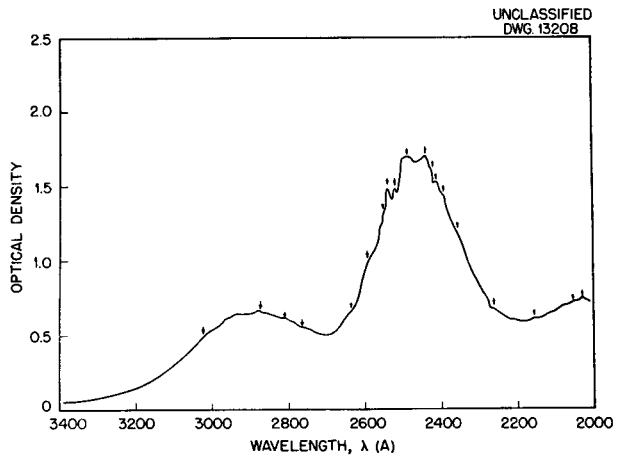

Fig. 2.8 - Ultraviolet Absorption Spectrum of 3 × 10^{-4} *M* NH_4TcO_4 in H_2O at 25°C. Determined with Beckman model DU spectrophotometer using variable slit width and constant sensitivity; source, H_2 discharge lamp; molar extinction coefficient at 2470 A = 4000.

salt formed. Pure NH_4TcO_4 is nonhygroscopic and shows no decomposition on heating to 100°C for several hours. Gravimetric results from two yellow oxide preparations are compared in Table 2.4 with the titers expected from the following:

$$Tc_2O_7 + 2OH^- = 2TcO_4^- + H_2O$$

$$TcO_3 + 2OH^- = TcO_4^{--} + H_2O$$

It was concluded that the correct formula for the yellow oxide is Tc_2O_7.

The intense ultraviolet absorption (Fig. 2.8) of TcO_4 ion in aqueous solution may be employed for the spectrophotometric determination of Tc(VII). Beer's law was found to hold rather well up to concentrations of 10^{-3} *M* for wavelengths near both maxima (e.g., 2470 and 2890 A). As

TABLE 2.4

Gravimetric Measurements on Formula of Yellow Oxide of Technetium (Tc_2O_7)

WEIGHT OF OXIDE (mg)	AMOUNT AS Tc_2O_7 (mmoles*)	AMOUNT AS Tc_2O_7 (meq)	AMOUNT AS TcO_3 (mmoles)	AMOUNT AS TcO_3 (meq)	OH^- REQUIRED (meq)	NH_4TcO_4 FOUND (meq)
157.7	0.5087	1.017	1.073	2.146	1.019	1.020
70.11	0.2262	0.4524	0.4769	0.9538	0.4561	0.4564

*We have used 99.0 as the theoretical isotopic weight[35] for Tc^{99}, although the fission product Tc may contain small quantities of other isotopes. Such amounts, however, will cause negligible error in the above calculations.

titration was performed on this solution using 0.05 *f* ammonium hydroxide. The titration curve showed only one inflection point characteristic of a strong monobasic acid. The whole of the neutralized solution was next taken to dryness at 95°C in platinum to determine the weight of technetium little as 10^{-8} g of technetium may be detected, which sensitivity compares quite favorably with that observed using a copper spark spectrochemical

[35] N. Metropolis and G. Reitwiesner, *Table of Atomic Masses*, U. S. Atomic Energy Commission, Report NP-1980 (March, 1950).

method. The occurrence of a third absorption band in the far ultraviolet is suggested by Fig. 2.8.

NUCLEAR CHEMISTRY OF TECHNETIUM

G. E. Boyd and B. H. Ketelle

Further search has been made for Tc^{98} and Tc^{100}. As yet no indication of an activity assignable to Tc has been obtained from the decay of a technetium fraction separated from an intense 15-Mev deuteron irradiation of an enriched molybdenum isotope preparation (95.0% Mo^{98}). A technetium fraction separated from a deuteron bombardment of 90.2% Mo^{100}, however, showed four distinct gamma-ray lines at approximately 80, 140, 230, and 400 kev after 212 days decay (Fig. 2.8). Interestingly, gamma-ray levels closely approximating three of these energies have been reported in the decay of 4.2-day Rh^{101}. Possibly this latter isotope should be assigned to mass 100.

Additional studies on the short-lived technetium isotopes formed in U^{235} fission are in progress.

An attempt was made to prepare a source of 50-min Tc^{94} which could be examined conveniently by irradiating an enriched molybdenum target (92.1% Mo^{92}) with 28-Mev alpha particles to produce a relatively long-lived Ru^{94} parent by an $(\alpha,2n)$ reaction. Despite an intense irradiation no ruthenium activity was found not previously assigned to other mass numbers. Good yields of the positron-emitting 1.65-hr Ru^{95} radioisotope were produced, presumably by an (α,n) reaction. Smaller amounts of the 2.9-day Ru^{97} were formed also by (α,n) or $(\alpha,2n)$ reactions on 1.7% Mo^{94} or 2.4% Mo^{95} present, respectively, in the enriched Mo^{92} preparation. The 215-kev gamma ray emitted in the decay of 2.9-day Ru^{97} was confirmed. Further, a considerably less abundant gamma ray of about 320 kev was found. The long-time decay of these ruthenium sources will be determined in the continuation of the search for Ru^{94}.

A preliminary magnetic lens spectrometer examination was made using a high-level technetium source prepared by deuteron irradiation of natural molybdenum in order to determine the character of the positron distribution emitted in about 1% of the decays of the 60.0-day Tc^{95m}. Owing to scattering effects it is not yet possible to check the prediction, based on shell theory, that this β^+ transition is first forbidden. The maximum positron energy, however, was about 650 kev, which is appreciably higher than the reported 400-kev value. Additional measurements to determine the positron spectrum shape are planned.

DECAY SCHEMES OF AU^{198} AND I^{131}

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

Decay scheme work in the last quarter has been concentrated on two isotopes. Au^{198} was studied because it is used as a standard in the measurement of neutron fluxes and in the calibration of a variety of instruments used in assay work. Recent publications have indicated that the decay of Au^{198} was not as simple as previously reported. I^{131} was studied because of the discrepancies in various methods of assay of this isotope.

Au^{198}. A 1.09-Mev level in Hg^{198} has recently been reported,[36-38] with gamma transitions in Au^{198} decay between the 1.09-Mev and the 0.411-Mev levels and between the 1.09-Mev level and the ground state. These transitions have been confirmed using Oak Ridge National Laboratory reactor-bombarded gold which was purified after bombardment by the method given by Noyes and Bray.[39] The NaI-TlI scintillation-spectrometer pulse distribution in Fig. 2.9 shows the presence of the recently reported 1.09- and 0.680-Mev gamma rays in addition to the well-known 0.411-Mev gamma ray. The shoulder on the curve corresponding to a gamma-ray energy of 0.820 Mev was shown to be the result of random coincidences between two 0.411-Mev gamma rays.

Further evidence that the 0.680-Mev gamma transition is part of the Au^{198} decay scheme was obtained by measuring the electron-energy distribution coincident with it. This was done by mounting an essentially weightless source in a thin magnetic lens spectrometer on a beryllium disk thick enough to absorb the 0.97-Mev beta group. A 13 g/cm^2 platinum absorber was placed between the beryllium disk and a NaI-TlI counter to reduce the counting rate of the 0.411-Mev gamma ray relative to that of the 0.680-Mev gamma ray by a factor of 25. With this reduction in intensity the random coincidences of the 0.411-Mev gamma ray were essentially eliminated.

Coincidences were recorded between pulses from the detector on the thin lens spectrometer and the pulses produced by the 0.680-Mev gamma ray in the NaI-TlI scintillation spectrometer. The energy distribution of the coincident-electron pulses is shown as an N/I vs. E plot in Fig. 2.9. These data show that the 0.680-Mev gamma ray is coincident with both a low-energy beta group and the K-conversion-electron peak of the 0.411-Mev gamma ray. The Kurie plot of the beta-energy distribution shown in Fig. 2.10 indicates a maximum energy of 290 ± 15 kev for the coincident beta group. These results are consistent with the coincidence absorption measurements of Cavanagh[37] and the decay scheme shown in Fig. 2.10. No attempt was made to confirm the low-intensity beta transition to the ground state reported by Elliott and Wolfson.[38]

Approximate measurements indicate that about 1% of the disintegrations are through the 0.680-Mev gamma ray and about 0.2% are through the 1.09-Mev gamma ray. These intensities are so low that the presence of these gamma rays has caused errors of only a few percent in previous work where Au^{198} was used as a standard.

I^{131}. In a study of I^{131} decay the beta-energy distributions coincident with particular gamma rays were measured. This was done by mounting an essentially weightless iodine source on a beryllium disk in a thin-magnetic-lens spectrometer. The NaI-TlI crystal of a scintillation

[36] P. E. Cavanagh, J. F. Turner, D. V. Booker, and H. J. Dunster, "An Investigation of the Secondary Electron Spectrum of ^{198}Au," *Proc. Phys. Soc. London* A64, 13 (1951).

[37] P. E. Cavanagh, "The Application of Proportional Scintillation γ-Ray Counters to the Determination of the Decay Scheme of Au^{198}," *Phys. Rev.* 82, 791 (1951).

[38] L. G. Elliott and J. L. Wolfson "The Disintegration of Au^{198}," *Phys. Rev.* 82, 333 (1951).

[39] A. A. Noyes and W. C. Bray, *A System of Qualitative Analysis for the Rare Elements*, Macmillan, 1943.

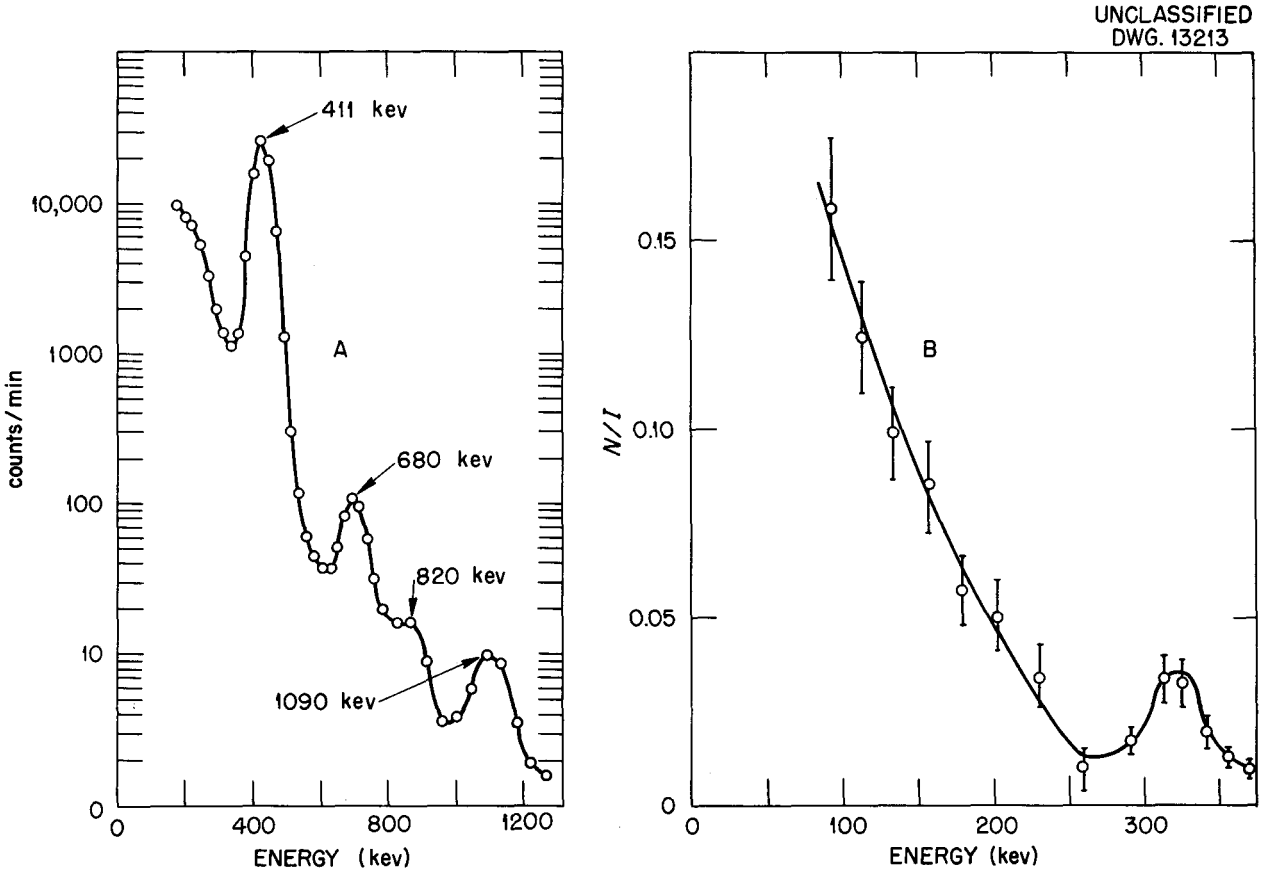

Fig. 2.9 - (*A*) Scintillation-Spectrometer Pulse-Height Distribution of Au^{198} Gamma Radiation. (*B*) Electron-Energy Distribution Coincident with 680-kev gamma Radiation.

spectrometer was mounted immediately behind the beryllium disk. Coincidences between pulses in the proportional counter detector and pulses from the scintillation spectrometer corresponding to a definite gamma-ray energy were measured. A delay in the differential discriminator of the scintillation spectrometer was matched by a 1-μsec delay line between the proportional counter and the coincidence circuit. A resolving time of about 0.3 μsec was used in the coincidence circuit.

The pulse-height distribution from the scintillation counter is shown in Fig. 2.11. It can be seen that pulses arising from the individual 720-, 635-, and 364-kev gamma rays can be counted without including more than a few percent of pulses arising from a second gamma ray. In the case of the 284-kev gamma ray, on the order of 10%

[redacted]

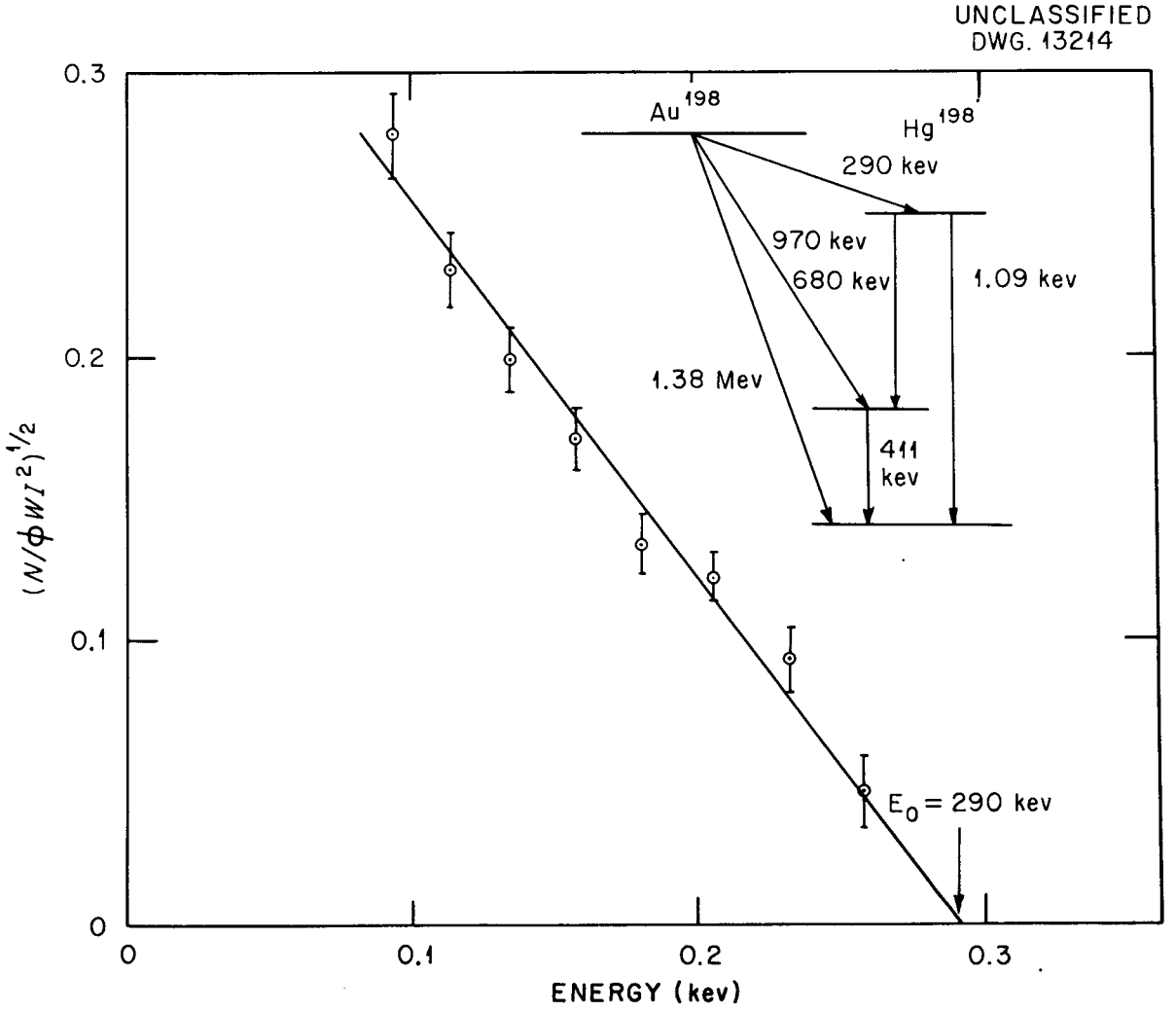

Fig. 2.10 - Kurie Plot of Au^{198} Beta-Energy Distribution Coincident with 680-kev Gamma Radiation.

of the pulses will result from the Compton electron distribution of the 364-kev gamma ray.

Only the 284-kev gamma ray is definitely coincident with the K-conversion electrons of the 80-kev gamma ray. The energy distribution of electrons coincident with the 284-kev gamma ray is compared with the energy distribution of all electrons in curve *B* of Fig. 2.11. Because of statistical fluctuations in the coincidence counting rates it cannot be stated that the 364-, 635-, or 720-kev gamma rays are in no case coincident with conversion electrons of the 80-kev gamma ray. The data do indicate that not more than 15% of the transitions of these gamma rays are coincident with the 80-kev gamma ray.

[redacted]

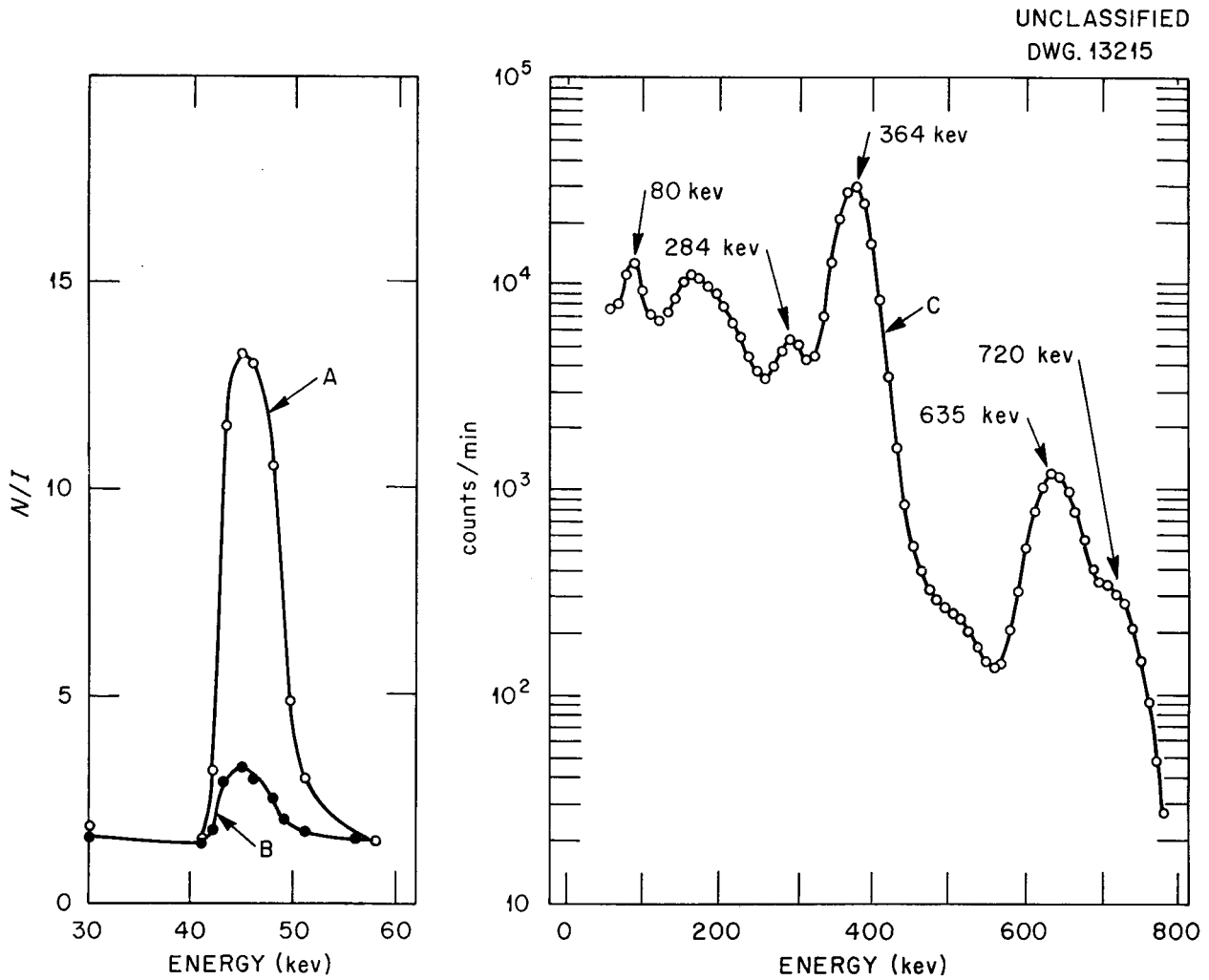

Fig. 2.11 - (*A*) K-Conversion-Electron Peak of 80-kev Gamma Ray Coincident with the 284-kev Gamma Ray. (*B*) K-Conversion-Electron Peak of 80-kev Gamma Ray. (*C*) Scintillation-Spectrometer Pulse-Height Distribution of I^{131} Gamma Radiation.

Kurie plots of the coincident-electron energy distribution in Fig. 2.12 show that the 720-, 635-, and 364-kev gamma rays are in coincidence with beta groups with maximum energies of 250 , 335 , and 606 kev, respectively. The 284-kev gamma ray also is coincident with a 606-kev maximum-energy beta group. The excess of low-energy electrons in the 606-kev beta curve was shown to be the result of back scattering from the beryllium source mount. Energy-distribution curves of several well-known beta emitters mounted on beryllium indicate that the energy at which

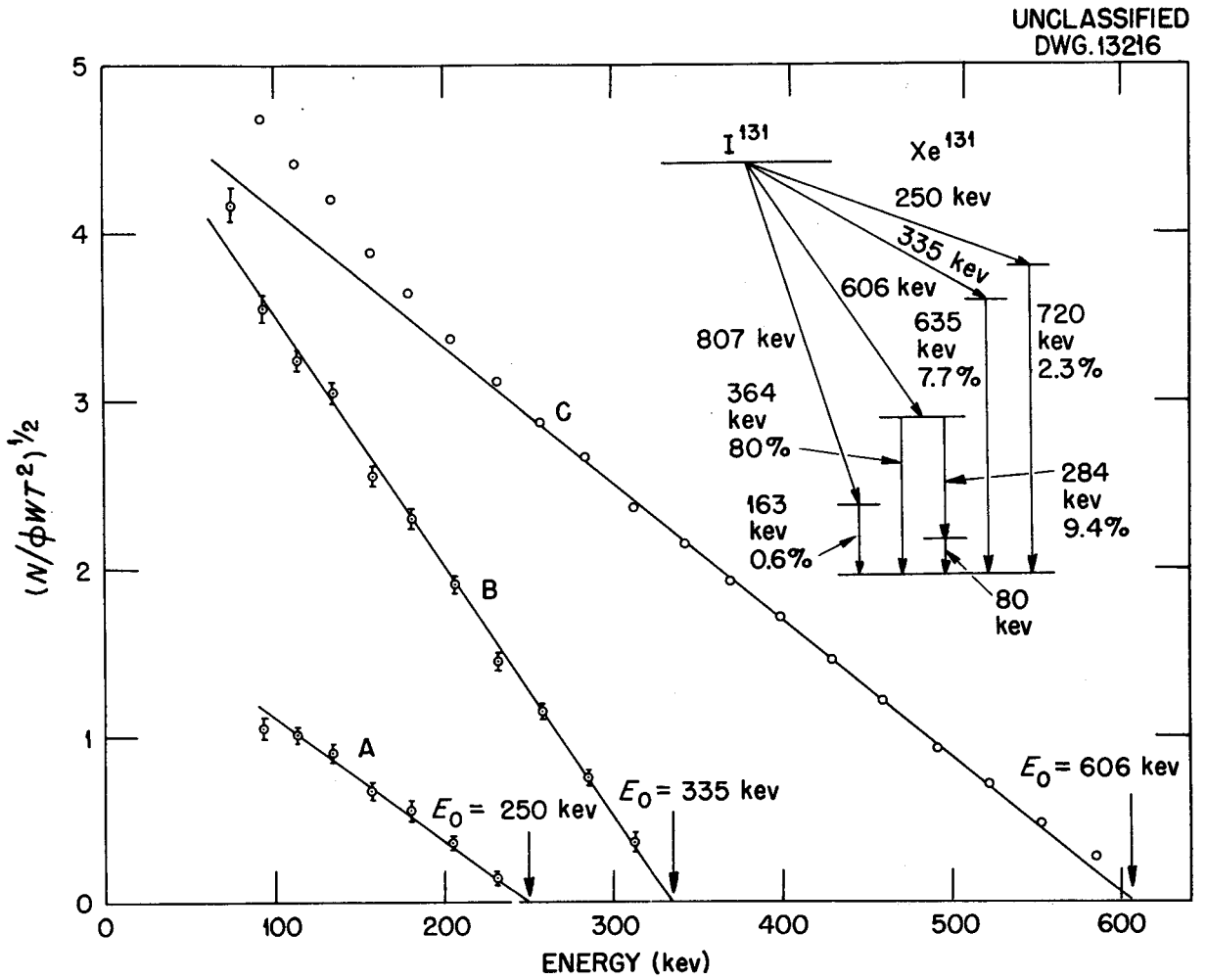

Fig. 2.12 - Kurie Plot of I^{131} Beta-Energy Distributions. (*A*) Coincident with 720-kev gamma rays. (*B*) Coincident with 635-kev gamma rays. (*C*) Coincident with either 364- or 284-kev gamma rays.

scattering becomes important is a function of the maximum energy of the beta emitter. In the case of the 250- and 335-kev beta groups this scattering becomes important only at energies lower than those plotted in Fig. 2.12.

These data support the decay scheme for I^{131} shown in Fig. 2.12. This scheme shows beta transitions to both a 635- and a 720-kev level in Xe^{131} whereas previous authors have reported only one low-energy beta transition.

[redacted]

3. RADIO-ORGANIC CHEMISTRY

RADIATION, ANALYTICAL, AND PREPARATIVE CHEMISTRY

Radiation Chemistry (E. J. Dowling, A. R. Jones, and W. J. Skraba). The effects of gamma radiation from a 300-curie Co^{60} source upon aqueous solutions of C^{14}-labeled benzoic and acetic acids have been studied. In both systems the volatile products have been identified and the relative amounts of these products have been determined. Three nonvolatile products have been isolated and identified from the irradiated benzoic acid solutions; from the irradiated acetic acid solutions three compounds have been isolated and two have been identified. The isolations and identifications were effected by means of paper chromatography followed by radiographic determinations of the chromatograms. The inhibitory effect of sodium chloride and sodium bromide upon benzoic acid decomposition during irradiation has been studied.

Experiments with Aqueous Benzoic Acid. Fifty-two separate irradiations of aqueous benzoic acid solutions have been carried out during the past quarter. Many of these were exploratory experiments, necessary to show what precautions must be taken to obtain duplicable results. Standard irradiation cells have been devised which, when cleaned in hot sulfuric acid for a given period of time, rinsed in a standard fashion with triply distilled water, filled with a standardized benzoic acid solution in triply distilled water, and then purged for a given time with pure hydrogen gas, will give highly precise duplicable results upon irradiation. In Fig. 3.1 is shown a plot of the rate of carbon-C^{14} dioxide evolution vs. irradiation time for (*a*) 0.01 *M* benzoic acid solution, (*b*) 0.01 *M* benzoic acid solution which is also 0.10 *M* in sodium chloride, and (*c*) 0.01 *M* benzoic acid solution which is also 0.10 *M* in sodium bromide. Although no inhibitory action is demonstrated by the addition of sodium chloride, the inhibitory action of sodium bromide is clearly demonstrated by this graph.

In Fig. 3.2 is shown a radiograph of a paper chromatogram of the nonvolatile products formed after irradiation of aqueous benzoic acid solution prepurged with hydrogen. Of five peaks, four have been identified as benzoic, salicylic, *m*-hydroxybenzoic, and *p*-hydroxybenzoic acids. The method for obtaining such radiographs is described in the analytical section of the report (p. 45).

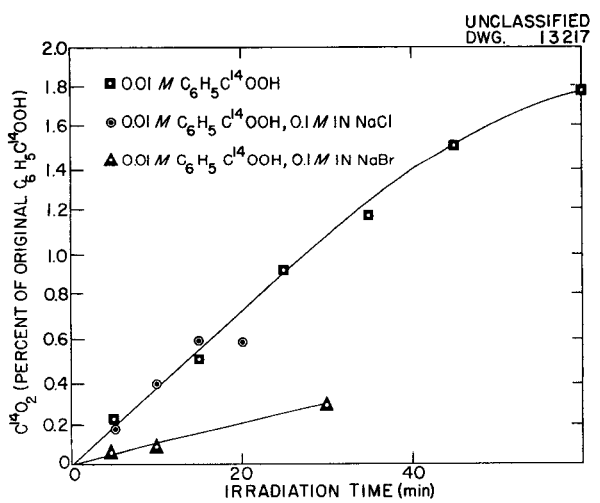

Fig. 3.1 - Plot of Irradiation Time vs. $C^{14}O_2$ Evolution for Aqueous C_6H_5-$C^{14}OOH$ Solution.

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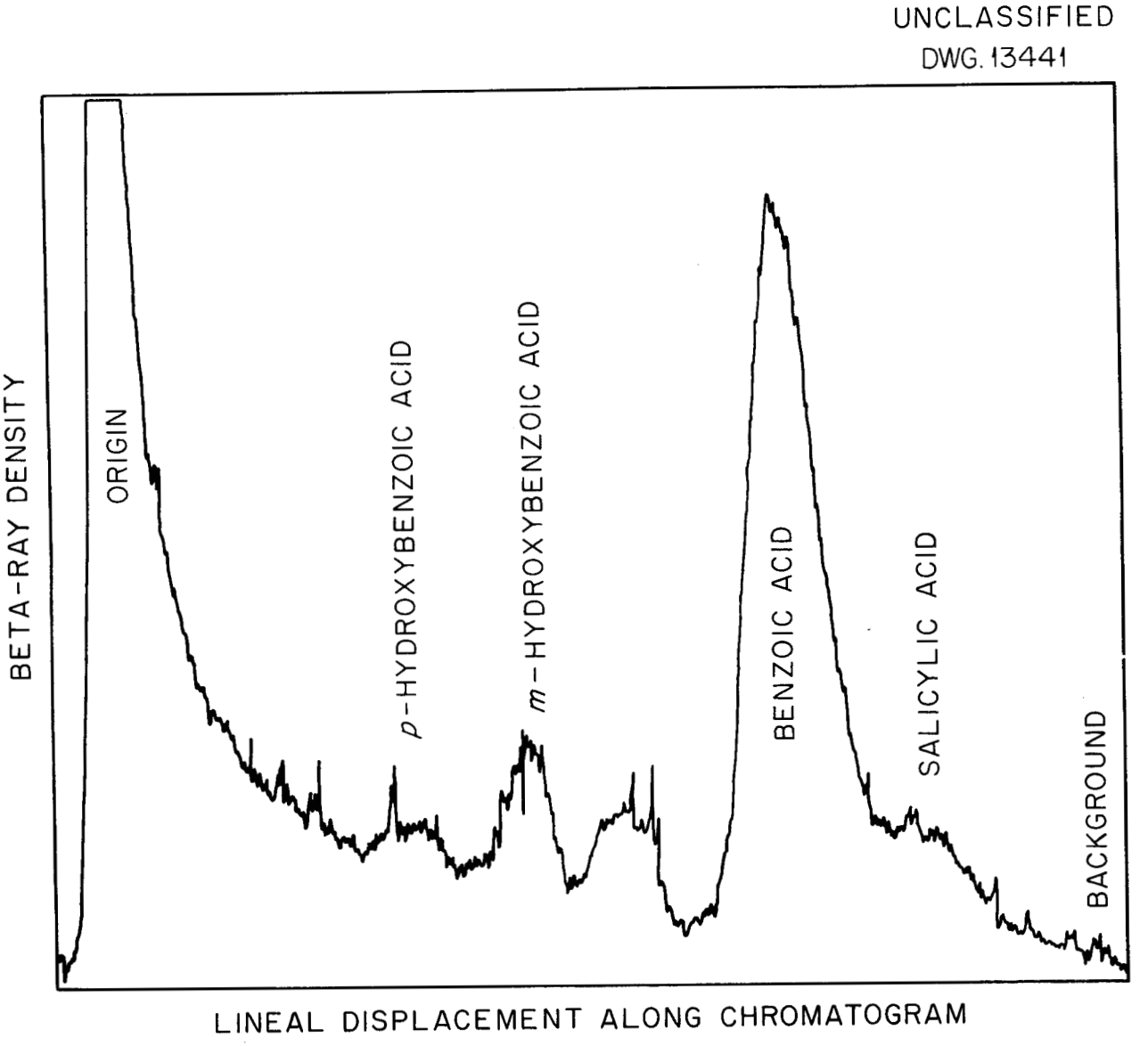


Fig. 3.2 - Radiograph of Paper Chromatogram of Products of Irradiation of Aqueous Benzoic-7-C^{14} Acid.

Experiments with Aqueous Acetic Acid. Five separate 20-min irradiations of aqueous acetic-1-C^{14} acid were carried out before duplicable results were obtained. One 15-min irradiation of aqueous acetic-2-C^{14} acid was performed, which checked very closely the results obtained with the carboxyl-labeled acid. From the carboxyl-labeled acetic acid were obtained carbon-C^{14} dioxide plus traces of a radioactive gas believed

to be carbon-C^{14} monoxide. Methyl-labeled acetic acid produced only traces of radioactive gases.

Paper chromatography of the non-volatile products formed upon irradiation of acetic-1-C^{14} acid, followed by a radiograph of the chromatogram, have demonstrated the presence of three compounds, two of which have been identified as succinic and glycolic acids. A third undetermined constituent of the mixture gives a color test for a carbonyl group but not a carboxyl group.

In Fig. 3.3 is shown a radiograph of a typical chromatogram of the

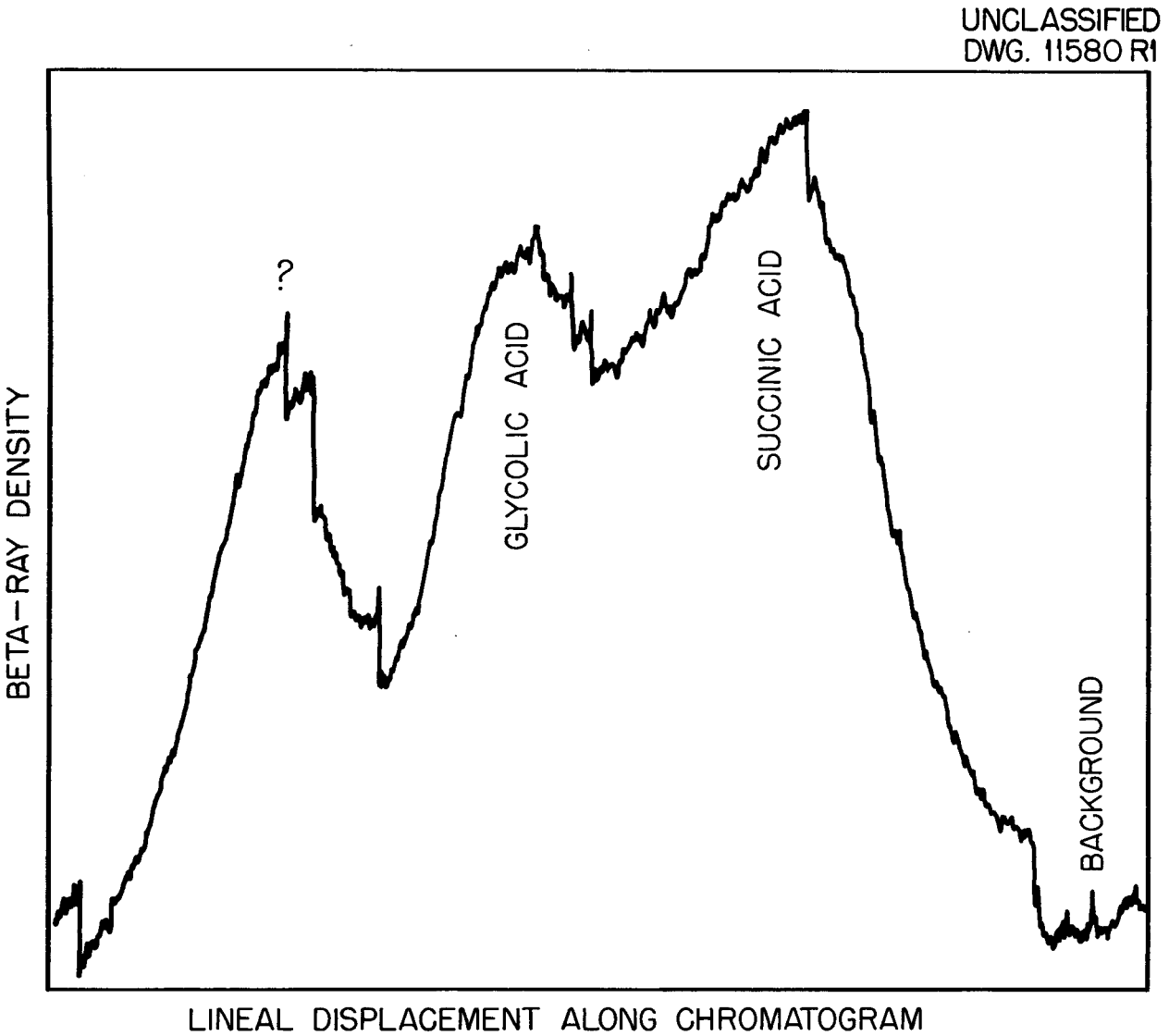


Fig. 3.3 - Radiograph of Paper Chromatogram of Products of Irradiation of Aqueous Acetic-1-C^{14} Acid.

nonvolatile irradiation products of acetic-1-C^{14} acid.

Irradiation of Aqueous Benzoic-7-C^{14} Acid. In a typical run a 22.05-g aliquot of a pure water solution of benzoic-7-C^{14} acid, 0.186 mmoles, 19.92 μc, purged with oxygen-free hydrogen gas for 15 min at 23°C was placed in a pyrex tube sealed at both ends. Only a tiny bubble of gas space remained. The sample was irradiated with gamma rays from a Co^{60} source (dose approximately 5×10^6 r).

The carbon dioxide formed was determined by oxygen purge as described in ORNL-1053. Decarboxylation had occurred to the extent of 12.05%. Carbon monoxide formation was negligible (radioactivity barely above background).

The degassed irradiated solution and the contents of the dry ice trap were ether-extracted continuously overnight. The ether solution was concentrated to approximately 15 ml and aliquots of 100 to 500 λ were ascendingly chromatographed on a sheet of Whatman No. 1 filter paper with a solvent composed of 93 parts of ethanol, 5 parts of 15 *N* ammonium hydroxide, and 2 parts of water. Benzoic-7-C^{14} acid, benzoic acid, salicylic acid, *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, *p*-phenylbenzoic acid, *p*-benzoyl acid, and a mixture of the nonradioactive acids were similarly chromatographed on the same sheet of paper at the same time as the irradiated material. The paper was dried overnight and sectioned vertically to separate the chromatograms due to each starting spot. The inert chromatograms and one of the radioactive chromatograms were sprayed with chlorophenol red indicator solution (40 mg per 100 ml, made basic). The nonradioactive acids gave clearly defined spots separately and together. However, the irradiated solution gave a smear of acidic color.

A radiograph (Fig. 3.2) of the chromatogram of the irradiated solution showed five clearly defined peaks together with a very radioactive starting spot. Since the starting spot for the benzoic-7-C^{14} acid was no longer radioactive, this is not a characteristic of radioactive chromatograms, and evidently some substance is formed by irradiation which is not moved by the solvent used.

The absence of carbonyl compounds as major products was indicated by the lack of spot formation when a radioactive chromatogram was sprayed with 2,4-dinitrophenylhydrazine solution. However, a 1-cm^2 spot formed by 800 λ of the ether solution gave a definite indication of the presence of carbonyl-containing material.

The respraying of the chlorophenol red—sprayed radioactive chromatogram confirmed the presence of salicylic acid as the cause of the small peak just ahead of the benzoic acid peak.

Irradiation of Aqueous Acetic-1-C^{14} Acid. In a typical run a 24.58-g aliquot of a pure water solution of acetic-1-C^{14} acid (0.0984 mmoles, 14.2 μc), prepurged with oxygen-free hydrogen gas for 20 min at 23°C, was placed in a pyrex tube sealed at both ends. Only a tiny bubble of gas space remained. The sample was irradiated with gamma rays from a Co^{60} source (dose approximately 10^7 r).

The irradiated solution was purged with oxygen containing some carbon

dioxide, and the exit gas, after passing through a dry ice trap, was washed with dilute sodium hydroxide solution to remove the carbon dioxide. The remaining gas was burned over copper oxide at 750°C, and the carbon dioxide formed by this combustion was removed by a second scrubbing with dilute sodium hydroxide.

Acidification of aliquots from the bubblers and radioassay of the gas evolved and swept into ion chambers with inert carbon dioxide showed 31.2% (4.43 μc) of the initial activity in the first scrubbing solution. Thus 31.2% of the acetic acid was decarboxylated. Only 0.075% (0.0108 μc) of the initial activity was found in the second scrubbing solution.

The degassed irradiated solution and the contents of the dry ice trap were ether-extracted continuously overnight. The ether solution was concentrated to approximately 15 ml and small aliquots (100 to 500 λ) were ascendingly chromatographed on a sheet of Whatman filter paper with ether saturated with a mixture of acetic acid and water (75:25 by volume). Glycolic and succinic acids were similarly chromatographed separately and together on the same sheet of paper at the same time as the radioactive material. The paper was dried overnight and sectioned vertically to separate the chromatograms due to each starting spot. Those of inert materials were sprayed with bromcresol green indicator solution (40 mg per 100 ml, made basic), as was also one of several radioactive chromatograms. Two acidic spots appeared on the latter at R_f values identical with the spots formed by glycolic and succinic acids when chromatographed separately or together. The radioactive chromatogram from irradiated acetic-1-C^{14} acid solution was drawn through the beta-ray scanner described below. The radiograph (Fig. 3.3) had three peaks, two of which correspond exactly with the acidic spots found for glycolic and succinic acids. The substance causing the third peak was not acidic and did not form a spot with 2,4-dinitrophenylhydrazine solution. However, a 1-cm^2 spot formed by 800 λ of the ether solution gave a definite indication of the presence of carbonyl-containing material.

Irradiation of Aqueous Acetic-2-C^{14} Acid. In a typical run a 26.82-g aliquot of a pure water solution of acetic-2-C^{14} acid (0.278 mmole, 3.94 μc), prepurged with oxygen-free hydrogen gas for 15 min at 23°C was placed in a pyrex tube and sealed at both ends. Only a tiny bubble of gas space remained. The sample was irradiated with gamma rays from a Co^{60} source (dose 10^6 r).

The carbon dioxide formed was determined by oxygen purge as described above, and a value of 0.0169 μc, 0.43% of the initial activity, was obtained. Similarly, the contents of the second bubbler contained only 0.0025 μc, 0.06% of the original activity.

Analytical Chemistry (E. J. Dowling, A. R. Jones, and W. J. Skraba). *Use of Beta-Ray Densitometry in Paper Chromatography.* For some time it has been customary to detect colorless chromatographic zones by placing the finished chromatogram in contact with

photographic film.[1] Whenever a zone contains a radioactive tracer such as I^{131} or C^{14} a developable image will result. Since long periods of time, up to a month, are required for this procedure a method for direct scanning and recording was urgently needed. Such a method for the recording of the position of activity on paper chromatograms has been described.[2] The setup consisted of a methane type ionization chamber and a pulse-integrating counter driving a Brown recorder.

An improvement upon this system has been developed employing a vibrating reed electrometer and a novel pickup which is described below. A 5-mm slit was milled lengthwise into each of two ion chambers. The chambers were mounted with the slits opposed and approximately 0.5 mm apart. The chambers were mounted horizontally, and the paper strip was inserted between them and attached with Scotch tape to the end of the recording chart of the Brown recorder. This permitted the chromatogram to be drawn across the slits of the ion chambers at a uniform rate and in exact synchronization with the chart motion. A photograph of this device is shown in Fig. 3.4.

A typical record is shown in Fig. 3.2. The peaks represent the counting of C^{14} beta particles, and by virtue of the scanning mechanism they give the exact lineal displacement of activity along the chromatogram. A peak height of half the chart width is shown by 0.001 μc of C^{14}. After the positions of the radioactive materials along the paper strip have been determined, the active portions can be excised and burned to give a radioassay.

Application of Paper Chromatography to Nonvolatile Ketones. It has been shown that the 2,4-dinitrophenylhydrazones of aldehydes and ketones can be separated by paper chromatography.[3] It is interesting that although the determinations of the positions of carbonyl compounds in adsorption chromatography have been shown by streaking the expelled cylinder of adsorbent material with a solution of 2,4-dinitrophenylhydrazine, the technique of spraying a paper chromatogram of colorless carbonyl compounds with the reagent has not been exploited.

In the course of our investigations of the products of radiation-degradation of organic compounds we have found it possible to indicate the formation of certain carbonyl compounds from their positions on a paper chromatogram. It was not necessary to prepare and then chromatograph the 2,4-dinitrophenylhydrazones, since spot formation occurred when the chromatogram was sprayed with a saturated solution of 2,4-dinitrophenylhydrazine in 6 *N* hydrochloric acid. The R_f values of a number of a number of aldehydes, ketones, and keto acids are being determined.

Application of Paper Chromatography to Carboxylic Acids. It has been found that the acidic degradation products from the irradiation of aqueous benzoic acid solutions can be

[1] D. L. Clegg, "Paper Chromatography," *Anal. Chem.* 22, 48 (1950).

[2] R. H. Müller and E. N. Wise, "Use of Beta-Ray Densitometry in Paper Chromatography," *Anal. Chem.* 23, 207 (1951).

[3] R. G. Rice, G. J. Keller, and J. G. Kirch, "Separation and Identification of 2,4-Dinitrophenylhydrazones of Aldehydes and Ketones, and 3,5-Dinitrobenzoates of Alcohols by Filter Paper Chromatography," *Anal. Chem.* 23, 194 (1951).

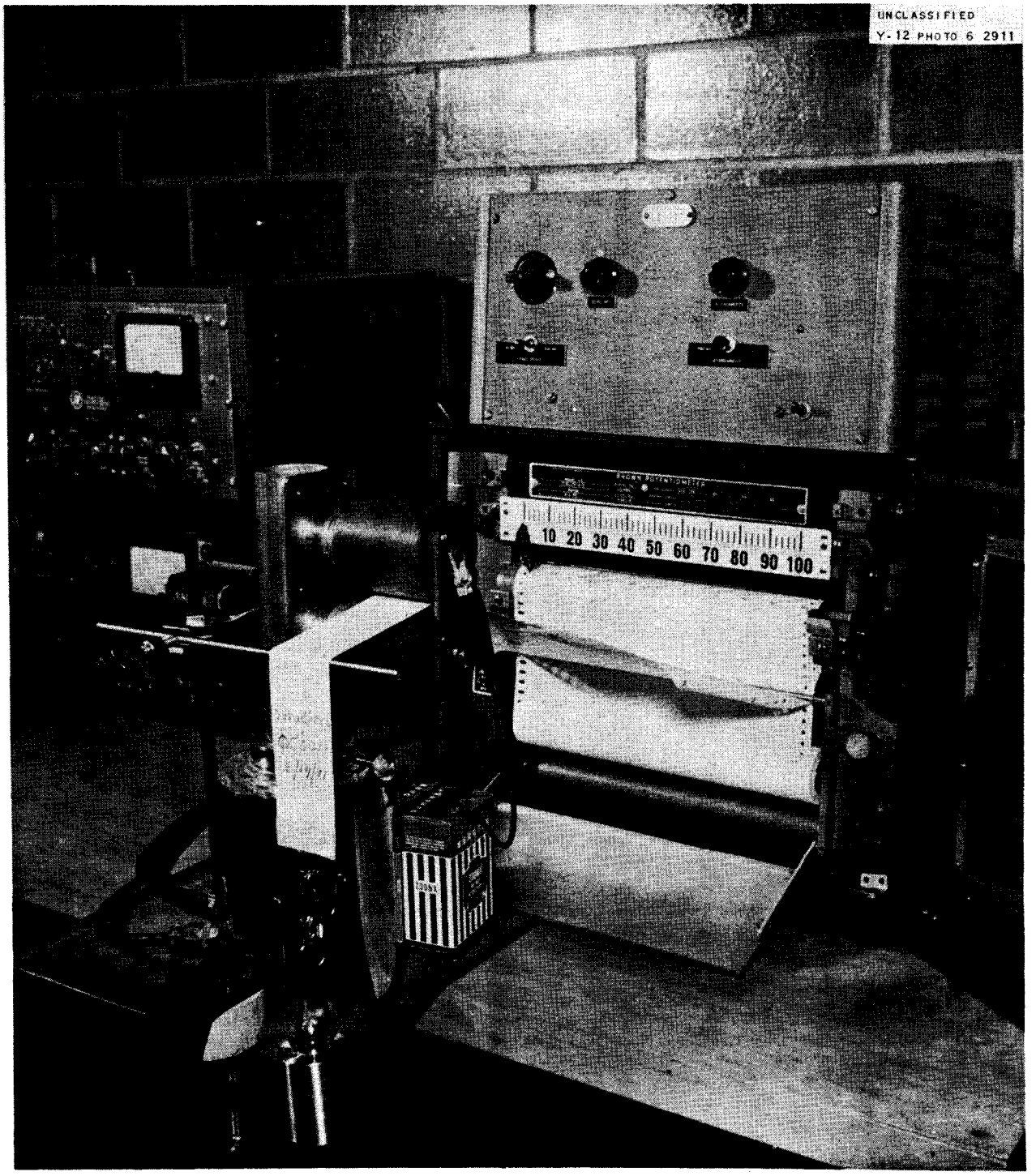


Fig. 3.4 - Improved Device for Direct Scanning and Recording of Paper Chromatograms of Radioactive Compounds.

TABLE 3.1

Radiochemical Yields of Sodium Acetate-2-C^{14}

BATCH	METHANOL USED (mc)	METHANOL USED (mmoles)	SODIUM ACETATE-2-C^{14} (mc)	YIELD (%)
1	50.6	10.7	24	48
2	93.4	11.1	59	63
3	96.2	11.4	56	58
4	130.5	15.9	94	72
5	48.4	17.2	40	84
6	62.2	14.9	45.5	73
7	81.6	25.0	64	78
8	63.1	18.3	51	81
9	91.0	29.6	70	77
Combined residues			70	

readily separated by chromatographing their ammonium salts with an elution solvent composed of various proportions of 95% alcohol, 15 *N* ammonium hydroxide, and water[4] (usually 95 parts of alcohol, 5 parts of ammonium hydroxide). The acidic products from the radiation degradation of acetic acid were determined by paper chromatography using as an elution solvent diethyl ether saturated with a mixture of 75% glacial acetic acid and 25% water.

Preparative Chemistry (O. K. Neville, V. F. Raaen, G. A. Ropp, A. J. Weinberger, and D. N. Hess). *Methanol-C^{14}* (A. J. Weinberger). A total of 600 mc of methanol-C^{14} was produced from catalytic reduction of carbon-C^{14} dioxide by a previously described procedure.[5]

Sodium Acetate-2-C^{14} (V. F. Raaen, D. N. Hess, and G. A. Ropp). By the method developed by Hess[6] 574.5 mc of high-specific-activity sodium acetate-2-C^{14} was prepared from methanol-C^{14} in 80% overall radiochemical yield. The yields from the various batches are listed in Table 3.1.

Sodium-2-C^{14} acetate aliquots of the following sizes were prepared in

[4] F. Brown, "Application of Paper Chromatography to the Separation of Nonvolatile Carboxylic Acids," *Nature* 167, 441 (1951).

[5] B. M. Tolbert, "Synthesis of Carbon Radioactive Methyl Iodide and Methanol from Carbon Dioxide," *J. Am. Chem. Soc.* 69, 1529 (1947).

[6] D. N. Hess, "Preparation of Acetic-2-C^{14} Acid," *J. Am. Chem. Soc.* 73, 4038 (1951).

flask from which acetic acid may be readily distilled after addition of phosphoric acid: sixteen 1-mc batches, six 10-mc batches, one 9-mc batch, and one 28-mc batch.

Acetic-2-C^{14} Acid. A total of 421 mc of sodium acetate-2-C^{14} was heated in high vacuum with excess phosphoric acid saturated with phosphorus pentoxide, and 380 mc (estimated on the basis of the measured volume of acetic acid) of triple-distilled acetic acid was collected.

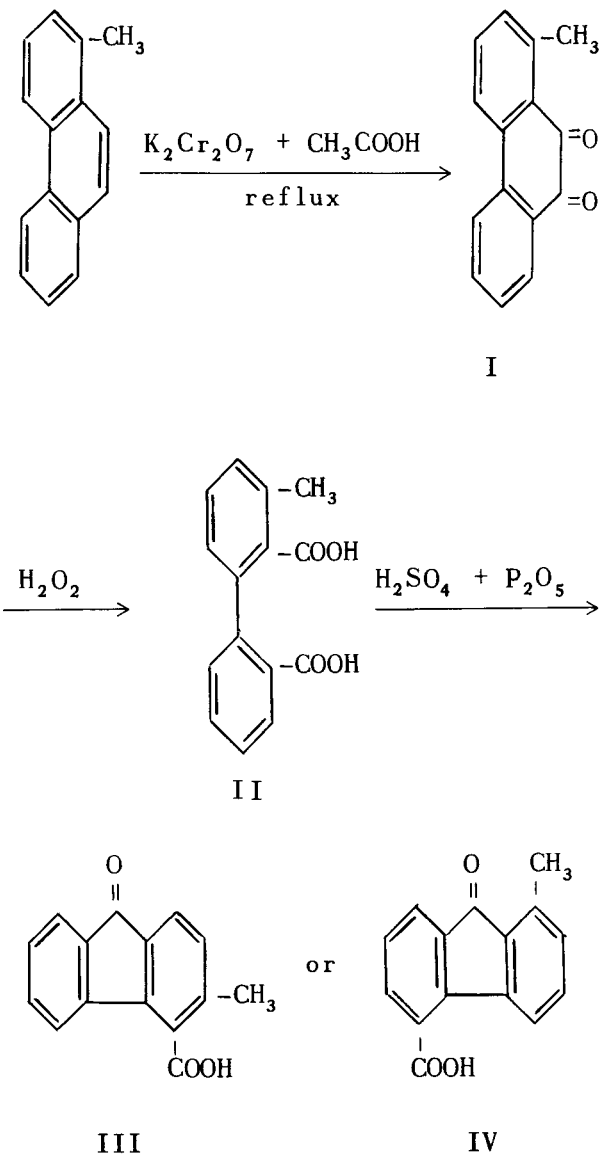
Chloroacetic-2-C^{14} Acid (V. F. Raaen and G. A. Ropp). By the procedure previously described[7] 380 mc of acetic-2-C^{14} acid was chlorinated in sealed tubes at 140°C in the presence of added acetyl chloride, red phosphorus, and iodine.

Malonic-2-C^{14} Acid (G. A. Ropp and V. F. Raaen). By the procedure developed by Gal and Shulgin[8] and modified by A. R. Jones and T. C. Weeks[7] 92 mc of malonic-2-C^{14} acid was prepared from sodium acetate-2-C^{14} via chloroacetic-2-C^{14} acid.

SYNTHESIS OF HIGH-MOLECULAR-WEIGHT COMPOUNDS CONTAINING C^{14}

Synthesis and Determination of Structure of C^{14}-Labeled 1-Methylphenanthrene (B. M. Benjamin* and C. J. Collins). The synthesis of 1-methylphenanthrene by the Wagner rearrangement of 1-methyl-9-fluorenemethanol was previously reported.[9]

With the purpose of determining the position of C^{14} in the corresponding labeled hydrocarbon, a means for degrading the substance has been developed. The course of the degradation reactions which have been carried out are indicated in the following flow diagram:



[7] E. J. Dowling, A. R. Jones, W. J. Skraba, and T. C. Weeks, "Radiation, Analytical, and Preparative Chemistry," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1951*, ORNL-1053, (Oct. 5, 1951).

[8] E. M. Gal and A. T. Shulgin, "Improved Syntheses of C^{14}-Labeled Malonic Acid and Malonitrile," *J. Am. Chem. Soc.* 73, 2938 (1951).

*Oak Ridge Institute of Nuclear Studies graduate fellow from the University of Florida, Gainesville.

[9] B. M. Benjamin and C. J. Collins, "Model Runs with Nonradioactive Material," ORNL-1053, *op. cit.*, p. 76.

1-Methylphenanthrenequinone (I). A mixture of 0.957 g of 1-methylphenanthrene and 5.29 g of potassium dichromate in 20 ml of acetic acid was refluxed for 5 hr with a magnetic stirring bar. The cooled solution was diluted with water and extracted continuously with ether for 4 hr. The residue from the ether extract was treated with excess sodium bicarbonate to remove acidic compounds. A second continuous ether extraction gave 0.7827 g, 59% yield of impure 1-methylphenanthrenequinone. Recrystallization from ethanol gave an orange product melting at 186 to 196°C; Pschorr[10] gives a melting point of 196°C.

The bicarbonate solution was acidified and extracted with ether to give 0.1623 g of an acid melting at 191 to 192°C after washing with benzene. The acid has a neutralization equivalent of 94.7 and is probably 3-carboxydiphenic acid which has a theoretical neutralization equivalent of 95.4.

3-Methyldiphenic Acid (II). A solution of 0.2846 g of 1-methylphenanthrenequinone in 20 ml of acetic acid containing 0.2 ml of 30% hydrogen peroxide was heated under reflux. After ½ hr 1 ml more of hydrogen peroxide was added. Refluxing was continued for 1½ hr, and then the reaction mixture was allowed to stand at room temperature for 14 hr. The acetic acid was evaporated and the residue was taken up in sodium bicarbonate and extracted with ether. Acidification of the solution and ether extraction of this produced 0.2674 g, 85% yield, of a light yellow solid. Recrystallization from ether gave an almost white product melting at 180 to 181°C. Its neutralization equivalent was 133 (theoretical for 3-methyldiphenic acid is 128).

3-Methylfluorenone-4-carboxylic Acid (III) or 1-Methylfluorenone-5-carboxylic Acid (IV). To a flask containing 15 ml of 96% sulfuric acid and 1 g of phosphorus pentoxide was added 0.1058 g of 3-methyldiphenic acid. The flask was stoppered and stirred with a magnetic bar for 21 hr. Addition of 300 ml of ice and water caused separation of a yellow precipitate. This suspension was continuously extracted with ether until no more yellow color appeared in the ether layer. After evaporation of the ether, washing with water, and drying, 0.0756 g, 76.8% of theoretical yield, of product melting at 197 to 225°C was obtained. Recrystallization from benzene gave 0.062 g of yellow crystals melting at 198.4 to 200°C. Decarboxylation of this acid with basic copper carbonate and quinoline gave a product (presumably a crude methylfluorene) which has not yet been identified.

MECHANISM STUDIES OF ORGANIC REACTIONS

Isotope Exchange Reactions Involving the Carbon-Carbon Bond (C. D. Douglass and O. K. Neville). The reversibility of the Friedel-Crafts alkylation reaction is well known. Though not definitely proved, the acylation reaction has been considered to be irreversible. A determination of the reversibility is being made by studying the extent of interaction between aromatic ketones and labeled acid chloride in the presence of

[10] R. Pschorr, "Synthesen und Verhalten einiger neuer Phenanthrenderivate," *Ber.* 39, 3106, esp. p. 3111 (1906).

strong Lewis acids, such as aluminum chloride:

$$R'COR + RC^*OCl \underset{}{\overset{AlCl_3}{\rightleftharpoons}} R'C^*OR + RCOCl$$

Isolation of the original ketone and determination of its radioactivity will indicate the degree of exchange.

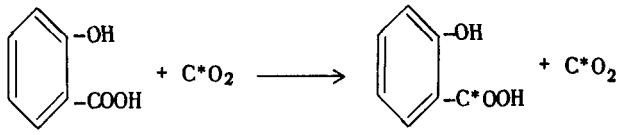
Under a number of catalytic conditions, in a variety of solvents, acetophenone was found not to exchange with acetyl chloride. Similar results were obtained with the benzophenone—benzoyl chloride pair. Activation by ring substitution of hydroxy or methoxy groups has failed to cause exchange. Table 3.2 shows the compounds and conditions which have been used in this study.

Preliminary experiments have been carried out on the reversibility of the Kolbe reaction, in which carbon dioxide reacts with a phenol salt to produce the corresponding *o*-phenolic

TABLE 3.2
Exchange of Ketones with Acid Chlorides

KETONE	ACID CHLORIDE	CATALYST	MOLAR PROPORTION OF CATALYST	SOLVENT	TEMPERATURE	TIME FOR REACTION
$C_6H_5COCH_3$	CH_3COCl	$AlCl_3$	2	$C_6H_5ND_2$	Room	92 hr
$C_6H_5COCH_3$	CH_3COCl	$AlCl_3$	2	CS_2	Room	92 hr
$C_6H_5COCH_3$	CH_3COCl	HCl		None	110°C	31 hr
$C_6H_5COCH_3$	CH_3COCl	$AlBr_3$	2	CS_2	Room	16 hr
$C_6H_5COCH_3$	CH_3COCl	$AlCl_3$	4	CS_2	Room	44 hr
p-$CH_3OC_6H_4COCH_3$	CH_3COCl	H_3PO_4	Catalytic amount	None	50°C	3 hr
p-$CH_3OC_6H_4COCH_3$	CH_3COCl	H_3PO_4	Catalytic amount	None	Room	16 hr
2,4-$(OH)_2C_6H_3COCH_3$	CH_3COCl	H_3PO_4	Catalytic amount	None	50°C	2 hr
2,4-$(OH)_2C_6H_3COCH_3$	CH_3COCl	$AlCl_3$	3	CS_2	40°C	5 days
2,4-$(OH)_2C_6H_3COCH_3$	CH_3COCl	$SnCl_4$	4	CS_2	Room	3 days
$C_6H_5COC_6H_5$	C_6H_5COCl	$AlCl_3$	3	$C_6H_5NO_2$	Room	16 hr
$C_6H_5COC_6H_5$	C_6H_5COCl	$AlCl_3$	3	CS_2	Room	16 hr
$C_6H_5COC_6H_5$	C_6H_5COCl	H_3PO_4	Catalytic amount	None	100°C	45 min
2,4,6-$(OH)_3C_6H_2COCH_3$	CH_3COCl	$AlCl_3$	3	CS_2	Room	16 hr
$(C_6H_5)_3CCOC_6H_5$	C_6H_5COCl	$AlCl_3$	3	$C_6H_5NO_2$	Room	16 hr
$(C_6H_5)_3CCOC_6H_5$	C_6H_5COCl	$AlCl_3$	3	$C_6H_5NO_2$	100°C	1 hr

carboxylic acid. This reaction is being studied by determination of the radioactivity associated with the acid product after equilibration with carbon-C^{14} dioxide:



Results to date are inconclusive.

Acetyl-1-C^{14} Chloride. The method of Fieser[11] was used to convert acetic-1-C^{14} acid (2 μc/mmole) to acetyl chloride. The crude acetyl-1-C^{14} chloride was purified by the addition of a small amount of dimethylaniline and distillation.

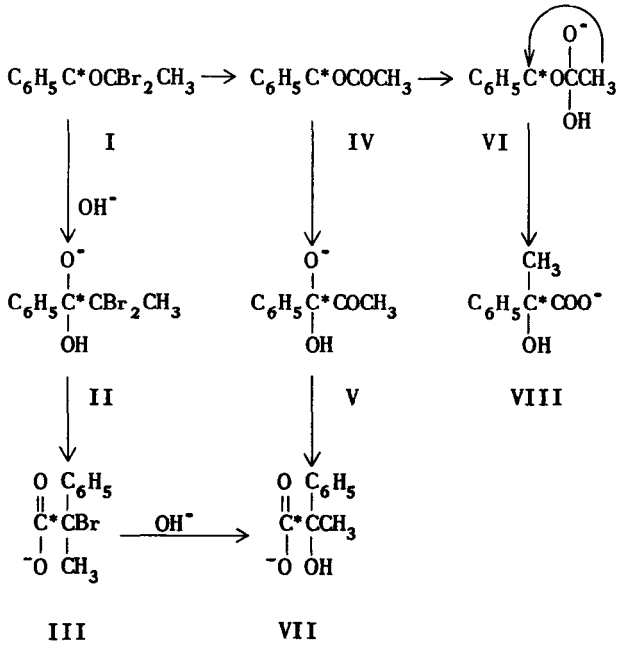
Benzoyl-7-C^{14} Chloride. A twofold excess of thionyl chloride was added to benzoic-7-C^{14} acid of approximately 2 μc/mmole activity, and the mixture was allowed to stand overnight. The mixture was heated for 1 hr at 100°C under reflux. The excess thionyl chloride was distilled off and the benzoyl-7-C^{14} chloride was distilled in vacuo at 125 to 126°C.

Attempted Exchange Reactions. The conditions and results of the attempted exchange reactions are presented in Table 3.2. In every case the reaction mixtures were decomposed by adding dilute hydrochloric acid and ice. The ketones were extracted with ether. In the cases of the ketones that are liquid at room temperature, solid derivatives were prepared (usually the 2,4-dinitrophenylhydrazones). The ketone derivative was purified by recrystallization and decolorization with charcoal and was then assayed for radioactivity.

The compounds isolated were examined critically as to identity and purity by use of paper chromatography, infrared and ultraviolet spectra, and conventional chemical methods.

Exchange has not been demonstrated in any of the reactions studied.

Rearrangement of α,α-Dibromopropiophenone (K. S. Warren and O. K. Neville). α,α-Dibromopropiophenone (I) rearranges to atrolactic acid (VII or VIII) in concentrated alkaline solution. The reaction has been postulated[12] to occur by the intermediate formation of the diketone acetylbenzoyl (IV) which then undergoes a benzilic acid type of rearrangement (paths 2 or 3 below):



Path 1: I ⟶ II ⟶ III ⟶ VII

Path 2: I ⟶ IV ⟶ V ⟶ VII

Path 3: I ⟶ IV ⟶ VI ⟶ VIII

(11) L. F. Fieser, *Experiments in Organic Chemistry*, p. 76, Heath, New York, 1941.

(12) R. Levine and J. R. Stephens, "The Course of the Oxidation of Propiophenone with Alkaline Hypobromite Solution and Certain Related Reactions," *J. Am. Chem. Soc.* 72, 1642 (1950).

An alternate reaction sequence which does not involve the formation of the intermediate diketone (IV) is that shown in path I.

By carrying out the rearrangement with the dibromide and with the diketones, each labeled in a carbonyl group, and determining the position of the C^{14} in the acid product the identity of the migrating group (phenyl or methyl) may be determined. By this at least one and perhaps two of the reaction paths above may be excluded. The experiments with labeled α,α-dibromopropiophenone (I), labeled in the carbonyl group, are complete. Degradation of the atrolactic acid formed from this compound has shown the rearrangement to involve only phenyl group migration, thus eliminating path 3 as a reaction sequence. The work on methyl phenyl diketone is in progress.

Carbonyl-labeled propiophenone was prepared by treatment of carbonyl-labeled benzamide with ethyl magnesium bromide. The ketone was converted by direct bromination.

(α,α-Dibromopropio-1-C^{14})-phenone. To 9.7 g (0.4 mole) of magnesium turnings contained in a 250-ml round-bottomed three-necked flask was added slowly a solution of 53.6 g (0.5 mole) of ethyl bromide in 95 ml of ether. While the flask was cooled in ice, 12.1 g (0.1 mole) of carbonyl-labeled benzamide was slowly added under dry nitrogen. After a reflux period of 24 hr the reaction mixture was hydrolyzed with ice and sulfuric acid and extracted with ether. From the extract was obtained 7.5 g (56% yield) of propiophenone (II).

One gram of the unpurified propiophenone was treated with a solution of 2.50 g of bromine in 7.5 ml of chloroform and allowed to stand at 25.5°C for ½ hr before it was refluxed for 4 hr. The solvent was carefully removed to give 2.13 g (97% theoretical yield) of crude α,α-dibromopropiophenone.

Hydrolysis and Rearrangement of α,α-Dibromopropiophenone (III). The crude dibromide was vigorously stirred with 42.6 g of 20% aqueous sodium hydroxide for 3½ hr. The aqueous phase was extracted with ether and acidified with concentrated hydrochloric acid. The precipitated crystalline atrolactic acid was removed by filtration and sublimed at 70 to 75°C; m.p. 91 to 92°C.[13]

Oxidation of Atrolactic Acid and Radioassay of the Products. A small portion (83 mg) of IV was decarboxylated at room temperature by treating with a mixture of 44 mg of chromium trioxide and 2.0 ml of glacial acetic acid in a small flask connected to a barium hydroxide absorption train. The apparatus was swept with nitrogen gas, and the evolved carbon dioxide was converted to barium carbonate. The residue in the flask was extracted with ether, and the ether extract was washed with sodium bicarbonate and then evaporated. The residual acetophenone was converted to the semicarbazone, which after two crystallizations from 25% alcohol melted at 198°C.[14]

The radioassays were conducted by the wet combustion of small samples

[13] Cf. M. V. Grignard, "Action des combinaisons organomagnésiemes mixtes sur les éthers d'acides cétoniques," *Ann. chim. et phys.* [7] 27, 548, esp. p. 557 (1902).

[14] Cf. R. L. Shriner and R. C. Fuson, *Systematic Identification of Organic Compounds*, p. 110, Wiley, New York, 1935.

to carbon dioxide and ion chamber assay of the carbon dioxide on the vibrating-reed electrometer. The acetophenone contained 0.00579 μc of C^{14} per millimole, and the $BaCO_3$ from the absorption train gave, on acidification, carbon dioxide with 0.909 μc of C^{14} per millimole. The starting material, benzamide, contained 1.028 μc of C^{14} per millimole.

Rearrangement of *p*-Methoxybenzil (E. C. Hendley[a] and O. K. Neville). The alkaline rearrangement of C^{14}-labeled *p*-methoxybenzil (I) has been found to give *p*-methoxybenzophenone (III) containing 35% of the initial activity. Since the C^{14} content of the carbonyl group in compound (III) is a measure of the degree of migration of the *p*-methoxyphenyl group, the percent migration of the phenyl group was 65%.

$$C_6H_5C^*OCOC_6H_4\text{-}p\text{-}OCH_3 \xrightarrow[C_2H_5OH]{NaOH}$$

I

$$C_6H_5\underset{\underset{C_6H_4\text{-}p\text{-}OCH_3}{|}}{\overset{\overset{C^*OOH}{|}}{C}}{}^*OH \xrightarrow[CH_3COOH]{CrO_3}$$

0.542 μc/mmole

II

$$C_6H_5C^*OC_6H_4\text{-}p\text{-}OCH_3 \quad + \quad C^*O_2$$

0.1895 μc/mmole

III

p-Methoxybenzil. A mixture of 128 mg of selenium dioxide, 260 mg of *p*-methoxybenzyl phenyl ketone, 5 ml of dioxane, and 2 drops of water was refluxed for 24 hr, after which the selenium was removed by filtration. Most of the dioxane was removed by evaporation, 5 ml of water was added, and the benzil was extracted with ether. After the ether was removed, recrystallization of the benzil from an ethanol-water mixture yielded 132 mg (47.8% of the theoretical yield) of the benzil, m.p. 61 to 62°C.

Rearrangement of p-Methoxybenzil. A solution containing 5 ml of alcohol, 10 ml of water, 2.2 g of sodium hydroxide, and 132 mg of *p*-methoxybenzil was stirred for 24 hr at room temperature, after which it was decolorized with Darco and filtered. When the acidified solution was cooled, *p*-methoxybenzilic acid precipitated. Recrystallization of this acid from a petroleum ether—chloroform mixture gave 68 mg of white solid, m.p. 147 to 148°C.

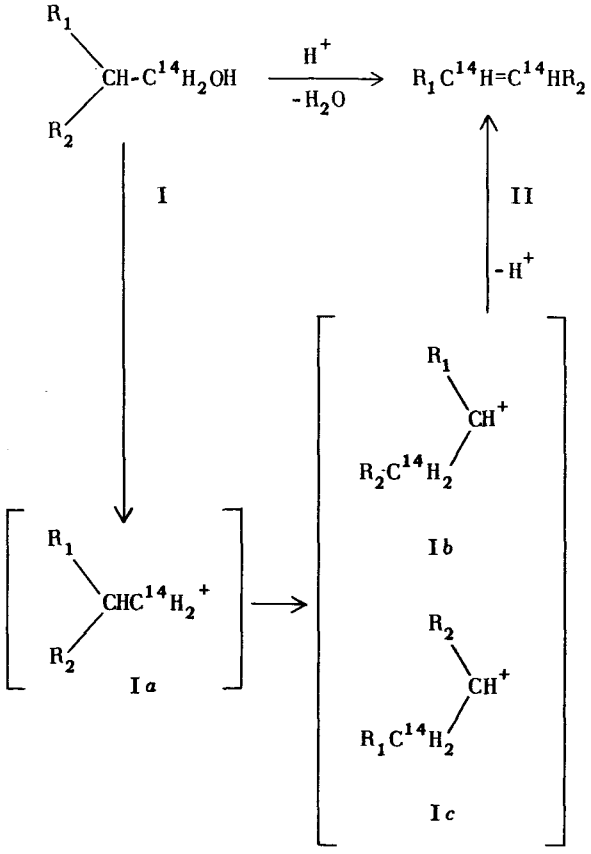
Decarboxylation of the p-Methoxybenzilic Acid. A mixture of 60 mg of the acid, 16 mg of chromic oxide, and 3 mg of glacial acetic acid was stirred for 1½ hr. The carbon dioxide from the decarboxylation was swept into half-saturated barium hydroxide solution, contained in two centrifuge tubes arranged in series. The precipitated barium carbonate was centrifuged, washed carefully with water, and dried.

After decarboxylation the mixture which remained in the reaction flask was added to 10 ml of water, neutralized with sodium bicarbonate, and extracted with ether. Removal of the ether left a clear glass, which when crystallized from a methanol-water solution yielded 30.1 mg of

[a] Member of the Research Participation Program sponsored jointly by the Oak Ridge Institute of Nuclear Studies and Oak Ridge National Laboratory; permanent address, Mississippi State College, State College, Mississippi.

crystals of the *p*-methoxybenzophenone, m.p. 61 to 62°C.

Rearrangement of β,β-Disubstituted Ethanols (John G. Burr, Jr.). The acid-catalyzed rearrangement of β,β-disubstituted ethanols (I) is known[15] to give in part or entirely (depending upon the nature of the substituent groups) symmetrical ethylenes (II).



These rearrangements presumably proceed through the carbonium ion intermediate, I*a*. The ethylene (II) is postulated to be formed through one or both of the intermediates, I*b* or I*c*, arising by migration of R_1 and R_2, respectively. The relative amounts of migration of these two groups can be determined by studying the rearrangement with a β,β-disubstituted ethanol containing a labeled carbon atom in either the α or β position.

Efforts thus far have been devoted to the attempt to obtain a method of preparation which would be broadly applicable to the preparation of ethanols such as I with a number of different types of R′ and R″.

Reaction of Hydroxymethylene Ketones with Alkaline Formalin Solutions (John G. Burr, Jr.). In an extension of the previously reported reaction[16] of alkaline formalin solutions with hydroxymethylene desoxybenzoin, the preparation of several novel hydroxymethylene ketones has been investigated.

It has been shown that the reaction of phenylacetaldehyde and anthrone with ethyl formate in the presence of sodium methoxide gives only those products which are known to result from the action of alkoxides upon these compounds.

Effect of Aluminum Chloride on Ethylbenzene-8-C^{14} (Royston Roberts,[a] Gus A. Ropp, and O. K. Neville). (Ethyl-2-C^{14})-benzene has been prepared in 85% radiochemical yield by catalytic reduction of aceto-2-C^{14}-phenone. A study is being made of the isomerization of this compound on treatment with aluminum chloride. The isomerization involves the shift of the labeled carbon from the β to the α position.

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[15] P. Remart and P. Amagat, "Sur quelques transpositions moléculaires," *Ann. chim.* [10] 8, 263 (1927); M. S. Kharasch and R. Clapp, "The Reactions of Epoxy Compounds with Reagents. I. The Interaction of Phenylepoxyethane (Styrene Oxide) and Arylmagnesium Halides," *J. Org. Chem.* 3, 355 (1938-39).

[16] J. G. Burr, Jr., "The Reaction of 9-Formylfluorene-10-C^{14} with Formaldehyde," *J. Am. Chem. Soc.* 73, 823 (1951).

[a] Research Participant, University of Texas, Austin.

Preparation of (Ethyl-2-C^{14})-benzene. Aceto-2-C^{14}-phenone (2.1 ml, 18 mmoles, 1.74 μc/mmole) dissolved in 6 ml of glacial acetic acid containing 5 drops of 70% perchloric acid was stirred for 72 hr with 2 g of 5% palladium on charcoal catalyst in hydrogen at 25 psi pressure. One hundred milliliters of c.p. ethylbenzene was added to the reaction mixture, and chemically pure (ethyl-2-C^{14}-benzene was isolated. Two successive distillations through a 36-in. 10-mm Vigreux column did not change its specific activity (1.71 μc/mmole, b.p. 132 to 134°C at 743 mm Hg). The radiochemical yield from aceto-2-C^{14}-phenone was 85%.

Degradation of (Ethyl-2-C^{14})-benzene. To demonstrate that the C^{14} activity of the (ethyl-2-C^{14})-benzene was present only in the position β to the ring, a sample was oxidized by nitric acid to *p*-nitrobenzoic acid which was shown to be nonradioactive. Three milliliters of (ethyl-2-C^{14})-benzene was heated for 40 hr at 125°C with 30 ml of c.p. nitric acid. Excess water was added, and the precipitated yellow solid was filtered and washed thoroughly with water. The collected product was dissolved in sodium bicarbonate solution and extracted with ether to remove nonacidic by-products of the oxidation. The product was reprecipitated from the bicarbonate solution with sulfuric acid. It was recrystallized from boiling water and dried at 70°C to give 100 mg (24% yield) of *p*-nitrobenzoic acid, m.p. 231 to 236°C, which was found to contain only background activity.

[redacted]

4. CHEMISTRY OF SEPARATION PROCESSES

FLUORIDE STUDIES

P. A. Agron

Removal of Pa^{233} from Neutron-Irradiated ThF_4. The work proposed in the last quarterly report[1] on the removal of protactinium from the pelleted sample of thorium fluoride (surface area = 0.48 m^2/g) is in progress.

Fluoride Solubility Studies. Experimental procedures are being considered for determining the solubilities of metal fluorides in anhydrous HF; in particular, this study will concern the fluorides of uranium and fission products.

The phase study of UO_2F_2-HF-H_2O has been carried out up to a 42% concentration of HF[2] at 25°C. It is proposed to complete this phase study by extending the range to higher concentrations of HF. The solubility of UO_2F_2 in anhydrous HF as a function of temperature will also be studied.

ORGANIC CHEMISTRY OF SOLVENTS

W. H. Baldwin and C. E. Higgins

Abstract. The kerosene diluent currently used in the Purex process reacts with 5 *M* HNO_3 above 100°C to give nitration products and carboxylic acids. These products could adversely affect the process if elevated temperatures were used.

A counting technique for solutions containing P^{32} has speeded the estimation of the organic phosphates being studied.

The solubility of tributyl phosphate is low in most of the aqueous solutions tested, but the apparent solubility may appear higher because of emulsification by processes that are not yet controlled.

The rate of hydrolysis of TBP is slow at 25°C but is much faster at 75°C. Hydrochloric acid hydrolyzed TBP faster than did nitric acid at 75°C.

Acid. Tributyl phosphate, the solvent used in the Purex purification process, is diluted with kerosene to extract uranium and plutonium. During hydrolysis rate studies at elevated temperatures, it was observed that the kerosene reacted with nitric acid. A test was made to determine the extent of this reaction.

Kerosene (500 ml of Amsco 123-15) was allowed to react with 500 ml of 6.1 *M* HNO_3 at reflux temperature for 6 hr. The aqueous phase was removed, and a fresh portion of nitric acid was added. This was repeated until 10 portions of 6.1 *M* HNO_3 had been used. Copious quantities of the brown fumes of nitrogen dioxide were liberated during the reaction, and both phases had a yellow color. Titration of the aqueous phases revealed that a total of 13.3 moles of nitric acid had disappeared (43% of the total nitric acid employed).

The aqueous phase on cooling deposited a white powder that weighed a

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[1] P. A. Agron, "Removal of Pa^{233} from Neutron-Irradiated ThF_4," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1951*, ORNL-1053, p. 78 (Oct. 5, 1951).

[2] R. Kunin, *The System UO_2F_2-HF-H_2O*, Carbide and Carbon, S.A.M. Laboratories, report A-3255 (May 8, 1945).

[redacted]

total of 28 g when combined with the material that was obtained by concentration of the mother liquors. This powder is a mixture of aromatic carboxylic acids which result from the oxidation of the methyl groups that are attached to aromatic rings.

From the white powder it was possible to pick out by hand several large sugar-like crystals (0.1 g). After crystallization from water, these crystals were identified as oxalic acid.

The kerosene fraction that remained after treatment with 9 portions of 6.1 *M* HNO_3 contained 65 mg of nitrogen per milliliter. This corresponds to 4.6 moles of nitrogen per liter, or nearly 1 mole of nitrogen (as nitrate) per mole of reacted kerosene (average molecular weight assumed to be 200).

The rate of reaction seemed to be as great at the end of these treatments as at the beginning. Several precautions might be taken in the use of kerosene-diluted TBP:

1. Operate at temperatures near 25°C.
2. Use purified kerosenes from which most aromatic compounds have been removed.
3. Make certain that the products formed in the reaction between nitric acid and kerosene do not interfere in the proposed process.

Counting Techniques for Use with TBP^{32} and Its Decomposition Products. Previous encouraging results with the counting of P^{32} in solution using thin-walled glass Geiger-Mueller tubes[3] have been confirmed, and a routine method of estimation has been adopted. Tri-*n*-butyl phosphate containing radioactive P^{32}[4] and its decomposition products dissolved in 15 ml of solution were placed in a 25-ml graduated cylinder (19 mm i.d., 110 mm high). Into this solution was dipped a thin-walled glass Geiger-Mueller tube (R.C.L., Mark 1, model 80; length of active section 75 mm, diameter 14 mm) so that the silvered section of the tube was covered by the solution. The counting efficiency was about 8% of the disintegration rate. The observed counting rate was corrected for the density of the solution. The background count of the tube and cylinder remained constant when the glass surfaces were rinsed with distilled water and acetone.

Solubility Tests. The loss of TBP in process streams is of practical importance in plant operation from the standpoint of solvent loss and contamination of products. Tests on the solubility of TBP have shown that emulsification and dispersion make significant differences in the observed amount of TBP in the aqueous phase.

The observed solubility of TBP (100%) was the same in 0.1 *M* NaOH and H_2O (0.0015 mole/liter). In 4 *M* HNO_3 the solubility was about half this value (0.00083 mole/liter) and in 2.3 *M* uranyl nitrate solution it was still less (<0.00005 mole/liter) (see Table 4.1).

Distribution of TBP between Water and Organic Solvents as a Function of Concentration. The concentration of

[3] W. H. Baldwin and C. E. Higgins, "Organic Chemistry of Solvents," ORNL-1053, *op. cit.*, p. 83.

[4] W. H. Baldwin and C. E. Higgins, *The Preparation of Tri-n-butyl Phosphate-P^{32}*, ORNL-887 (Feb. 5, 1951).

TABLE 4.1

Solubility of Tributyl Phosphate-P^{32} at 25°C

SOLUTION	SOLUBILITY (moles/liter)
0.1 *M* NaOH	0.0015
H_2O	0.0015, 0.0015*
4 *M* HNO_3	0.00083
2.3 *M* uranyl nitrate	<0.00005

*Hanford Engineer Works, private communication.

TABLE 4.2

Distribution of Tributyl Phosphate-P^{32} between Solvents and Water at 25°C

TBP^{32} (moles/liter)	TBP^{32} IN WATER (moles/liter)		
	OURS		
	PREP. 1	PREP. 2	HANFORD*
In Amsco 123-15			
0.01	0.000034		
0.1	0.00029		
0.31			0.00064
0.47	0.00060		
0.64			0.00090
0.94	0.00083		
1.25			0.00105
1.88			0.00109
2.91			0.00124
3.76	0.00154		0.00147
In CCl_4			
0.001		3.3×10^{-7}	
0.01		3.5×10^{-6}, 2.6×10^{-6}	
0.1		0.000035	
0.48	0.00019	0.00019	
0.96	0.00026	0.00049	
1.96		0.00094	
3.76	0.00154	0.00177	

*Private communication.

tributyl phosphate in water that has been equilibrated with organic solutions varies directly with the concentration of the TBP in the organic phase. Concentrations were higher in those aqueous phases that had been contacted with kerosene solutions than in those that had been equilibrated with carbon tetrachloride solutions.

The data presented in Table 4.2 represent the most reliable that are available; they illustrate the difficulty of getting samples that truly represent the solubility of TBP in water. The amount of TBP found in water equilibrated with TBP in Amsco solvent was found to be higher by workers at Hanford than those found here (see Table 4.2).

Rate of Hydrolysis of TBP by Nitric Acid. Tributyl phosphate has been favored as an extraction solvent because of its stability toward nitric acid. Empirical tests in semi-works and pilot plant—scale equipment have indicated no ill effects on the process from repeated use of solvent. An effort has been made to supply quantitative data on the hydrolysis rate.

Equal volumes of TBP^{32} and 8 *M* HNO_3 have been equilibrated at 25°C for 29 days. The concentration of nitric acid was chosen at 8 *M* to give about 5 *M* HNO_3 in the aqueous phase at equilibrium. In this time 0.28% of the TBP has been hydrolyzed. It is planned to continue this experiment by allowing the hydrolysis to

proceed and obtain data over longer periods of time.

Preliminary measurements on the rate of hydrolysis of TBP (0.0004 *M*) by 5 *M* HNO_3 (homogeneous phase) at 75°C indicate the half-time of the reaction to be of the order of 50 hr. It can be calculated from this that the fraction decomposed per day is 0.33, which agrees with the estimate calculated from the formula of Slansky.[5]

Hydrolysis with 5 *M* HCl was more rapid (by a factor of 4 or 5) than with 5 *M* HNO_3 at 75°C.

[5] Hanford Engineer Works, *Hanford Chemical Research Section Quarterly Report for Period January through March 1951*, HW-20863 (Apr. 16, 1951).

ELECTROCHEMICAL ION-EXCHANGE SEPARATION

J. H. Gross

During this quarter equipment was assembled for more refined determinations of the separation factor in the electromigration of mixtures of Na^+ and Li^+ (as the chlorides) through a bed of Dowex-50 resin. Preliminary data were obtained on variation of bed resistance with current density and on variation in bed solution concentration during start-up.

Work on this separation method has been suspended in favor of more urgent problems. The electromigration work may be continued by another group.

5. CHEMICAL PHYSICS

CHEMISTRY OF SOLID STATE

High-Temperature X-Ray Diffraction (M. A. Bredig). The construction of the vacuum chamber for the high-temperature X-ray-diffraction spectrometer, briefly described in the preceding quarterly report,[1] has been completed, and a few runs have been made at elevated temperatures. During heating periods approximating 30 min, sections of the diffraction pattern up to a Bragg angle of 60° were recorded. On the basis of these first tests a number of improvements, particularly in the design of the graphite heating element and of the heat shield, are being made. Whereas with the present arrangement a maximum temperature of 1540°C was reached with a power input of approximately 4.5 kva (or approximately 3 kw), preliminary tests indicate that it will be possible with the new design to reach temperatures well in excess of 2000°C, with a higher power input.

The present experiments were carried out with hafnium dioxide and zirconium dioxide, i.e., highly refractory compounds of interest because of exceptionally high, and low, neutron-absorption cross-sections, respectively. Significantly, the cubic, fluorite type, phase, with a lattice parameter of 5.1 A, which has been assigned by various authors[2] to solid solutions of zirconium dioxide with other oxides rather than to the pure ZrO_2,[3] appeared prominently beside the tetragonal phase in the pattern taken at 1540°C whereas at 1340°C only the tetragonal phase[3] was obtained. Spectrographic analysis limited the amounts of impurities such as MgO, which are known to stabilize the cubic phase, to traces, with the exception of hafnium oxide (2.8%) and calcium oxide (0.1%). In both zirconium and hafnium oxide the cubic and tetragonal phases after cooling to room temperature were found only partially reconverted to the monoclinic, low-temperature form. These results somewhat favor the views of Goldschmidt[3] on the nature of the cubic phase as a crystal modification of pure ZrO_2 (and HfO_2).

Remotely Controlled X-Ray-Diffraction Spectrometer (M. A. Bredig; B. S. Borie, Metallurgy Division; G. Klein, Physics of Solids Institute; and F. A. Sherrill, Physics of Solids Institute). The work in the research and instrument shops on the construction of the instrument mentioned in previous reports[1,4] is nearing completion. The Hilger X-ray generating equipment has been set up in the vicinity of the concrete cell which will house the spectrometer.

Effects of Radiation on Crystal Structure. *Lead Oxide* (M. A.

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[1] M. A. Bredig, "Solids and High-Temperature Chemistry," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1951*, ORNL-1053, p. 114 (Oct. 5, 1951).

[2] E.g., P. Duwez and F. Odell, "Phase Relationships in the System Zirconia-Ceria," *J. Am. Ceram. Soc.* 33, 274 (1950).

[3] V. M. Goldschmidt, *Geochemische Verteilungsgesetze*, 1926; see *Strukturbericht* I, 208 (1931).

[4] M. A. Bredig and B. S. Borie, Jr., "X-Ray Diffraction Spectrometer for High-Level Radioactive Specimens," *Physics Division Quarterly Progress Report for Period Ending June 15, 1950*, ORNL-782, p. 88 (Oct. 4, 1950).

Bredig[5,6]). The first group of specimens which was irradiated for 17,719 megawatt-hr (approximately 3×10^{19} fast neutrons per square centimeter) in an air current as coolant inside the water-cooled uranium cylinder of the fast-neutron facility at Chalk River was returned to X-10 in April. It consisted of one specimen each of the red and yellow crystal modifications of PbO. The originally bright red sample was, after irradiation, dark brown in color, whereas the yellow specimen had changed only slightly toward a grayish yellow. The X-ray-diffraction patterns, on the other hand, showed that no trace of the yellow, orthorhombic, modification was present in the red-brown specimen, but that a considerable quantity, approximately 25%, of the red modification had formed in the originally pure yellow specimen (Fig. 5.1). A trace of minium, Pb_3O_4, was also formed in both specimens, either by oxidation by the small amount of air left in the quartz capsule on sealing, or by disproportionation of the PbO into metallic lead and the higher oxide.

Pending an examination of the second group of specimens, which are receiving a four times larger dosage of pile radiation, the following conclusions may be drawn from the present result:

1. So-called "thermal spikes," i.e., lattice vibrations due to collisions of fast neutrons and recoil atoms with lattice atoms sufficient to raise above the inversion temperature of 488°C the temperature of a sufficiently large volume element of the crystal for a sufficiently long time to produce the conversion red → yellow, which occurs on ordinary heating, did not occur under the conditions of the experiment. The possible objection that a similar mechanism might also cause annealing and reconversion of the yellow form produced in such a way into the red low-temperature modification, thus concealing the occurence of the original process, does not appear very plausible, because very long time periods of annealing were found to be necessary for the purely thermal inversion yellow → red below the enantiotropic transition temperature of 488°C. However, a study of this particular question with variation of the fast-neutron flux (nv) rather than dosage (nvt) seems indicated.

The partial conversion of the metastable yellow form into the stable red form, as observed, may at this stage of the investigation be attributed to two different causes: (1) it may be the result of collisions of fast neutrons with the atoms of the lattice with subsequent displacement and rearrangement in the most stable structure; and (2) it may be caused by ionization by either recoil atoms (e.g., oxygen) or by beta and gamma radiation. The effect of gamma rays on red and yellow lead oxide is at present being tested in the cobalt gamma-ray source at X-10. Other experiments will include X-ray and

[5] M. A. Bredig, "Phase Transition on Neutron Bombardment," *Physics Division Quarterly Progress Report for Period Ending September 20, 1950*, ORNL-865, p. 77 (Jan. 8, 1951).

[6] M. A. Bredig, ORNL-1053, *op. cit.*, p. 118.

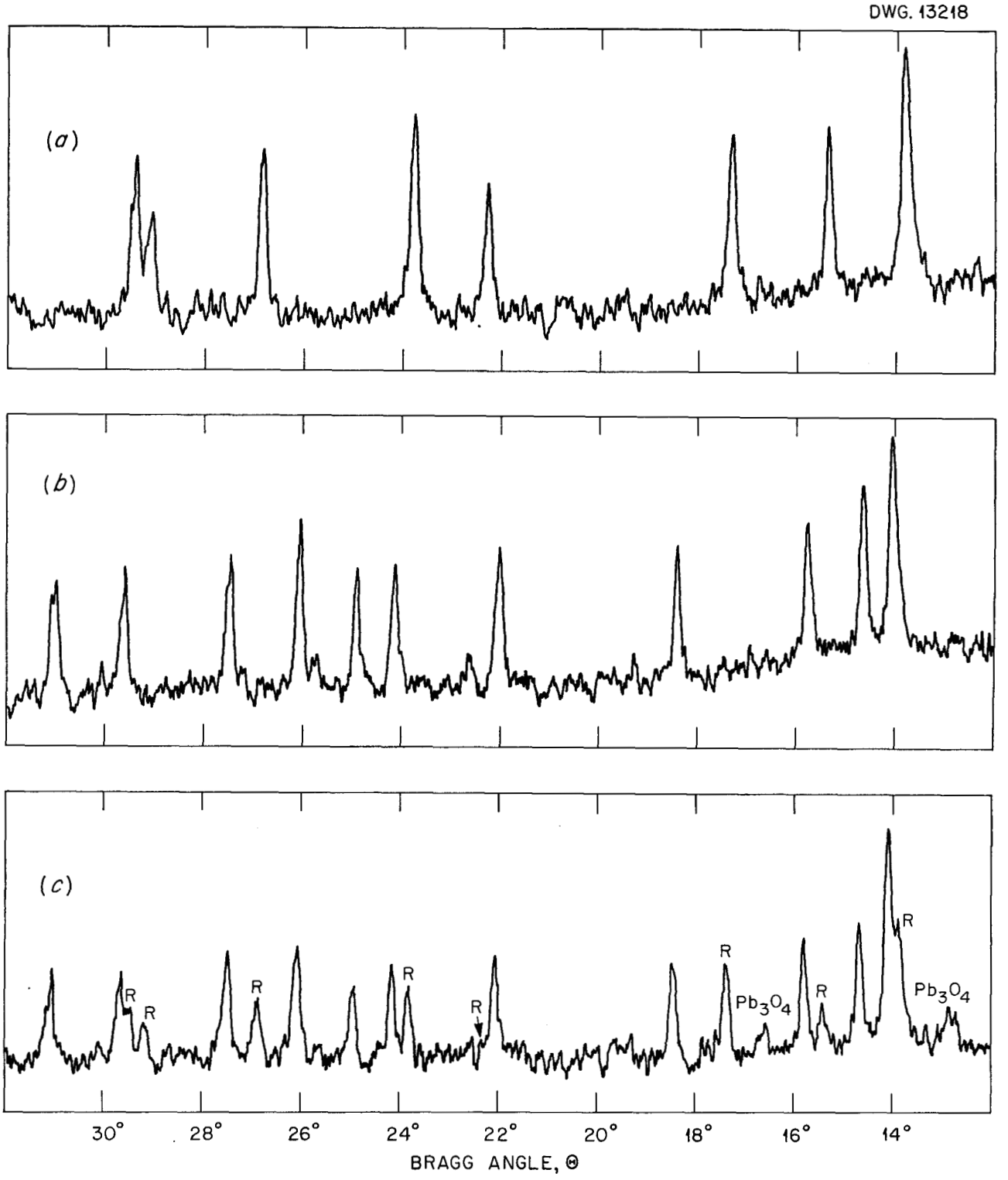

Fig. 5.1 - Powder X-Ray Diffraction Patterns (Cu Kα). (*a*) Lead oxide (PbO), red, tetragonal; (*b*) lead oxide (PbO), yellow, orthorhombic; before irradiation; (*c*) lead oxide (PbO), yellow; irradiated at Chalk River, nvt = 3×10^{19} fast neutrons/cm^2. Note red form, R.

ultraviolet irradiations. A somewhat preliminary search of the literature makes it appear that yellow lead oxide is the only substance, besides yellow phosphorus,[7] thus far found to undergo a change of crystal form under irradiation.[8] Microscopic observation, rather Than X-ray diffraction, was employed in the previous investigation, and the remark found there that the red form changed to orange and yellow on exposure to beta and gamma rays remains unexplained, particularly in view of the failure of the red form to change its structure in the recent pile irradiation experiment. Another case, that of hexagonal zinc sulfide allegedly converted in an environment of water into the cubic phase by ultraviolet radiation,[9] has in common with the earlier lead oxide study the fact that no X-ray-diffraction evidence was obtained. It is difficult to see on what evidence, then, the statement regarding such a conversion was actually based. Thus, the effects of ionizing radiation (as against collisions) cannot be considered proven in either PbO or ZnS. The conversion by such radiation of yellow phosphorus is probably that of a molecular type crystal from one degree of polymerization, P_x, to another one, P_y. As such, it is somewhat easier to understand through the absorption of one energy quantum per molecule, dissociation, and recombination than is a phase change in a largely ionic crystal such as PbO or ZnS. This consideration tends to emphasize the significance of the phase change observed in the pile irradiation of lead oxide and of the elucidation of its mechanism, which is now being attempted.

Organic Acid Salts and Miscellaneous Compounds (M. A. Bredig, D. S. Jesseman). An irradiation for three weeks in the X-10 reactor of sodium bitartrate had led to the destruction of the crystal lattice, probably with simultaneous partial chemical decomposition.[10] The irradiation is being repeated in the X-10 cobalt gamma-ray source. Included in the samples thus being exposed is sodium bioxalate hydrate, $NaHC_2O_4 \cdot H_2O$. The anhydrous neutral salt, $Na_2C_2O_4$, had shown no effect of fast-neutron irradiation at X-10,[10] whereas it had been reported previously by W. Bothe, Heidelberg, to undergo a reversible change to the amorphous state on bombardment with alpha particles. Still another specimen, arsenic trioxide (As_2O_3), was included on the suggestion of K. Lark-Horowitz who reported the observation by Bothe of its reversible conversion to an amorphous state with alpha particle.[11] An exposure of six months has been scheduled. Irradiation experiments with X rays are also being considered.

[7] H. Becquerel, "Sur quelques effets chimiques produits par le rayonnement du radium," *Compt. rend.* 133, 709 (1901).

[8] J. Hoffmann, "Anderungen der Bleioxyde durch Licht und Druck," *Z. anorg. allgem. Chem.* 228, 160 (1936).

[9] H. Platz and P. W. Schenk, "Über die Verfärbung des Zinksulfids im Licht," *Z. angew. Chem.* 49, 822 (1936).

[10] M. A. Bredig, ORNL-1053, *op. cit.*, p. 119.

[11] K. Lark-Horovitz, letter to M. A. Bredig, June 6, 1951.

High-Temperature Chemistry (M. A. Bredig, J. W. Johnson, and D. S. Jesseman). Work in the field of high-temperature chemistry is at present concerned with these two first objectives: (1) an experimental study of salt type melts and solids containing excess metal in liquid and/or solid solution, and (2) a computation of thermodynamic properties of systems of interest in connection with the possible use of molten sodium hydroxide as a moderator, coolant, or fuel carrier in nuclear reactors.

Fused Salt, Excess Metal Systems. It was proposed some time ago[12] that melts containing excess metal either as ions in unusual low valence states, or as metal in liquid solution, might exhibit advantages with respect to corrosive attack. Among fluoride systems, which would merit particular attention, a calcium solution in molten calcium fluoride had received early attention (1909) by previous investigators (Wöhler and Rodewald[13]) who also believed that they had prepared a solid subfluoride, CaF, besides other subhalides such as CaCl, CaI, and Ag_2F. Whereas the structure and properties of Ag_2F have been studied since and are now quite well known, the existence of neither the other usually very deeply colored subhalides, and of suboxides, or subsulfides (see, for example, Guntz and Benoit[14]) nor of true metal solutions in salt melts has been generally accepted.[15] More recent studies have confirmed part of the earlier work. Cubicciotti and Thurmond[16] found solubilities of alkaline earth metals in their halide melts at temperatures up to 1100°C as high as 30 to 40 mole %, whereas Rinck[17] does not report any quantitative data on solubility of sodium and potassium metals in their fluoride melts. Halla and Tompa[18] found the solubility of sodium metal in a melt of sodium hydroxide[19] to be due to the formation of sodium oxide and sodium hydride:

$$NaOH + 2Na \longrightarrow Na_2O + NaH$$

Lorenz and Winzer[20] found sodium to be soluble in molten sodium chloride in amounts of approximately 4 wt % at 800°C, and of 15 wt % at 850°C. These last figures might indicate a rather low solubility of alkaline metals in their salt melts at low temperature, e.g., in eutectic fluoride melts. No work on the crystal structure of quenched melts has been found in the literature.

A study of such systems has been started in the laboratory by the preliminary step of collecting and

(12) M. A. Bredig, oral communication to A. M. Weinberg, October, 1950.

(13) L. Wöhler and G. Rodewald, "Bekannte und neue Subhaloide," *Z. anorg. allgem. Chem.* 61, 54 (1909).

(14) A. Guntz and F. Benoit, "Sur les sous-sels alcalino-terreux," *Bull. soc. chim. France* 35, 709 (1924).

(15) A summary of the earlier work is found in the Book *Pyrosole* by R. Lorenz and W. Eitel, Akadem. Verlagsges., Leipzig, 1926.

(16) D. D. Cubicciotti and C. D. Thurmond, *J. Am. Chem. Soc.* 71, 2149 (1949).

(17) E. Rinck, "Equilibres à l'état fondu entre sels et metaux alcalins et alcalino-terreaux," *Ann. chim.* [10] 18, 395 (1932).

(18) F. Halla and H. Tompa, "Uber den Zustand des in NaOH-Schmelzen gelösten Natriums," *Z. anorg. allgem. Chem.* 219, 321 (1934).

(19) G. v. Hevesy, "Uber die schmelzelektrolytische Abscheidung der Alkalimetalle aus Atzalkalien und die Löslichkeit dieser Metalle in der Schmelze," *Z. Elektrochem.* 15, 529 (1909).

(20) R. Lorenz and R. Winzer, "Die Löslichkeit von Natrium und Calcium in ihren Chloriden und Chloridgemischen," *Z. anorg. allgem. Chem.* 183, 121 (1929).

TABLE 5.1

Calculated Free Energies of Reaction

REACTION	ΔF REACTION (kilocalories per mole of oxide)			
	AT 25°C	AT 500°C	AT 800°C	AT 900°C
$2NaOH + Fe = FeO + Na_2O + H_2$	+33	+22	+17	+15
$2NaOH + Ni = NiO + Na_2O + H_2$	+41	+32	+30	+29
$2NaOH + Co = CoO + Na_2O + H_2$	+41	+30	+26	+24
$2NaOH + C = CO + Na_2O + H_2$	+50	+29	+14	+8
$2NaOH + Mn = MnO + Na_2O + H_2$	+5	-6	-11	-12
$2NaOH + 2Cu = Cu_2O + Na_2O + H_2$	+57	+44	+39	+37
$6NaOH + 2Cr = Cr_2O_3 + 3Na_2O + 3H_2$	+27	-3	-13	-18
$6NaOH + 2V = V_2O_3 + 3Na_2O + 3H_2$	-16	-48	-59	-64
$4NaOH + Mo = MoO_2 + 2Na_2O + 2H_2$	+63	+44	+38	+34
$4NaOH + Si = SiO_2 + 2Na_2O + 2H_2$	-11	-30	-36	-39
$4NaOH + Ti = TiO_2 + 2Na_2O + 2H_2$	-21	-40	-48	-51
$4NaOH + W = WO_2 + 2Na_2O + 2H_2$	+64	+43	+35	+32
$4NaOH + C = CO_2 + 2Na_2O + 2H_2$	+90	+50	+31	+24

computing thermodynamic data on metal—metal chloride systems which would be pertinent to a selection of suitable container materials. In addition, a stainless steel cylinder, with one closed and one flanged and water-cooled end, for differential thermal analysis experiments has been designed and is being constructed. A vacuum system for operation of this and similar apparatus has been assembled. Actual experiments in which extensive use will be made of X-ray diffraction for possible identification of solid subhalides (greatly neglected in the previous studies) are expected to be underway soon.

Free-Energy Calculations for Reactions with Sodium Hydroxide. The free energy of formation of sodium hydroxide from the elements in their standard states, as a function of temperature, has been calculated with existing data from 298 to 900°K and extrapolated to 1173°K (900°C). The accuracy of the extrapolation is estimated to be ±15%. These values were used with the free energies of formation of several oxides to calculate the free energy of reaction of sodium hydroxide with the elements. The general reaction investigated was of the following type with reactants and products in their standard states:

$$2NaOH + xM = M_xO + Na_2O + H_2$$

Table 5.1 contains the free energies of reaction in kilocalories. The accuracy of these values is probably of the order of ±20%. Inspection of the tabular values indicates that iron, nickel, cobalt, copper, molybdenum, and tungsten are resistant to attack by sodium hydroxide under these conditions up to a temperature of 900°C. However, chromium, vanadium, silicon, manganese, and titanium show a tendency to react at 500°C, and the tendency increases with temperature.

It should be pointed out that (1) these results only serve to eliminate from further consideration those elements with which this reaction is possible and does not indicate that iron, nickel, etc. are not corroded by some other process, (2) no account has been taken of the activities of the various reactants and products under actual test conditions, and (3) possible compounds of the elements with sodium and oxygen, i.e., sodium ferrite, sodium tungstate, and sodium molybdate, have not been considered at the present writing owing to the meager data available. Adtional data are now being compiled for convenient reference on the basis of more recent literature, particularly for metallic oxides and metal-sodium double oxides.

STORAGE AND RELEASE OF ENERGY IN IONIC SOLIDS SUBJECTED TO IONIZING RADIATION

J. A. Ghormley (with H. A. Levy)

This work is being written up as a thesis and will appear shortly.

ORNL-1116
6/51

[redacted]

CHEMISTRY DIVISION QUARTERLY PROGRESS REPORT

6. REACTOR CHEMISTRY

AQUEOUS SOLUTION CHEMISTRY OF REACTOR FUELS

H. O. Day W. L. Marshall
J. S. Gill H. W. Wright

The Uranium Trioxide—Orthophosphoric Acid—Water System. The experimental work on the uranium trioxide—orthophosphoric acid—water system is given elsewhere.[1]

The study is being confined to the range 150 to 250°C to determine the feasibility of uranium phosphate as a reactor fuel. At the present time no precise solubility data have been obtained owing to the slow equilibration rates and the complexity of the solid phases. However, from current experimental work the following tentative solubilities of uranium in aqueous orthophosphoric acid are given at 250°C:

H_3PO_4 (*M*)	SOLUBILITY OF URANIUM (moles/liter)	MOLE RATIO, PO_4/U
1.0	0.050	20
2.1	0.25	8.4
3.1	0.60	5.2
3.8	~0.85	~4.5
5.8	~1.67	~3.5

Effect of Ferric Oxide on the Critical Solution Temperatures of Aqueous Uranyl Sulfate. The effect of ferric oxide on critical solution temperatures of aqueous uranyl sulfate is reported in reference (1). In summary, the temperature appeared to be lowered 3 or 4°C; however, this is not certain because of the difficulty of observation of solution and solid in silica tubes.

Additional Investigations in Progress. Emphasis is now placed on the investigation of vapor pressure of aqueous solutions of uranium salts [namely, UO_2SO_4, $UO_2(NO_3)_2$, and UO_2F_2] between 150 and 300°C. Consequently, experiments from room temperature to 150°C have been postponed (although the equipment is complete) in order to devote full time to the higher temperature investigation.

Conductivity apparatus is being devised by Bunger to measure conductivities of aqueous uranyl sulfate and other uranium salts between 100 and 300°C.

An extended study of fission product solubilities in uranyl sulfate solutions above 100°C has been started. E. V. Jones will continue the investigation initiated by Lietzke and Stoughton.[2]

RADIATION STABILITY

H. F. McDuffie

The result of work done this quarter by the Radiation Stability Group is summarized below. A detailed discussion will appear in the

[1] J. A. Swartout *et al.*, *Homogeneous Reactor Project Quarterly Progress Report for Period Ending May 15, 1951*, ORNL-1057 (in press).

[2] M. H. Lietzke and R. W. Stoughton, *The Measurement of the Solubility of Fission Product Sulfates at High Temperatures and Pressures*, ORNL-970 (March 13, 1951).

[redacted]

Homogeneous Reactor Project quarterly report.

Efforts of the Radiation Stability Group have been directed toward the following general investigations:

1. Out-of-pile ampoule studies of passive films on 347 stainless steel in contact with uranyl sulfate solution.
2. Out-of-pile studies of corrosion and solution stability using the bomb-fitting-tubing assemblies designed for in-pile testing.
3. Long-term radiation stability tests at the maximum flux of the graphite pile.
4. Short-term exploratory tests at the much higher fluxes of the LITR.
5. Preliminary radiation stability studies of uranyl nitrate solutions.
6. Preliminary radiation stability studies of the components of the heavy-water reflector system of the HRE.

The conclusions of principal interest to the HRE which have arisen from the work of the group during the quarter are as follows:

1. The presence of oxygen is necessary for the maintenance of the passivity of 347 stainless steel surfaces in contact with uranyl sulfate solutions at temperatures of 250°C and may possibly be sufficient for the achievement and maintenance of passivity. (This finding is supported by the work of other groups approaching the problem from different points of view, and it is not intended that any credit should be taken away from their findings. The conclusion, nevertheless, is presented here because the work of this group has been sufficient to establish it with certainty).
2. Surfaces pretreated with chromic acid appear outstandingly better than those pretreated with nitric acid when tested for ability to maintain passivity in contact with degassed solutions of uranyl sulfate.
3. A group of five stainless steel bombs containing enriched uranyl sulfate solutions has been exposed to the full flux of the X-10 pile for seven weeks with maintenance of pressures substantially in excess of steam pressure, thus indicating that the bombs continue to maintain their uranium in solution.
4. A preliminary experiment in the LITR has been carried out successfully.

Projected Work for Next Quarter. Additional preliminary experiments will be carried out at the higher fluxes obtainable in the LITR, using the vertical hole into the active lattice. Apparatus for long-term experiments in the horizontal thimble holes will be completed and experiments will be started. An exploration of uranium peroxide formation as a function of temperature and flux will be carried out in the LITR using the vertical experimental hole.

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Long-term experiments will be continued in the horizontal hole (No. 60) of the X-10 pile throughout the quarter. If the present set of bombs is removed for any reason, a new set will be inserted.

Exploration of the radiation decomposition of the heavy-water reflector system of the HRE will be carried out by means of experiments in hole 12 of the X-10 pile.

Preliminary exploration of the radiation decomposition of uranyl nitrate solutions will be continued, and studies on uranyl fluoride and possibly uranyl phosphate solutions will be initiated, using hole 12 of the X-10 pile.

Out-of-pile studies of bomb-fitting-tubing assemblies will be continued as a basis for interpretation of the in-pile radiation results. Solutions of higher concentration will be checked, following which radiation studies will be initiated in hole 12.

Out-of-pile studies of the rates of recombination of hydrogen and oxygen in our bomb-fitting-tubing assemblies at high pressures may be initiated in order to provide better interpretation of the significance of data obtained in the presence of radiation, particularly in the pressure "hump" frequently observed in radiation experiments.

If possible, work on the interaction of oxygen with stainless steel surfaces, both using O^{18} as a tracer and measuring the rates of consumption of ordinary oxygen, will be initiated for its significance in connection with passivity. Also, work will be started on the interaction of stainless steel components with uranyl sulfate solutions under a variety of conditions, using irradiated stainless steel as a source of radioactive components. This technique should provide a very sensitive measurement of the ability of protective measures to prevent the escape of the stainless steel metallic components, i.e., to prevent corrosion.

SOLUBILITIES OF FISSION PRODUCT SULFATES IN AQUEOUS SOLUTIONS

B. Zemel and R. W. Stoughton

The solubilities of $La_2(SO_4)_3$ and of $Ce_2(SO_4)_3$ in H_2O have been determined as a function of temperature up to about 350°C, and will be reported in detail in the HRE quarterly progress report.

Several solubility curves for data obtained in the presence of UO_2SO_4 were discarded when it was found that the stock UO_2SO_4 used contained appreciable amounts of ammonia. It was further shown that the solubility of the alundum filter disks employed and temperature variations across the bomb were causing spurious results owing to precipitation of uranium and distillation of water, respectively.

In order to obviate these factors three measures were taken: the alundum filter disks were replaced by platinum sponge filters, the bomb furnaces were so arranged that the upper or sample end of the bomb was kept a few degrees hotter than the lower or reaction side, and the temperature differential for filtration was kept low enough to favor filtrations over distillation.

[redacted]

ELECTROCHEMICAL CORROSION STUDIES

J. C. Griess

Studies of the corrosion in connection with the HRE have been continued. As previously reported,[3] the majority of the results obtained to date for corrosion of 347 stainless steel and stability of UO_2SO_4 solutions can be explained on an electrochemical basis. Hence most of the work during the past quarter has been directed toward the establishment of a general mechanism of the corrosion of certain metals and the effects of the different variables on the corrosion rate.

Experiments have been carried out in an attempt to show the effect of the presence of oxygen in preventing the precipitation of uranium from solution. The data definitely showed that oxygen was consumed when uranyl sulfate was heated at 250°C in the presence of air in a passivated stainless steel container. It was also shown that in the absence of oxygen at least some of the uranium was precipitated from solution either as UO_2 or U_3O_8.

Recently, however, some doubt has been cast on the validity of the results owing to the presence of impurities in the uranyl sulfate. Careful analyses of the supposedly pure uranyl sulfate have shown that the ratio of sulfate to uranium was greater than unity. The odor of the uranyl sulfate solutions used also indicated the presence of small amounts of organic material.

An attempt is being made to prepare pure uranyl sulfate by reacting stoichiometric amounts of uranium trioxide and sulfuric acid. When pure uranyl sulfate is available, the experiments concerning the consumption of oxygen will be repeated.

ANODIC TREATMENT OF TYPE 347 STAINLESS STEEL DURING PASSIVATION WITH NITRIC OR CHROMIC ACID SOLUTION

M. H. Lietzke and R. W. Stoughton

The type 347 stainless steel to be used in the X-10 homogeneous reactor experiment can be passivated by heating in either 1% HNO_3 or 2% CrO_3 solution at 250°C for 24 hr. Since either treatment is believed to produce a passive oxide film on the surface of the steel, it seemed of interest to determine whether anodic treatment of the steel during either of the passivation processes might not produce a superior passive film.

Specimens of No. 347 stainless steel freshly passivated in either HNO_3 or CrO_3 solutions show a potential greater than 700 mv more positive than the saturated calomel electrode (SCE) when immersed in a 0.13 *f* UO_2SO_4 solution (corresponding to 30 g of uranium per liter). The potential becomes somewhat less positive when the passivated steel specimen is maintained at 100°C in the UO_2SO_4 solution under reflux conditions. As long as the film is intact the curve obtained by plotting potential vs. time does not show any sudden breaks. However, if sufficient KCl is added to the uranyl sulfate solution the potential of the passivated steel with respect to the SCE may suddenly become much less positive, indicating failure of the passive film. The length of time before sudden breaks are observed in

[3] ORNL-1057, *op. cit.*

the potential-vs.-time curve when the uranyl sulfate solution at 100°C is made 0.2 *M* in KCl is taken as a measure of the quality of the passivated film being studied. The potential is measured using a vibrating-reed electrometer and recorded by a Brown recording potentiometer.

It was observed in the first experiments that HNO_3-passivated specimens failed almost immediately when placed directly in uranyl sulfate solution 0.2 *M* in KCl. However, the passive films appeared much more resistant to the chloride when they were maintained in contact with the UO_2SO_4 solution at 100°C for 48 hr prior to the addition of the KCl. Hence all specimens used in subsequent experiments were subjected to this preliminary treatment before KCl was added to the solution. The actual changes that occur in the film during this conditioning period will be investigated further.

Figure 6.1 shows the potential-vs.-time curves obtained with specimens of nitrate-passivated No. 347 stainless steel. The initial decrease in potential probably corresponds to the removal of oxygen from the passive film. When the chloride was added (as KCl dissolved in a small amount of UO_2SO_4 solution) some oxygen was also introduced into the system which caused the sudden humps in the curve. As far as the curves were followed after the addition of the KCl, no breaks were observed in the case of the specimens conditioned in the

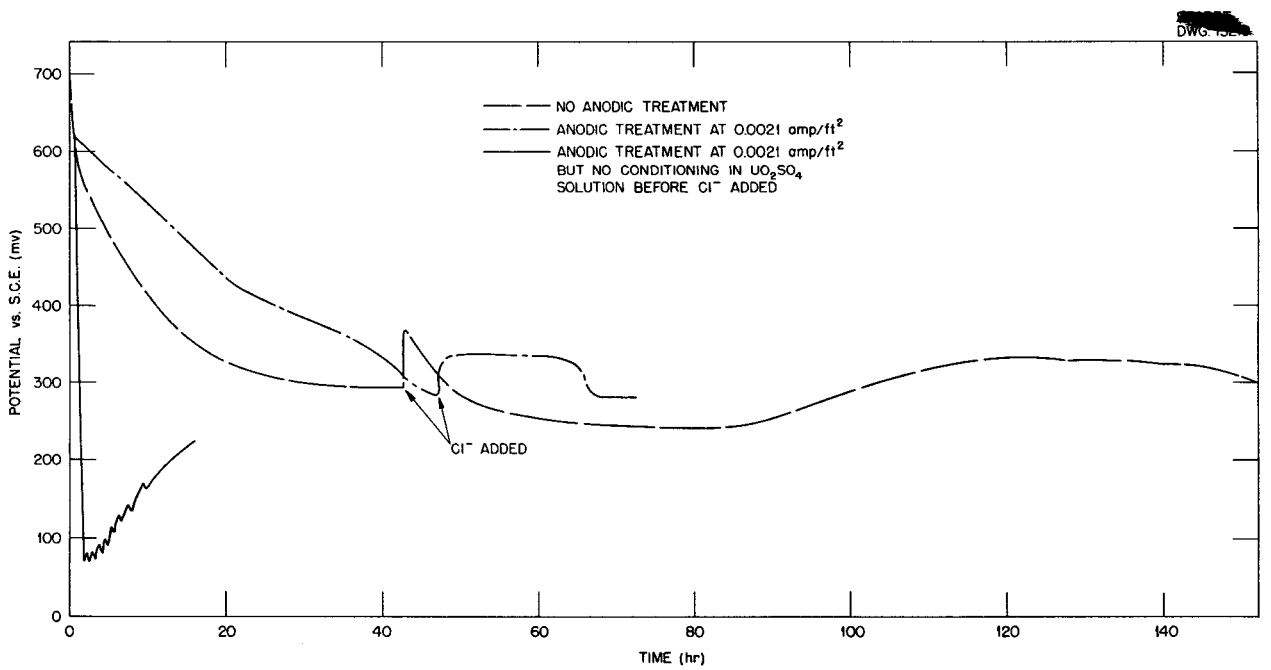

Fig. 6.1 - Effect of Anodic Treatment of Type 347 Stainless Steel During Passivation in 1% HNO_3 Solution.

UO_2SO_4 solution before the addition of the chloride. The specimen that was not conditioned in the UO_2SO_4 solution failed almost immediately.

Figure 6.2 shows the effect of anodic treatment of 347 stainless steel at various current densities during passivation in 2% CrO_3 solution. The specimen that received no anodic treatment lasted for more than 62 hr before it failed. The length of time the anodized specimens remained good decreased with increasing anodic current density during passivation. Hence it appears from these experiments that the passive film produced on 347 stainless steel anodized in 2% CrO_3 at 250°C is inferior to that produced under the same conditions but without anodic treatment.

Further experiments involving anodic treatment in HNO_3 and cathodic treatment in CrO_3 solution are being carried out at present.

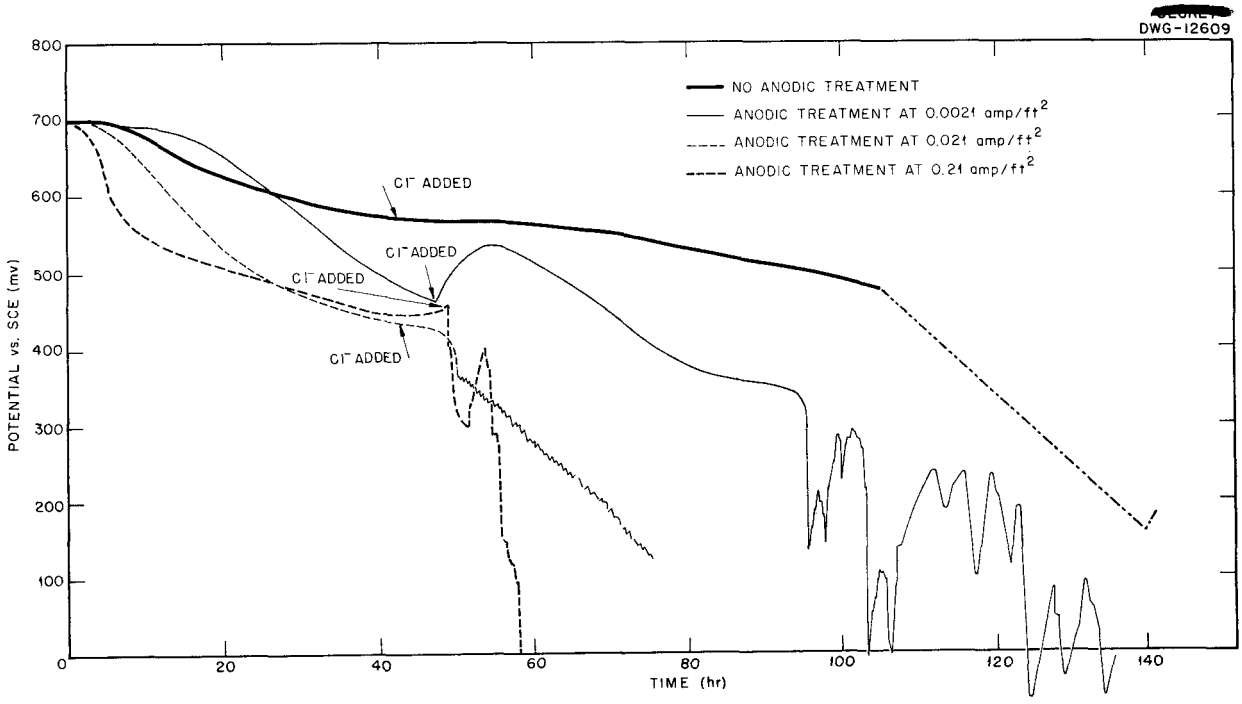

Fig. 6.2 - Effect of Anodic Treatment of Type 347 Stainless Steel at Various Current Densities During Passivation in 2% CrO_3 Solution.

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7. RADIATION CHEMISTRY

RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS

C. J. Hochanadel and J. A. Ghormley

Actinometry of Gamma Radiation. Additional measurements were made on the yield for ferrous sulfate oxidation by gamma radiation in order to resolve the difference between our value[1] of $G = 15.5 \pm 0.3$ Fe^{++} oxidized per 100 ev determined calorimetrically and that obtained by Miller[2] and Hardwick[3] of $G = 20.8$ determined by ion-chamber measurement of energy absorption.

New calorimetric measurements of intensities of 1500, 4500, and 15,000 r/min gave the same yield as that obtained previously. In addition, the yield was measured using an ion chamber made of polystyrene, giving a value of $G = 15.5$ at 4500 r/min and $G = 16.1$ at 270 r/min.

The yield for reduction of Ce^{4+} in air-saturated 0.4 *M* H_2SO_4 solution was found to be $G = 2.46$ Ce^{4+} reduced per 100 ev absorbed. The ratio of yields, $(15.5\ Fe^{++})/(2.46\ Ce^{4+}) = 6.4$, is the same as that obtained by Hardwick,[3] $(20.8\ Fe^{++})/(3.3\ Ce^{4+})$. This would indicate that the difference in yields results from an error in energy measurement.

The yield vs. concentration for ferrous oxidation was checked for concentrations from 5×10^{-5} to 1.6×10^{-2} *M* at intensities of 270, 4500, and 15,000 r/min. No significant difference in yield was found under these conditions. A short irradiation of 5×10^{-5} *M* solution at 4500 r/min showed that H_2O_2 builds up during irradiation and continues to react with Fe^{++} after the irradiation. To test whether a build-up of H_2O_2 affects the yield at the higher concentrations of Fe^{++} normally used in actinometry, samples were given a series of short irradiations with relatively long periods between. Pulsed exposures and equivalent continuous exposures showed no significant difference in yield at either 4500 or 15,000 r/min.

Incidental measurements showed the ratio for ferrous oxidation in air-saturated and O_2-free solution to be 2.02. Also, the yield was found to have a small temperature coefficient, the values being $G = 15.5$ at 25°C and 16.1 at 65°C.

Steady-State Concentrations in Various Inorganic Solutions Irradiated with Gamma Rays. A program was started to determine the steady-state concentrations of gases evolved in various solutions irradiated with gamma rays at several intensities and temperatures. At present Na_3PO_4, H_3PO_4, NaOH, acid and neutral KBr, and UO_2SO_4 solutions are being studied.

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[1] J. A. Ghormley and C. J. Hochanadel, "A Calorimetric Determination of the Yield for the Oxidation of Ferrous Sulfate by Cobalt Gamma Rays," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORNL-870, p. 121 (March 1, 1951).

[2] N. Miller, "Quantitative Studies of Radiation-Induced Reactions in Aqueous Solutions. I, *J. Chem. Phys.* 18, 79 (1950).

[3] In *Progress Report for September to November, 1950*, Montreal report PR-CE-8.

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RADIATION EFFECTS ON HETEROGENEOUS CATALYSTS

J. A. Wethington and E. H. Taylor

The apparent decrease in catalytic activity of a ZnO catalyst upon irradiation continues to be observed, but an unequivocal proof of the nature of the effect is still lacking. A number of experiments designed for this purpose are under way, and should be completed shortly.

EFFECTS OF GAMMA RADIATION ON AQUEOUS BENZENE SOLUTIONS

T. J. Sworski

Hydrogen peroxide production is observed in aqueous benzene solutions containing oxygen, which has not been reported in previous work.[4] This effect is shown in Fig. 7.1, where the hydrogen peroxide yield in aqueous benzene solution is compared with that in pure water.

Since hydrogen peroxide reportedly interferes with phenol determination by the Folin and Denis phenol reagent[5] and since biphenyl interferes with Carr's method[6] using the absorption of phenol at 270 mμ, the need for another analytical method arises. A new method has been developed using the change in the ultraviolet absorption spectrum when the solution is made alkaline, as shown in Fig. 7.2. The increase in optical density of a solution at 290 mμ when it is made

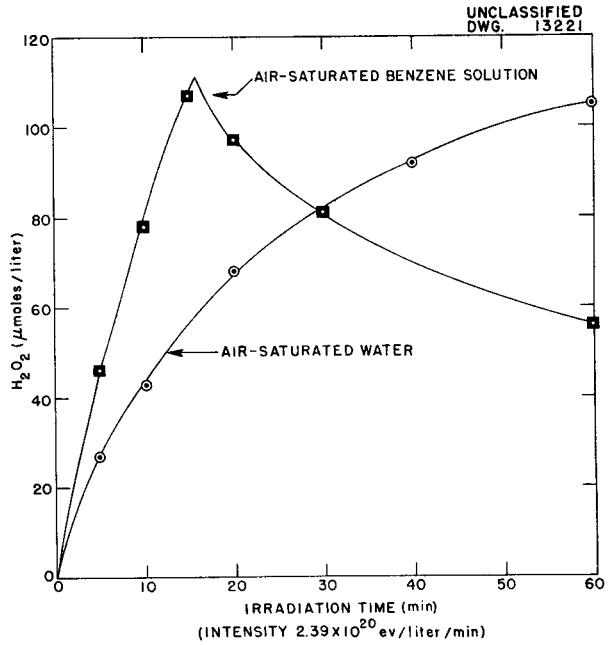

Fig. 7.1 - Effect of Benzene on H_2O_2 Production in Air-Saturated Water.

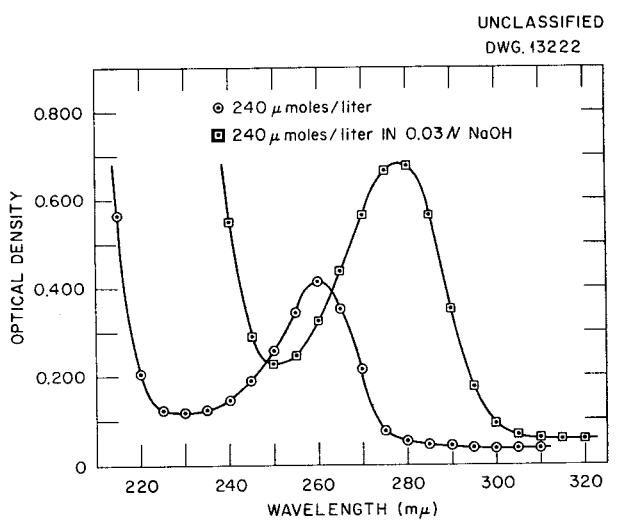

Fig. 7.2 - Ultraviolet Absorption Spectrum of Phenol.

[4] G. Stein and J. Weiss, "Chemical Actions of Ionising Radiations on Aqueous Solutions," *J. Chem. Soc. London* 1949, 3245 (1949).

[5] F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, vol. II, Van Nostrand, New York, 1937.

[6] M. E. J. Carr, "A Simplified Chemical Method of Radiation Dosimetry," *Nature* 167, 363 (1951).

0.03 *N* in sodium hydroxide is linearly related to the concentration of phenol. This determination is not interfered with by benzene or hydrogen peroxide. Interference by biphenyl formation is removed by using the irradiated solution as the blank.

The radiation exposures were carried out in a cobalt gamma-ray source.[7] Determination of the rate of energy absorption in solution was based on a calorimetric measurement[1] of the rate of energy absorption in water. The method for saturating solutions with O_2, H_2, or He and filling the irradiation cells was essentially that reported by Hochanadel.[8] Excess benzene was present over the aqueous solution while the solution was being saturated with the desired gases.

Hydrogen peroxide was determined using a colorimetric method developed by Ghormley.[9] The presence of benzene or phenol does not interfere in this method. Phenol was determined by measurements of optical density at 290 mμ. To 5 ml of irradiated sample was added 3 ml of 0.1 *N* NaOH, and the mixture was diluted to 10 ml. The blank consisted of 5 ml of irradiated solution diluted to 10 ml. The optical densities for sample and blank were measured on a Beckman Model DU spectrophotometer in the same 1-cm cell, using for comparison the intensity with no cell in the optical path. The concentration of phenol in the irradiated sample was calculated by the formula

$$\text{Concentration in } \mu\text{mole/liter} = 385(D_S' - D_B)(\text{dilution}).$$

The constant was evaluated by measurements on phenol solutions standardized by precipitation of iodophenol with I_2, the excess I_2 being determined with a thiosulfate solution standardized against arsenious oxide.

Water from a Barnstead still was redistilled from acid permanganate and then alkaline permanganate. A further distillation was made in an all-silica system, and the water was stored in silica vessels. Baker and Adamson thiophene-free benzene was used without further purification. Pure tank helium was passed over copper at 500°C and then through a charcoal trap at -196°C to ensure removal of oxygen. Pure tank oxygen was used without further purification.

Results and Discussion. In an oxygen-saturated solution of benzene the initial yield of phenol per 100 ev absorbed in solution is 2.80 as shown in Fig. 7.3. This is to be compared with the yield of 2.74 reported by Hochanadel[8] and 2.78 evaluated from the work of Hart[10] for OH radicals free to react with solute. From this comparison it may be concluded that each OH radical results in the formation of a molecule of phenol. In addition to phenol, hydrogen peroxide is produced in an initial yield of 2.91 as shown in Fig. 7.4. These results are consistent with the following mechanism:

[7] J. A. Ghormley and C. J. Hochanadel, *A Cobalt Gamma-Ray Source Used for Studies in Radiation Chemistry*, ORNL-897 (Feb. 6, 1951).

[8] C. J. Hochanadel, presented at 119th ACS Meeting, Cleveland, 1951.

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

[10] E. J. Hart, presented at 119th ACS Meeting, Cleveland, 1951.

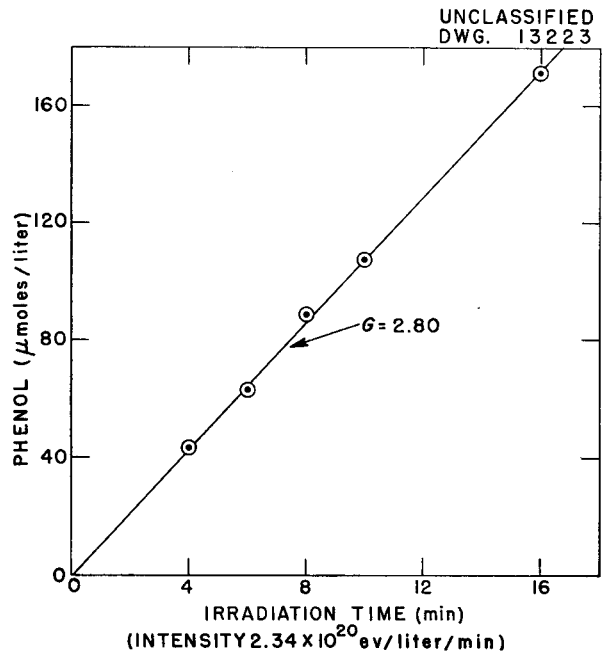

Fig. 7.3 - Initial Yield for Phenol Production in O_2-Saturated Benzene Solutions.

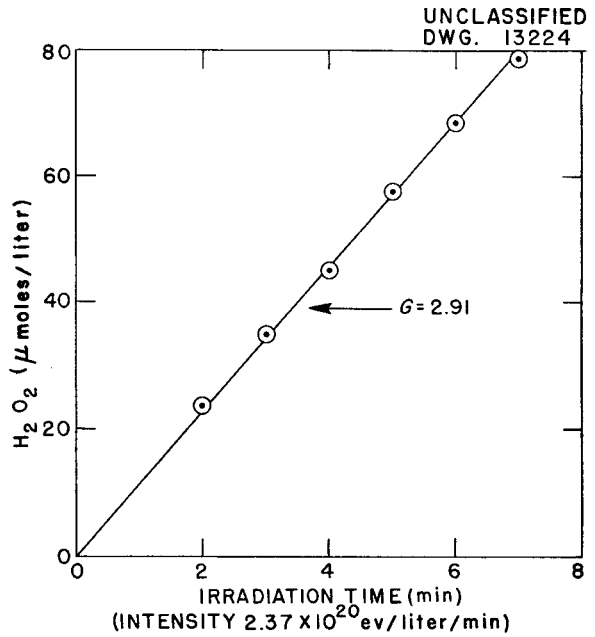

Fig. 7.4 - Initial Yield for H_2O_2 Production in O_2-Saturated Benzene Solutions.

$$2H_2O \rightsquigarrow H_2 + H_2O_2 \qquad (1)$$

$$H_2O \rightsquigarrow H + OH \qquad (2)$$

$$C_6H_6 + OH \longrightarrow C_6H_5OH + H \qquad (3)$$

$$H + O_2 \longrightarrow HO_2 \qquad (4)$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (5)$$

In a benzene solution saturated with a mixture of hydrogen and oxygen, there is no significant change in the above yields of phenol and hydrogen peroxide. This indicates that the reaction of hydrogen with the OH radical,

$$H_2 + OH \longrightarrow H_2O + H \qquad (6)$$

does not compete appreciably with reaction (3) under the conditions of this investigation.

In helium-saturated benzene solutions the initial yield of phenol is 0.31, as shown in Fig. 7.5. The ratio of initial phenol yields in oxygen and in helium-saturated solutions is observed as 9/1 as compared with 5/1 reported by Weiss.[4] The lower yield in helium-saturated solutions is evidently due to the recombination reaction:

$$H + OH \longrightarrow H_2O \qquad (7)$$

Figure 7.6 shows that a sharp change in the rate of phenol production in air-saturated solutions of benzene occurs at the same time that the decomposition of hydrogen peroxide is

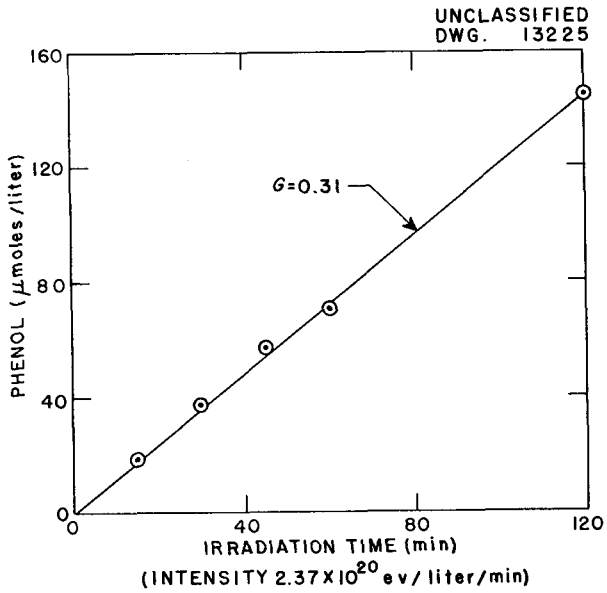

Fig. 7.5 - Yield for Phenol Production in Helium-Saturated Benzene Solutions.

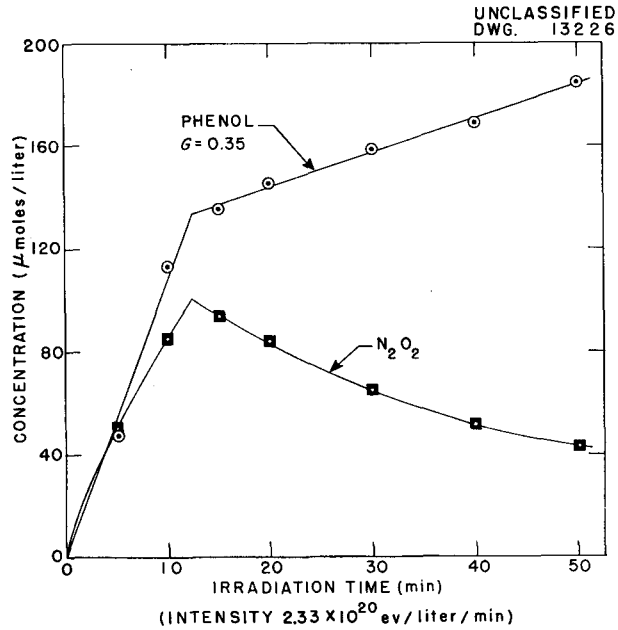

Fig. 7.6 - Comparison of H_2O_2 and Phenol Production in Air-Saturated Benzene Solutions.

induced. This presumably corresponds to oxygen depletion in solution. The rate of production of phenol after oxygen depletion corresponds to a yield of 0.35, which is higher than that observed in helium-saturated solutions. This higher rate is caused by the presence of hydrogen peroxide undergoing decomposition.

The effect of hydrogen peroxide on phenol production is shown in Fig. 7.7. A rapid initial rate is induced, followed by a higher rate of production than that observed in the absence of hydrogen peroxide. With an initial concentration of hydrogen peroxide of 111 μmoles per liter, the linear rate of phenol production corresponds to a yield of 0.35, which is the yield shown in Fig. 7.6.

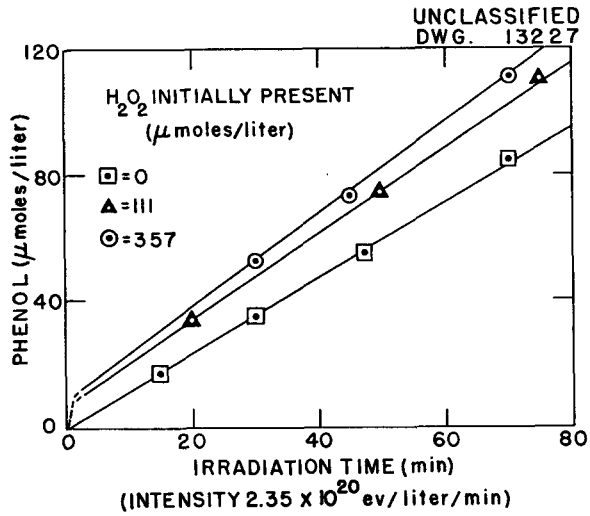

Fig. 7.7 - Effect of H_2O_2 on Phenol Production in Helium-Saturated Benzene Solutions.

8. INSTRUMENTATION

Edward Fairstein and Frank Porter

PULSE GENERATOR

A mercury-relay pulse generator for testing amplifiers and other equipment (Fig. 8.1) has been designed and tested which has some advantages over other types now in use at this laboratory. The advantages of the unit are:

1. It is small and light; its dimensions are 5 by 6 by 9 in.
2. It contains no batteries.
3. It is designed for an external terminating resistance of 100 ohms or less. This is advantageous in that long lengths of low-impedance connecting cable may be used with no degradation of the pulse shape. The voltage calibration is independent of the terminating resistance, for resistances of 100 ohms or less. Low-impedance uncompensated attenuator boxes may be used with the unit.

The voltage calibration of the generator may be checked with an external d-c voltmeter or potentiometer (the generator load must be removed when making this test). The warm-up drift is less than 0.05%. The long-time stability has not been checked.

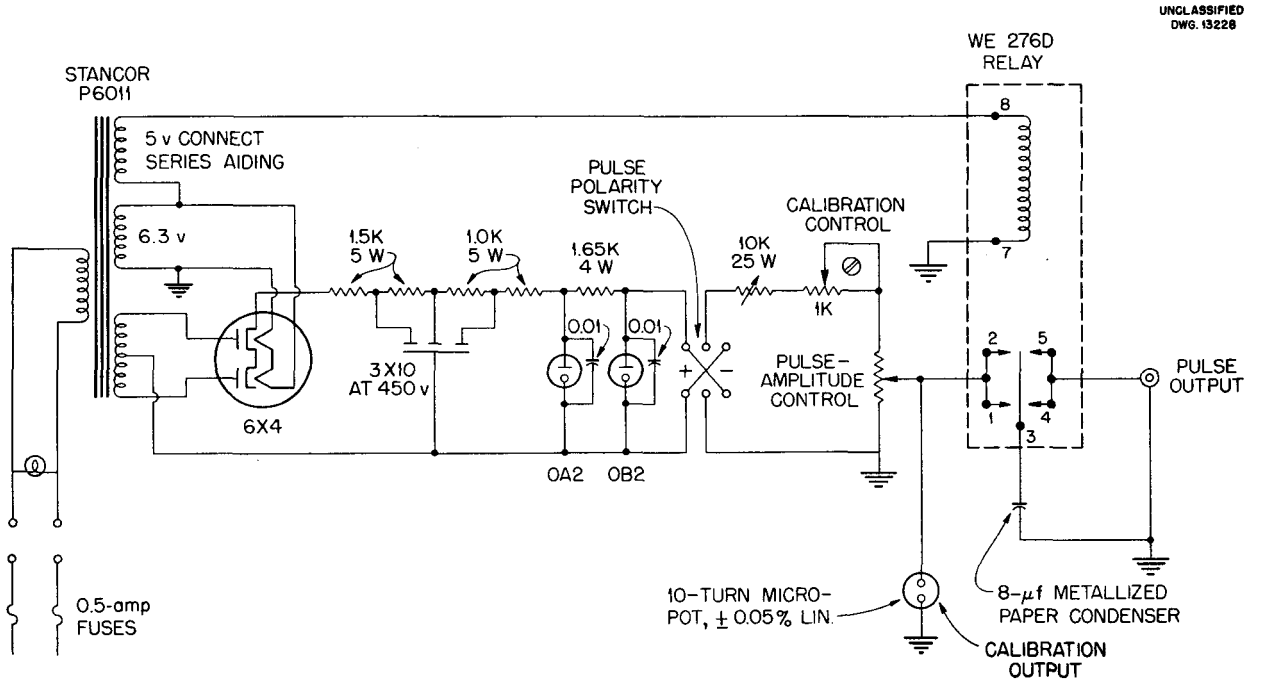

Fig. 8.1 - Mercury-Relay Pulse Generator.

The rise time is less than 0.007 μsec. If there is ringing present, it has a period which is less than this figure. With a 100-ohm load, the fall time is about 1700 μsec. The fall time is directly proportional to the load resistance. External loads of greater than 100 ohms will cause a voltage calibration error.

Contact potential differences between the relay contacts cause spurious pulses as they make and break. The connections as shown in the diagram appear to be optimum. The spurious pulses from a new relay are usually less than 1 mv in amplitude.

SINGLE-CHANNEL DIFFERENTIAL DISCRIMINATOR

The single-channel discriminator previously described[1] has been in operation for a sufficient length of time to obtain new information about its performance.

It was found necessary to replace the diodes in the shunt-compensating circuits of the trigger pairs with 4.7K damping resistors. It was also necessary to slightly increase the dead time of the lower trigger pair by means of a powdered iron slug in the compensating inductor. These changes materially improved the circuit operation at very high counting rates (3×10^6 counts/min).

The circuit has unfortunately proved to be unstable for long periods of operation. Both random and uniform drifts occur in the slit width. The trouble is caused by the extremely close grid-to-cathode spacing in the 404A tubes. Intermittent shorts cause randomly spaced drifts of large magnitude. Slow drifts are apparently caused by slow changes in the grid-to-cathode spacing. It is expected that an aging program for the tubes will materially improve the reliability of the circuit by making it possible to install sets of tubes with closely matched drift rates and by weeding out those tubes which develop shorts. An aging rack is now being constructed. Other tube types are also being investigated with the hope that a desirable substitution can be made.

20-CHANNEL ENERGY ANALYZER

A 20-channel pulse-height analyzer has been designed and is now under construction. The unit is expected to be a general-purpose energy analyzer, adaptable to all the types of energy measurements now being made by differential discriminators.

The basic circuit is that of the single-channel unit described above. The analyzer will be used with a window amplifier similar to that used in the Physics Division, to minimize channel width drift.

A condenser storage circuit will be substituted for the usually used scaler circuit. This will result in a considerable saving in space and cost and an increase in flexibility of operation. The data will be automatically plotted in the form of a histogram by a strip-chart recorder.

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[1] E. Fairstein, " A Differential and Integral Pulse-Height Selector for the A-1 Amplifier," *Instrument Department Research and Development Quarterly Progress Report for Period Ending January 20, 1951*, ORNL-1021, p. 7 (June 25, 1951); also in *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1950*, ORNL-1036, p. 65 (Sept. 10, 1951).

10-CHANNEL ENERGY ANALYZER

The Allen B. Du Mont Laboratories have made available a 10-channel gating tube for pulse-height analysis applications. The tube type is K 1059, and the original development work was sponsored by the University of California. The claims for it are high. If the tube meets specifications, it should be possible to construct a very stable, relatively inexpensive energy analyzer. An experimental circuit using this tube has been designed and is now under construction.

HIGH-VOLTAGE POWER SUPPLIES

Two power-supply designs are being considered with the hope that these will eventually become standard equipment for the Chemistry Division. One has an output adjustable between 500 and 1500 volts for use with scintillation counters, and the other will be adjustable between 500 and 5000 volts for proportional counters. Emphasis is being placed on those design factors which result in stable operation for long periods of time.

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