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CHEMISTRY DIVISION

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QUARTERLY PROGRESS REPORT

for Period Ending December 31, 1950

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ORNL-607	Period Ending December 31, 1949
ORNL-685	Period Ending March 31, 1950
ORNL-795	Period Ending June 30, 1950
ORNL-870	Period Ending September 30, 1950

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Beginning with this report, it is planned to reduce the amount of material included in the quarterly reports of the Chemistry Division. As far as possible the reports will merely abstract completed work, with references to appropriate completion reports or journal articles, and give the current status, with any significant results, of work in progress. This will avoid duplication between quarterly reports and completion reports and will eliminate the detailed presentation of work in progress. The latter will be the only material permanently lost from the literature, and it is thought that the advantages in economy and rapid readability outweighs this loss.

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ABSTRACT

CHEMISTRY OF SOURCE, FISSIONABLE, AND STRUCTURAL ELEMENTS

Under the heading of phase studies, work has been completed on the solubilities of a number of fission product sulfates and on the liquid-solid equilibria for the thorium nitrate-water system. The solubilities in water of the sulfates of Y, Cs, La, Cd, and Zn and the solubilities in aqueous UO_2SO_4 solution of the sulfates of Y, La, and Cd have been determined up to about 250°C.

Three methods for characterizing species in aqueous solution continue to receive attention: solvent extraction, anion exchange, and ultracentrifugation. Work on thorium-thenoyl trifluoroacetone complexes is about complete, but some experimental anomalies have delayed the work with zirconium. Ultracentrifuge studies indicate that a dimerized undissociated uranyl fluoride molecule is a major species in solutions of uranyl fluoride.

NUCLEAR CHEMISTRY

The current investigations of decay schemes of the fission chains going through rare gases have uncovered a new beta group in I^{133} , a new 720-Kev gamma ray in I^{131} , and a new 810-Kev beta group in the same isotope. It has also been found that a very small fraction of the disintegrations of 5-day Xe^{133} goes by a soft beta to a 380-Kev level in Cs^{133} .

In the separation of Np^{237} from the wastes from the Redox treatment of the Chalk River material, the neptunium is concentrated with the rare earth fission products and added cerium. It is planned to separate the cerium by precipitation as cerium iodate, and conditions have been worked out under which the loss of neptunium is only 1 to 2%.

RADIO-ORGANIC CHEMISTRY

One hundred and fifty-two millicuries of methanol- C^{14} has been prepared by catalytic reduction of carbon dioxide.

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Thirty-one and one-half millimoles of formic acid-C¹³ has been prepared by the catalytic reduction of potassium bicarbonate-C¹³.

The syntheses of glycine-1-C¹⁴, glycine-2-C¹⁴, and malonic acid-2-C¹⁴ are in progress.

A total of 1 millicurie of 2-heptadecylglyoxalidiazine-2-C¹⁴ has been prepared in 81% yield on a 1-mmole scale from stearic acid-1-C¹⁴.

Ten millicuries of chrysene-5,6-C¹⁴ has been prepared, and progress has been made in the high-level preparation of several other polynuclear hydrocarbons labeled with C¹⁴.

The reactions of formaldehyde with diphenylacetaldehyde and formyl-desoxybenzoin have been studied.

An isotope effect of the order of 8% at 25°C and of about 10% at 0°C has been demonstrated for the decomposition in concentrated sulfuric acid of formic acid-C¹⁴. A preliminary value of about 140 calories per mole has been calculated for the difference in activation energy of the reactions of C¹² and C¹⁴ formic acid.

A new method for the preparation of carbonyl-labeled unsymmetrical benzils is being studied.

CHEMISTRY OF SEPARATIONS PROCESSES

Experiments on the separation of lithium isotopes by conventional ion exchange have been finished and have shown that the method is not attractive for large-scale use.

The organic chemical studies in solvent extraction have been directed toward the organic phosphates which have assumed so important a role in recent process development. Tri-*n*-butyl phosphate labeled with P³² has been prepared and is being used in distribution studies. Samples have also been supplied to HEW and KAPL.

Studies of phosphorus fluorides as possible agents for facilitating removal of protactinium and uranium from irradiated ThF₄ have been extended to

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higher pressures and temperatures. Further indication of particle size reduction was obtained, but there was no evidence as to the mechanism of the attack or its effect on subsequent volatilization of uranium or protactinium.

Work on electrodeposition of traces of radiosilver has been completed. When less than a monolayer is present on the electrode, the deposition behavior does not obey the Nernst equation, varies with different electrode materials, and is apparently influenced by the heterogeneity of the surface of any given electrode.

CHEMICAL PHYSICS

Work on nuclear spins and magnetic moments has progressed in two directions. On the chemical side, an improvement in the foreign salt content of I^{131} preparations has been made by substituting hydrazine for sulfurous acid in the absorption of the elemental iodine and by instituting a solvent extraction step. On the side of measurements, nuclear induction has been used to give a more precise value of the nuclear magnetic moment of I^{129} . The value is 2.617 nuclear magnetons, to be compared with the microwave spectroscopic value of $2.74 \pm 5\%$.

The calorimetric determination of the rate of heat liberation by weighed samples of $C^{14}O_2$ has been completed, but the actual rate of energy production by the decay is still uncertain because of the possibility that some of the energy is stored in the charcoal used to adsorb the samples. This possibility will be explored in a separate experiment.

RADIATION CHEMISTRY

The recent work on the decomposition of water by gamma radiation and on the nature of various centers produced in alkali halide crystals by such radiation has been summarized for the Radiation Chemistry Symposium being held in Cleveland in April. The activity of a ZnO catalyst for ethylene hydrogenation has been found to be lowered by previous gamma-ray irradiation of the catalyst. In-pile radiation studies of uranyl sulfate solutions, now largely radiation-corrosion tests of stainless steel, have given encouraging results; 13 runs showed normal behavior, seven were inconclusive, and two were failures (apparent precipitation of the uranium as evidenced by absence of appreciable H_2-O_2 pressure).

INSTRUMENTATION

Most of the work of the quarter has been devoted to several aspects of the problem of measuring the energy distribution of ionizing radiations. To assist generally in such work a differential and integral pulse-height selector has been designed to replace the present integral selector of the A-1 linear amplifier.

A problem in energy measurements with proportional counters is to ensure constant gas multiplication regardless of the location in the counter of the ionizing event. One solution is to simulate an infinitely long counter by making the end walls of concentric insulated rings, each held at the appropriate potential to approach the field distribution in an infinitely long tube. This expedient has been studied in an electrolytic bath analog and found to give promising results in terms of uniformity of field. A proportional counter with such end walls is to be built.

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1. CHEMISTRY OF SOURCE, FISSIONABLE, AND STRUCTURAL ELEMENTS

PHASE STUDIES

The Thorium Nitrate—Water System (W. L. Marshall and J. S. Gill). The liquid-solid phase equilibria for the thorium nitrate—water system have been studied from room temperature to decomposition temperatures of the salt. The densities of the saturated solutions have been measured, and some observations concerning the vapor-liquid equilibria have been made. A detailed discussion of this work, together with the data, has been published in the HBE quarterly report ORNL-925, and only the significant results will be mentioned here.

A solution of thorium nitrate would show promise of utility for a breeder reactor if the following conditions were met:

1. The nitrate would have to be enriched in N^{15} .
2. A concentration of about 1 g of thorium per milliliter would have to be attained.
3. The solution would have to display reasonable thermal and phase stability.
4. A container material with high corrosion resistance and suitable in other respects would have to be found.

The purpose of this study was to determine the feasibility of items 2 and 3. The experimental data show that a solution containing 1 g of thorium per milliliter can be attained at and above 118°C. In a closed system such a solution does not deposit a solid phase until a temperature of about 225°C is reached. There is thus a temperature range of more than 100°C throughout which a breeder solution could be maintained thermally stable. The effects of radiation on the system have not been studied.

The $UO_2SO_4-UO_3-H_2O$ System in Relation to the Homogeneous Reactor Experiment (W. L. Marshall and J. S. Gill). A previous study^(1,2) has been made

- (1) "Phase Rule Work," *Homogeneous Reactor Experiment Report for the Quarter Ending February 28, 1950*, ORNL-630, p. 49 (Apr. 21, 1950).
- (2) W. L. Marshall, J. S. Gill, and C. H. Secoy, "The System $UO_2SO_4-UO_3-H_2O$ in Relation to the Homogeneous Reactor," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950*, ORNL-685, p. 32 (June 16, 1950).

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of the uranyl sulfate—uranium trioxide—water system from 25 to 300°C in which precipitation phenomena were determined as a function of temperature from solutions that were 0.168 *M* in uranium trioxide (40 g of uranium per liter) and contained variable amounts of sulfate ion up to a maximum concentration of 0.168 *M*. These results indicated that, with temperature increase, an increase of sulfate ion concentration was necessary to prevent precipitation of an unidentified yellow solid.

In this investigation we have extended the exploratory study to include similar solutions containing 0.126 and 0.0840 moles per liter (30 and 20 g of uranium per liter, respectively) of uranium trioxide. Acidity data are given at 25°C for the various solutions. These studies were initiated to determine the feasibility of decreasing the sulfate concentration in order both to reduce the acidity and to lower the neutron-absorption effect of the sulfur in a homogeneous reactor solution. In passing it should be mentioned that any increase in alkalinity of the solution due to the deficiency of sulfate ions would be expected to offer conditions more favorable for the radiation-induced precipitation of uranium peroxide. This would mean that the minimum temperature for operation without the risk of peroxide precipitation might be somewhat higher for the more alkaline, sulfate-deficient solution. A study of this factor is planned by the Radiation Group of the Chemistry Division.

Experimental. The experimental procedure has been described previously^(1,2) although a few modifications were used in this work. The solutions were studied in 3- and 6-mm-I.D. sealed quartz tubing rather than the capillary tubes used in the earlier work. These larger tubes afforded stirring without explosion danger up to about 270°C. The general procedure was to place a sealed tube containing a solution of known composition in a cylindrical aluminum heating block, increase the temperature slowly, and observe through a slit any phenomena occurring in the solution. Owing to some scattering in the experimental data an alternate procedure was used in which various solutions were held at 250°C for 16 to 24 hr to fix, within limits, the minimum concentration of sulfate ion necessary to prevent precipitation of the solid phase at this temperature.

Acidity data at 25°C were obtained with a Beckman pH meter.

Data and Discussion. The temperatures at which aqueous solutions containing constant amounts of uranium trioxide and varying concentrations of

sulfate ion deposit a yellow solid phase are given in Tables 1.1 and 1.2 and are shown in Fig. 1.1. Previous precipitation, acidity, and two-liquid phase data are included in Figs. 1.1 and 1.2 for comparison. The data in Fig. 1.1 are actually shown as a projection from a three-dimensional model on which the uranium trioxide concentration can be represented at right angles to temperature and sulfate ion concentration. Curves I, II, and III represent, respectively, constant uranium trioxide concentrations of 0.084, 0.126, and 0.168 moles per liter. These curves approach a 1:1 mole ratio of uranium trioxide to sulfate at lines A, B, and C.

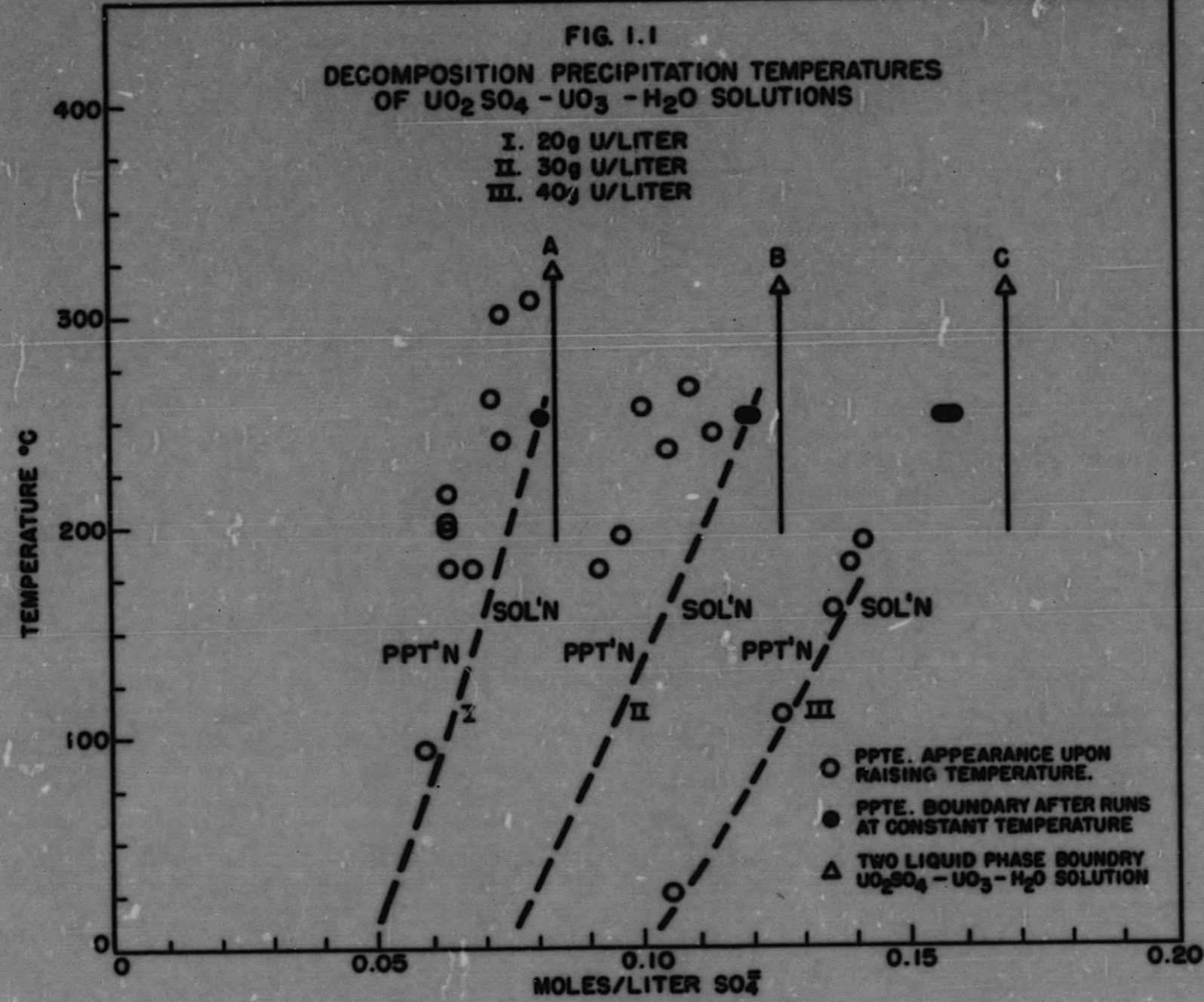
The scattering of the precipitation data shown by the open circles in Fig. 1.1 is due partly to the slow precipitation rate upon raising the solution temperature and to the apparently irreversible character of the process. Boundary data obtained from different solutions held at 250°C for extended periods are given by the shaded circles. We must then rely on these later data to a greater extent than on the earlier values. An allowance for this factor is included in dashed curves I, II, and III of Fig. 1.1.

The acidity data for the solutions are given in Table 1.1 and shown in Fig. 1.2. As in Fig. 1.1, the diagram is actually a projection, the uranium trioxide concentration being the third variable. Curves I, II, and III are then curves of constant uranium trioxide concentration and approach a 1:1 mole ratio of $\text{UO}_3/\text{SO}_4^{--}$ at points B, C, and D. Line AO represents a 1:1 mole ratio of $\text{UO}_3/\text{SO}_4^{--}$ at all concentrations of sulfate ion and, consequently, is the pH curve for stoichiometric UO_2SO_4 solutions. Line EF of Fig. 1.2 represents saturation values of uranium trioxide and sulfate at 25°C and indicates that a maximum pH of approximately 3.92 may be reached at this temperature. At 250°C the maximum attainable pH (measured at 25°C) before precipitation will occur is approximately 3.00.

This work is an exploratory study rather than a complete investigation of the system in that the solid phase is not identified, the irreversible aspects of the precipitation are not understood, the experimental data are incomplete, and the times of equilibria attainment are unknown.

X-Ray-Diffraction Data for the Compound Uranyl Orthosilicate Trihydrate (W. L. Marshall and J. S. Gill). In an earlier investigation⁽³⁾ a synthesis

(3) W. L. Marshall and J. S. Gill, "The Compound Uranyl Orthosilicate Trihydrate," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORNL-870, p. 25 (Mar. 1, 1951).



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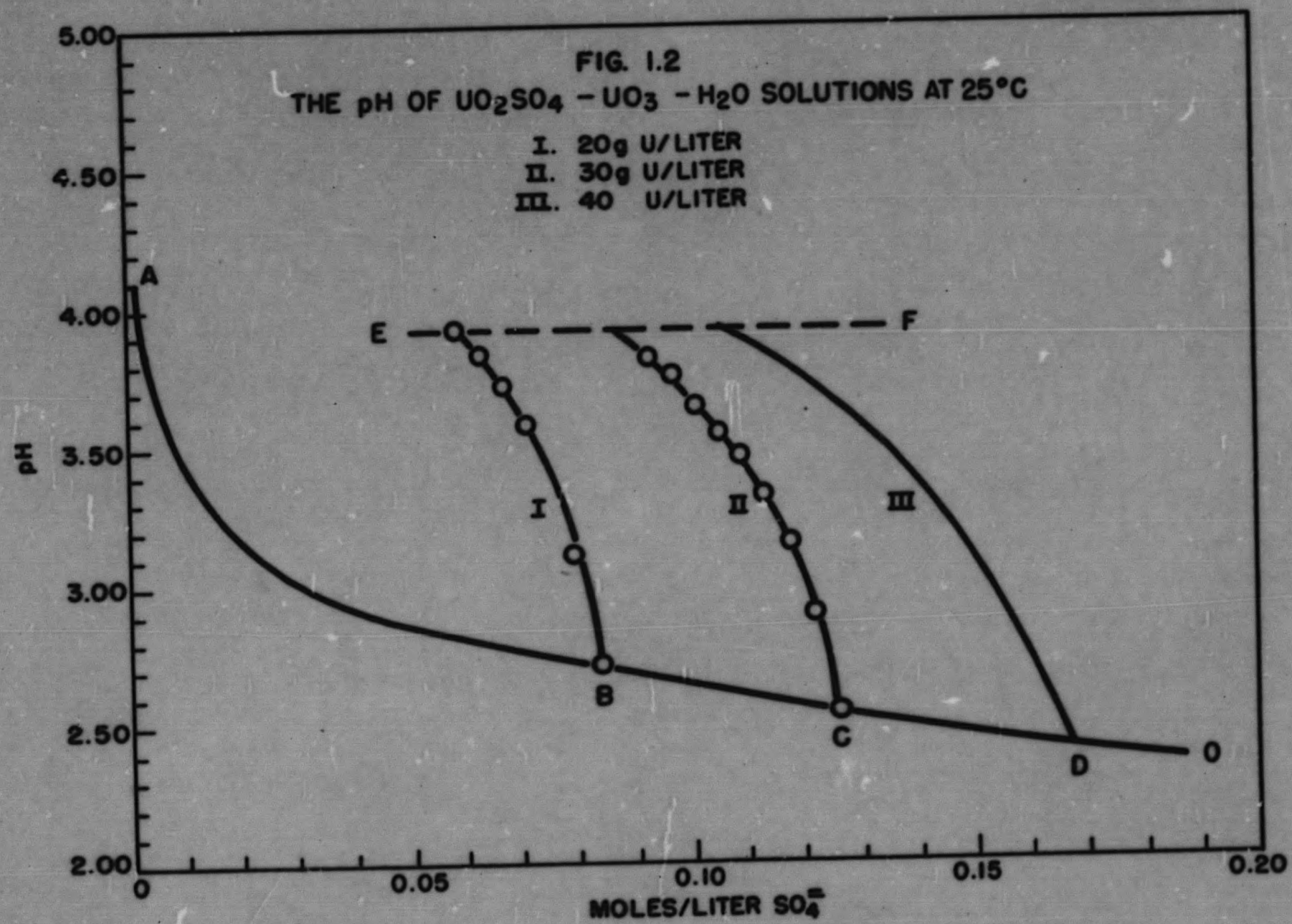


TABLE 1.1

Decomposition-Precipitation Temperatures and Acidity of
 $UO_2SO_4-UO_3-H_2O$ Solutions

UO_3 (moles/liter)	SO_4^{--} (moles/liter)	pH AT 25°C	PRECIPITATION TEMPERATURE (°C)
0.0840	0.0588	3.92	95
0.0840	0.0630	3.83	180
0.0840	0.0630	3.83	197
0.0840	0.0630	3.83	200
0.0840	0.0630	3.83	215
0.0840	0.0672	3.72	180
0.0840	0.0714	3.58	260
0.0840	0.0735		240
0.0840	0.0735		300
0.0840	0.0798	3.11	305
0.0840	0.0840	2.71	(no precipitation)
0.126	0.0924	3.81	178
0.126	0.0966	3.75	195
0.126	0.101	3.64	256
0.126	0.105	3.55	235
0.126	0.109	3.46	265
0.126	0.113	3.32	243
0.126	0.118	3.15	(no precipitation)
0.126	0.122	2.89	
0.126	0.126	2.54	(no precipitation)

TABLE 1.2

Decomposition-Precipitation Characteristics of $UO_2SO_4 \cdot UO_3 \cdot H_2O$
Solutions Stirred at 250°C

UO_3 (moles/liter)	SO_4^{--} (moles/liter)	STIRRING TIME (hr)	OBSERVATIONS
0.0840	0.0756	16	Yellow, crystalline precipitate
0.0840	0.0798	20	Very slight yellow crystalline precipitate
0.0840	0.0819	20	No precipitate
0.126	0.113	16	Yellow, crystalline precipitate
0.126	0.118	20	Very slight yellow crystalline precipitate
0.126	0.122	20	No precipitate
0.168	0.151	5	Yellow, crystalline precipitate
0.168	0.155	16	Very slight yellow crystalline precipitate
0.168	0.160	20	No precipitate

TABLE 1.3

X-Ray-Diffraction Data — Principal Lines for Uralyl Orthosilicate
Trihydrate (Cu K α Radiation)

RELATIVE PEAK HEIGHT	<i>d</i>	RELATIVE PEAK HEIGHT	<i>d</i>	RELATIVE PEAK HEIGHT	<i>d</i>
44	6.100	16	1.962	5	1.342
14	4.716	16	1.893	6	1.327
20	4.571	6	1.871	4	1.292
81	4.447	17	1.842	3	1.279
14	3.720	15	1.757	6	1.260
66	3.276	3	1.723	3	1.238
22	3.207	7	1.693	8	1.218
3	3.113	8	1.666	3	1.198
15	2.948	11	1.655	5	1.163
7	2.765	9 (?)	1.651	5	1.160
42	2.680	18	1.634	5	1.155
5	2.620	14	1.631	7	1.148
2	2.564	9	1.582	7	1.145
2	2.520	8	1.572	4	1.134
29	2.459	5	1.557		
15	2.434	4	1.544		
3	2.371	7	1.505		
10	2.307	4	1.488		
11	2.235	4	1.463		
8	2.189	4	1.448		
4	2.157	3	1.439		
3	2.139	12	1.400		
3	2.097	8	1.396		
17	2.074	2 (?)	1.378		
4	2.052	5	1.364		
8	2.025	6	1.348		

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and some general properties of uranyl orthosilicate trihydrate are given. In this report X-ray-diffraction data are given in Table 1.3 and Fig. 1.3. They were obtained from the crystalline powdered compound using a recording X-ray spectrometer and Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation. The work was done by B. S. Borie of the Metallurgical Division, Oak Ridge National Laboratory.

No attempt was made to analyze the structure.

Measurement of Solubility of Fission Product Salts at High Temperatures and Pressures (M. H. Lietzke). The high-temperature solubility curves for the sulfates of Y, Cs, La, Cd, and Zn in water and for those of Y, La, and Cd in UO_2SO_4 solution containing 30 g of uranium per liter have been determined over as wide a range of temperatures as is possible with the quartz tube synthetic method. The data will be described in detail in a forthcoming completion report.

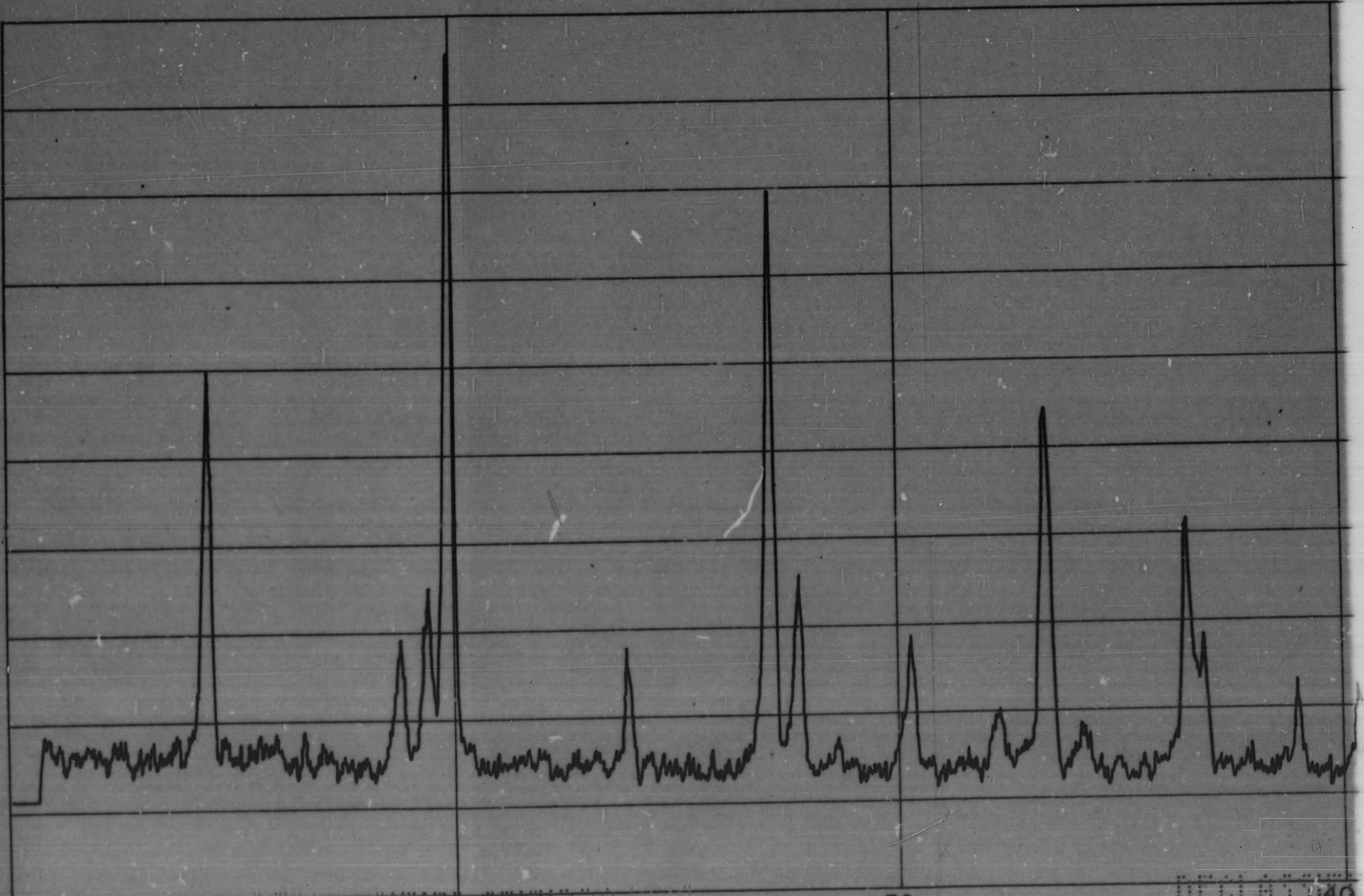
SOLUTION CHEMISTRY

TTA Complexing of Aqueous Thorium (W. C. Waggener and R. W. Stoughton). Aqueous TTA-thorium species are being studied by measuring the partition of TTA, under suitable conditions, between a benzene phase and an aqueous phase, as a function both of thorium concentration and of chloride concentration. A single complex, mono(thenoyltrifluoroacetone) thorium (i.e., ThT^{3+}), has been found, and a tentative value for k_T ($\text{Th}^{4+} + \text{HT}_{\text{TTA}} \rightleftharpoons \text{ThT}^{3+} + \text{H}^+$) at $\mu = 2.00$ is $6.6 \pm 5\%$. There is no evidence of a double complex involving both TTA and chloride, viz., ThClT^{++} , the question of which recently arose in this laboratory.

It is planned to issue a completion report covering this work within the next quarter.

Zirconium in Aqueous HCl-HClO_4 (J. P. McBride and R. W. Stoughton). The studies of the aqueous complexes of Zr^{4+} and Cl^- ions at ionic strength $\mu(\text{HClO}_4 + \text{NaClO}_4 + \text{NaCl}) = 3.00$ and $[\text{Zr}] = 10^{-5} \text{ M}$, reported in detail last quarter,⁽⁴⁾ were extended this quarter to acidities below 1 *M*. Zirconium

(4) J. P. McBride and R. W. Stoughton, "Zirconium in Aqueous HCl-HClO_4 ," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORO-870, p. 88 (Mar. 1, 1951).



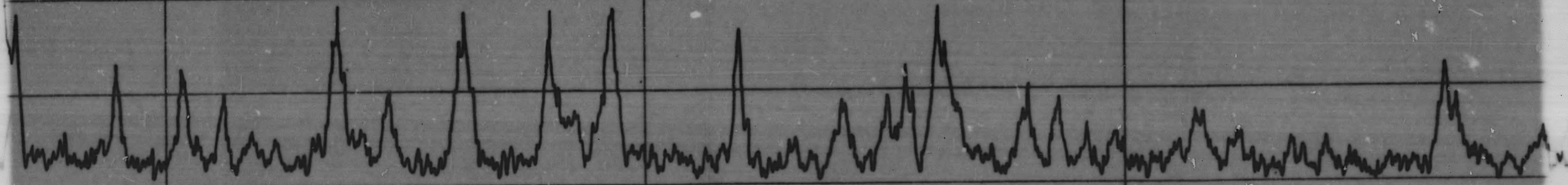
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FIG. 1.3
X-RAY DIFFRACTION PATTERN FOR
URANYL ORTHO SILICATE TRIHYDRATE



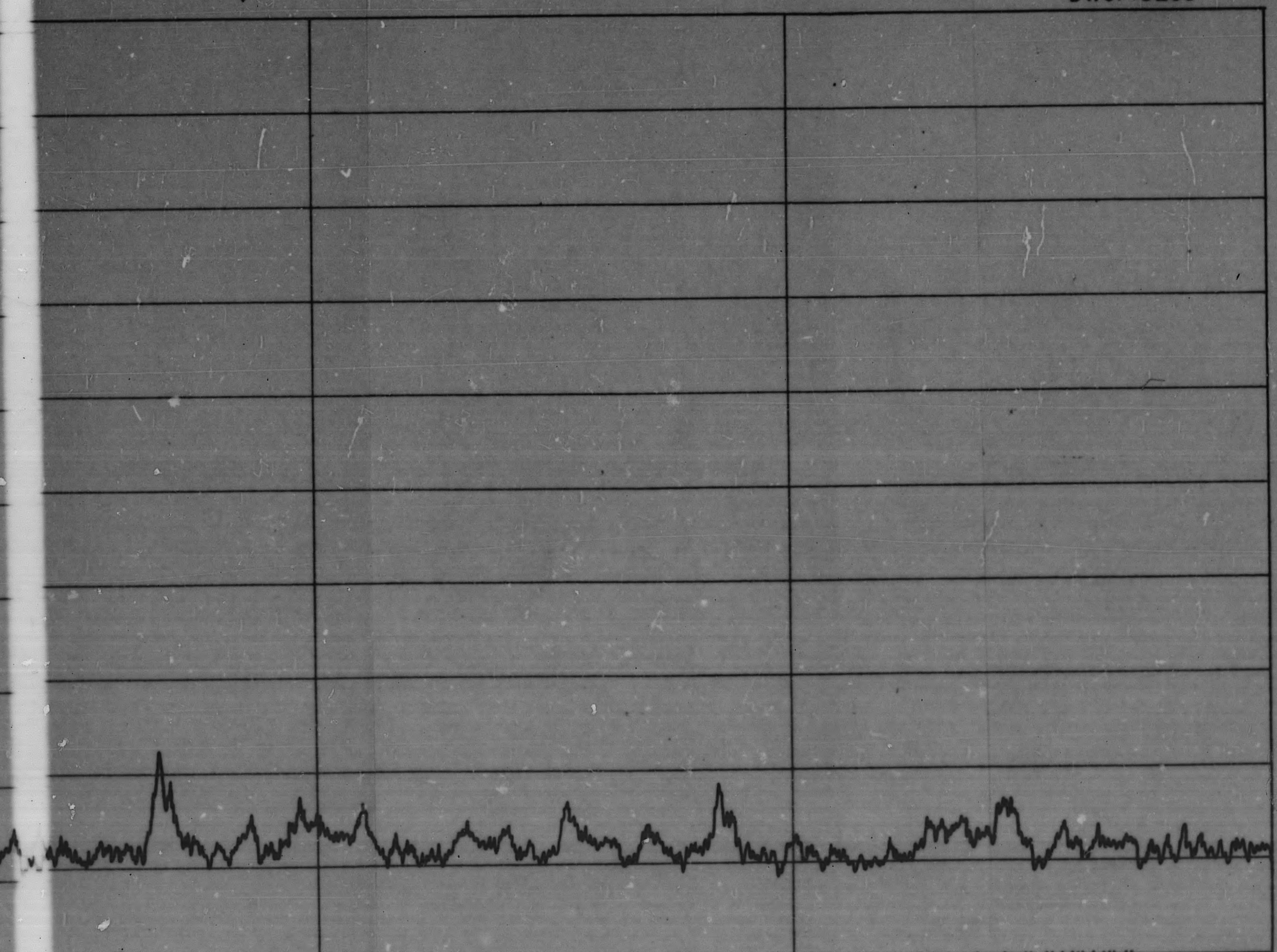
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concentrations lower than 10^{-5} M were used in order to reduce the likelihood of zirconium polymerization at the lower acidities. Considerable difficulty was encountered in obtaining reproducible and consistent results, and chloride complexing was revealed only in a qualitative manner. The distribution ratios, Zr aqueous/Zr benzene, were almost uniformly higher than were expected from previous data. The problem was further complicated by the fact that duplicate series of extractions (at $\mu = 3.00$) made at different zirconium concentrations and with extraction tubes cleaned by different methods showed radically different behaviors, as pointed out below. Additional experiments were run to determine the reasons for the discordant results.

The extractions were carried out in pyrex tubes with individually ground glass stoppers in a water bath at 25°C. A small amount of silicone grease was used on the stoppers of the extraction tubes in Series I (common practice in previous work). For Series II, however, and for all subsequent extractions, the stoppers were reground and used without grease. In all cases stoppering was satisfactory.

Stock solutions of TTA-benzene containing dead Zr at proper concentrations and Zr^{95} tracer were freshly prepared for each set of runs by equilibrating TTA-benzene with a dilute HNO_3 solution containing Zr and purified tracer. This aqueous HNO_3 solution was prepared as follows: A Zr-Nb tracer mixture was added to 8 M HNO_3 along with dead Zr in a 0.1 M oxalic acid solution. After the solution had been heated to 95 to 100°C, $KMnO_4$ was added to destroy the oxalate and to precipitate MnO_2 , which carries the Nb. The mixture was centrifuged, the supernatant was diluted, and the labeled Zr was ready for extraction.

The benzene phases for the subsequent partition experiments were then prepared by diluting the stock TTA-benzene solutions with benzene.

Counting plates for the organic phases and for aqueous phases containing no nonvolatile solute were prepared by direct evaporation of an appropriate aliquot. Aqueous phases containing nonvolatile solutes were extracted with benzene phases containing an excess of TTA, and the resulting organic phases were mounted for counting. All plates were counted on the third shelf of a standard Geiger-Mueller beta counter without using an absorber. A check of the change with time of the activity on the plates counted in this manner

revealed that the Nb produced from the Zr decay gave, in two weeks time, a positive error of only 4%. That is, the observed count was 4% higher than that expected from Zr^{95} activity alone (65-day half-life). Distribution ratios were obtained from the ratios of the aqueous to benzene activities.

Results. Following are the results that were obtained from the various experiments:

1. Partition of Zr as a function of chloride concentration. The conditions and results for the extractions using $ClO_4^- - Cl^-$ mixtures are summarized in Table 1.4.
2. Effects of time, zirconium concentration, and tube treatment on partition of zirconium. The effects of time of equilibration (at 25°C), Zr concentration, and tube surface treatment on the partition of Zr between 0.5 M HCl and 0.005 M TTA-benzene were investigated. The tubes used in these extraction experiments were treated with hot alcoholic KOH, boiled in concentrated HNO_3 , rinsed with distilled water, and dried at 110°C. Other treatment of the tubes is given in Table 1.5, which summarizes the results.
3. Effects of time, zirconium concentration, and tube treatment on the specific activity of a 0.005 M TTA-benzene solution. In order to test whether or not the zirconium concentration of a 0.005 M TTA-benzene solution containing dead Zr and tracer would change on standing (not in contact with an aqueous phase), three stock solutions were prepared containing 10^{-5} M, 10^{-6} M, and tracer Zr. Aliquots of the stock solution containing each concentration of Zr were placed in tubes receiving the three surface treatments described in Table 1.5 (nine tubes in all), and the zirconium concentration was determined as a function of time of standing at 25°C by counting aliquots. No significant change in concentration with time was noted in any of the solutions over a period of two weeks.

Discussion and Conclusions. The most significant feature of the partitions, aqueous over benzene, observed in the $ClO_4^- - Cl^-$ mixtures is that they are almost uniformly higher than expected. The partitions show a lack of consistency and, in the case of Series II, increase with time. Since the ClO_4^- solutions free of Cl^- and the pure HCl solutions show no increase in the distribution ratios with time, it is unlikely that zirconium hydrolysis produced the phenomena observed. The leaching of a complexing impurity (i.e., minute particles inducing radiocolloid formation or a chemical complexing agent) from the vessel walls might be the cause of the observed results. The

TABLE 1.4

Zirconium Partition Experiments at $\mu(\text{HClO}_4 + \text{NaClO}_4 + \text{NaCl}) = 3.00$

SERIES	TREATMENT OF EXTRACTION TUBES	[Zr]	[H ⁺]	[Cl ⁻]	[TTA]	SUMMARY OF RESULTS
I	Boiled in concentrated HNO ₃ ; rinsed with H ₂ O; dried at 110°C	1.7 x 10 ⁻⁶	1.0	0 to 1.0	0.0067	Chloride complexing indicated; D.R.'s (a/b) high, inconsistent, and show no change after 4 days (first obser- vation of D.R.)
		1.4 x 10 ⁻⁶	0.8	0 to 0.8	0.0053	
		1.0 x 10 ⁻⁶	0.6	0 to 0.6	0.0040	
II	Treated with hot alcoholic KOH; boiled in concentrated HNO ₃ ; rinsed with H ₂ O; dried at 110°C	3.5 x 10 ⁻⁷	1.0	0 to 1.0	0.0067	Chloride complexing indicated; D.R.'s, aqueous over benzene, increase with time in presence of Cl ⁻ ; rate of change increases with increasing concentration of Cl ⁻
		2.7 x 10 ⁻⁷	0.8	0 to 0.8	0.0053	
		2.0 x 10 ⁻⁷	0.6	0 to 0.6	0.0040	

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TABLE 1.5

Effect of Time of Equilibration and of Zirconium Concentration on Distribution Ratios
(Aqueous over Benzene)

Zirconium Partition Between 0.5 M HCl and 0.005 M TTA-Benzene at 25°C

TREATMENT OF EXTRACTION TUBES	DISTRIBUTION RATIOS								
	Zr = 10 ⁻⁵ M			Zr = 10 ⁻⁶ M			Zr = tracer		
	n = 5	n = 7	n = 15	n = 5	n = 7	n = 15	n = 5	n = 7	n = 15
None	0.241	0.247	0.247	0.394	0.394	0.348	0.372	0.386	0.321
Boiled in 10 ⁻³ M ZrOCl ₂ + 0.5 M HCl; let stand over night; rinsed with H ₂ O; dried at 110°C	0.194	0.206	(0.185)**	0.216	0.232	(0.186)**	0.273	0.330	0.282
Rinsed with 4% Dri-film (G.E. 9978) in methyl alcohol; dried 3 hr at 110°C	0.253	0.272	0.261	0.346	0.370	0.348	0.348	0.403	0.379

*n = time in days.

**Analytical data for the values in parentheses give material balances of 105 and 106%, and partitions are probably low.

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hot alcoholic KOH used in cleaning the extraction tubes of Series II would produce new glass surfaces which would be more susceptible to attack. The low values for the distribution ratios, aqueous over benzene, found initially in Series II (after two days of equilibration) and at low Cl^- concentrations may be due to the removal of the impurities from the walls by the more thorough cleaning procedure. The distribution ratios, however, increase with time. The rate of change with time increases with increasing Cl^- concentration.

No change with time is noted for the distributions of Series I, but the high values and lack of order point to the presence of impurities. Since the zirconium concentrations were higher, the concentration of impurity producing the largest change with time in Series II would change the values of Series I by more than 25%. It seems unlikely, therefore, that a significant amount of impurity is produced here with time.

The decreases in the ratios with increasing zirconium concentration shown in the extraction from 0.5 M HCl point to the presence of a low concentration of impurity even in these solutions. Similar changes in distribution ratios with change in zirconium concentration have been observed by Connick *et al.* (5,6) in HClO_4 solutions. They attributed the changes to low concentrations of impurities and suggested that they were leached from the walls of the flasks by the perchloric acid.

A further significant fact in these runs is seen in the decrease in partition carried out in tubes which had been treated with ZrOCl_2 . It would seem that this treatment either removed more of the impurity or conditioned the walls against attack. That some impurity is present even in these solutions, however, is demonstrated by a decrease in distribution ratio with decreasing zirconium concentration similar to that pointed out above. The change in ratio with change in zirconium concentration also indicates that no significant amount of dead Zr is introduced into the extraction system by the ZrOCl_2 treatment. It should be mentioned here that the extraction studies made last quarter were carried out in tubes which had been treated with ZrOCl_2 and at

(5) R. E. Connick and W. H. McVey, *The Aqueous Chemistry of Zirconium*, UCRL-101, p. 24 (Mar. 1, 1948).

(6) R. E. Connick and W. H. Rees, *The Hydrolytic Behavior of Zirconium in Perchloric Acid Solution*, UCRL-261, pp. 11, 19 (September, 1948).

a Zr concentration of 10^{-5} M. This may account in part for the fact that lower distribution ratios, aqueous over benzene, were obtained.

Anion-Exchange Studies (G. E. Moore, F. Nelson, and K. A. Kraus). Work on the anion-exchange behavior of chloride and sulfate complexes has continued. The major emphasis, however, was shifted from studies of separation efficiencies to determination of the charge of the adsorbed ions. At the same time experiments are being carried out to determine changes in activity-coefficient ratios of adsorbed ions in the resin phase as a function of loading.

Properties of Uranyl Fluoride Solutions (J. S. Johnson and K. A. Kraus). As mentioned in the previous quarterly report (ORNL-870), ultracentrifuge studies of uranyl fluoride solutions together with the activity coefficients calculated from freezing point depressions⁽⁷⁾ were found to be in agreement with the hypothesis that the solutions contain primarily the undissociated monomer UO_2F_2 . These activity coefficients, γ_f , were surprisingly low for an undissociated solute even at moderate concentrations where they might be expected to follow the equation⁽⁸⁾

$$\log \gamma_f = km \quad (1)$$

where k is a proportionality constant and m is the molality.

It appeared reasonable to assume that the observed low values of γ_f are due to partial association (e.g., dimerization) of the solute according to the equation



with the equilibrium constant

$$K = a_2/a_1^2 \quad (3)$$

where $a_1 = m_1\gamma_1$ and $a_2 = m_2\gamma_2$, the activities of the monomer and dimer, respectively.

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

(8) H. S. Harned and B. B. Owen, *Physical Chemistry of Electrolytic Solutions*, 2 ed., p. 209, Reinhold, New York, 1950.

Assuming for convenience that the monomer is the species at infinite dilution,* its activity can be evaluated from the equation**

$$a_f = m\gamma_f = a_1 \quad (4)$$

Assuming also [according to Eq. (1)] that

$$\log \gamma_1 = k_1 m \quad \text{and} \quad \log \gamma_2 = k_2 m \quad (5)$$

and, for further simplification, assuming that $k_1 = k_2 = k$ and remembering that $m = m_1 + 2m_2$, both K and k can be evaluated by trial and error from the observed activities a_f .

As shown in Table 1.6, a satisfactory dimerization constant K can be obtained using $k = 0.17$. The lower value of K at $m = 0.1$ is probably due to dissociation into ions which was not properly eliminated in the calculation of γ_f .

TABLE 1.6
Dimerization Constant of Uranyl Fluoride from Freezing Point Data
($k = 0.17$)

m	a_f	m_1	m_2	K
0.1	0.0894	0.086	0.007	0.91
0.5	0.283	0.233	0.133	2.02
1.0	0.481	0.325	0.338	2.16
1.5	0.688	0.382	0.559	2.13
2.0	0.892	0.408	0.796	2.19
3.0	1.374	0.425	1.288	2.21
4.0	1.972	0.412	1.794	2.21
5.0	2.84	0.401	2.300	2.02

*The same assumption was made in the evaluation of the activity coefficients γ_f from the freezing point data. This assumption, though surely not true at high dilution, where dissociation into UO_2F^+ , UO_2^{++} , and F^- must occur, is necessary to bound the problem.

**Equation 4 can be derived as follows:

$$\bar{F}_f = \gamma \bar{F}_1 + \frac{1-\gamma}{2} \bar{F}_2$$

where \bar{F}_f , \bar{F}_1 , and \bar{F}_2 are the partial molal free energies of the solute, monomer, and dimer, respectively, and γ is the fraction as monomer. At equilibrium $\Delta \bar{F} = 0 = \bar{F}_2 - 2\bar{F}_1$. Hence $\bar{F}_f = \bar{F}_1$ or $\bar{F}_f^\circ + RT \ln a_f = \bar{F}_1^\circ + RT \ln a_1$. Since at infinite dilution $a_1 = a_f$, $\bar{F}_1^\circ = \bar{F}_f^\circ$ must be true at all concentrations and $a_1 = a_f$ at all concentrations.

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When the results of the ultracentrifuge experiments were interpreted on the basis of the activity coefficients calculated from freezing point depressions, good agreement between the theoretical (308) and calculated values was found for the less concentrated solutions (see Table 1.7). At higher concentrations the calculated molecular weights tended to become increasingly higher. It seemed probable that this trend in molecular weights resulted from the use of activity coefficients which are applicable at the freezing point rather than at the experimental temperature (about 30°C). Reversing the procedure, activity-coefficient ratios can be calculated from the centrifuge data, assuming that the molecular weight is 308. For evaluation of activity coefficients from these ratios, it was assumed that the activity coefficients for 0.1 M UO_2F_2 solutions were the same at 0 and 30°C. This procedure is quite arbitrary and implies that K changes only little with temperature. It was adopted for convenience and should be revised after the pertinent data are available.

TABLE 1.7.

Observed Molecular Weights of UO_2F_2 , Using Activity Coefficients,
from Freezing Point Lowering

EXPERIMENT	INITIAL UO_2F_2 (M)	MEDIUM	OBSERVED MOLECULAR WEIGHT
1	0.153	1 M NaClO_4	283
2	0.239	Water	292
3	0.755	Water	352
4	1.56	Water	366
5	5.17	Water	369 - 482

The results of the calculation for 0.2 to 2 M UO_2F_2 solutions are shown in Table 1.8. It is interesting that the new (30°C) activity coefficients are also in fair agreement with a dimerization hypothesis. As also shown in the table, reasonably constant values of $K \approx 1.8$ are obtained using $k = 0.08$, which is considerably smaller than its value at the freezing point ($k = 0.17$). Using these constants for evaluation of activity coefficients at higher concentration, the "observed" molecular weight of uranyl fluoride in the

"saturated" solution was calculated to be between 286 and 228. Although these values are too low, a re-evaluation of K and k at 30°C does not appear necessary since with this very dense solution sufficient distortion of the quartz plates of the cell may occur to lead to errors of this order of magnitude.

TABLE 1.8

Activity Coefficients of UO_2F_2 at 30°C from Ultracentrifuge Data
(Assuming Molecular Weight = 308 and $\gamma_f = 0.750$ at $m = 0.2$)

m	γ_f	K (for $k = 0.08$)	MOLECULAR WEIGHT
0.2	(0.750)*	1.28	(308)
0.5	0.570	1.62	(308)
1.0	0.454	1.81	(308)
1.5	0.410	1.80	(308)
2.0	0.382	1.82	(308)
3.0	(0.357)**		286 (4 - 5 m)
4.0	(0.347)**		263 (5 - 5.5 m)
5.0	(0.348)**		228 (5.5 - 6 m)
6.0	(0.352)**		

*Assumed γ_f at 30°C equals γ_f at freezing point.

**Calculated assuming $K = 1.8$ and $k = 0.08$.

2. NUCLEAR CHEMISTRY

DECAY SCHEMES OF SOME IODINE AND XENON FISSION PRODUCTS

H. Zeldes B. H. Kettle
A. R. Brosi

Work has continued on the decay schemes of the mass 133 fission products. A new beta group has been found in I^{133} which is emitted in a transition to the 2-day metastable level in Xc^{133} . In a very small fraction of 5-day Xe^{133} disintegrations a soft beta group is emitted in a transition to a 380-Kev level in Cs^{133} .

Part of the work on I^{133} has been done with sources containing appreciable amounts of I^{131} . This has led to a study of the I^{131} decay scheme in which a new 720-Kev gamma ray and a new 810-Kev beta group have been found.

A considerable amount of time has been spent on instrumentation for the new short-lived isotopes laboratory. Equipment has been designed for the rapid separation of fission gases in order to study the radiations of short-lived gaseous isotopes and their descendants.

It is planned to reinvestigate the mass 135 chain because many improvements have been made in instruments and techniques since it was studied three years ago. In addition to decay scheme work, it is hoped that independent fission yields of some of the chain members can be determined in the new laboratory.

EVIDENCE FOR THE PRODUCTION OF Tc_2O_7

G. W. Parker and W. J. Martin

During the process of developing a routine purification method for technetium by subliming TcO_3 from process crudes, a white to pale yellow product was observed to deposit near the heated portion of the quartz assembly. This material, which can be melted and which will form yellow or green solutions, will also, upon standing, become dark red and resemble TcO_3 . A sharp detonation twice resulted when quartz tubes containing the sublimed oxides of technetium were heated with a torch to attach a collecting tube. The explosion blew out the ground stopper connected to the train, but, fortunately, detectable amounts of technetium apparently were not released outside the furnace.

In the future it is planned to collect some of the light-colored oxide for X-ray examination and for oxygen analysis.

**SEPARATION OF CERIUM FROM NEPTUNIUM AND RARE EARTHS
BY IODATE PRECIPITATION**

P. M. Lantz and G. W. Parker

In preceding reports (ORNL-685, p. 62, ORNL-695, p. 51) the initial steps in the large-scale separation of Np^{237} from the ORNL pilot plant Redox wastes were described. A summary of steps following the concentration of the fission rare earths and neptunium by coprecipitation with added $\text{Ce}(\text{OH})_3$ is:

1. Removal of chemical and radiochemical cerium by iodate precipitation.
2. Metathesis of the neptunium and the fission product rare earth nitrates to the chlorides by hydroxide precipitation and dissolution in HCl.
3. Removal of neptunium by reduction to $\text{Np}(\text{IV})$ and extraction into TTA-xylene.
4. Fractionation of gadolinium, europium, samarium, promethium, etc. by the usual ion-exchange elution with citrate buffers.

Removal of bulk cerium by means of the ceric iodate precipitation outlined by Boldridge and Hume⁽¹⁾ has been adapted to the first step. In the work described below, some of the variables affecting the quantitative removal of cerium, and the behavior of neptunium are described.

Solubility of Ceric Iodate. In the initial separation, after thorough washing, the neptunium, rare earths, and cerium hydroxides are to be dissolved out of the centrifuge tube with strong nitric acid and stored for later separation and purification.

In order to determine the effect of acid strength on the solubility of $\text{Ce}(\text{IO}_3)_4$, precipitations were made at five HNO_3 normalities (2, 4, 8, 10, and 12) using, per liter, 200 mg of $\text{Ce}(\text{III})$ carrier, 200 mg of La holdback carrier, and Ce^{144} tracer. To oxidize the cerium to $\text{Ce}(\text{IV})$ the solutions were made

(1) W. F. Boldridge and D. N. Hume, *A Study of the Separation of Cerium by Iodate Precipitations and the Improved Radiochemical Determination of Cerium and Rare Earth Activities*, Clinton Laboratories Report CC-R-2845 (June 30, 1945).

0.1 *M* with 1 *M* NaBrO₃ (about 60 times stoichiometric). After being digested several minutes on a hot plate, the solutions were cooled in an ice bath and then centrifuged. The precipitate was washed once with a volume of H₂O equivalent to 50% of the original, and the two supernatants were combined. Portions of the combined supernatants and the dissolved Ce(IO₃)₄ were counted. The results (Table 2.1) indicate that for all practical purposes the solubility of Ce(IO₃)₄ is unchanged over the range of 2 to 12 *N* HNO₃.

TABLE 2.1

Solubility of Ce(IO₃)₄ When Precipitated Out of 2, 4, 8, 10, and 12 *N* HNO₃

HNO ₃ (<i>N</i>)	Ce(III) CARRIER (g/liter)	La HOLDBACK (g/liter)	% Ce ¹⁴⁴ ACTIVITY IN PRECIPITATE
2	0.2	0.2	100
4	0.2	0.2	99.8
8	0.2	0.2	99.6
10	0.2	0.2	99.2
12	0.2	0.2	98.5

Separation of Rare Earths from Ceric Iodate. Since europium is one of the trivalent rare earths whose recovery from the fission products is sought, determinations of the extent of its recovery from the iodate precipitation at various acid normalities were conducted. The conditions were identical to those maintained for the previous Ce(IO₃)₄ solubility experiment except that Eu¹⁵⁵ tracer was used.

It can be observed from Table 2.2 that as the acid normality increased the recovery of europium improved.

Solubility of Np(IV) Iodate Compared with Np(V) Iodate. It was expected that the different states of neptunium should exhibit different solubilities in a HNO₃ solution, and hence the behavior of neptunium under the conditions of the ceric iodate separation was investigated.

TABLE 2.2

Recovery of Europium from $\text{Ce}(\text{IO}_3)_4$ When Precipitated Out of 2, 4, 8, 10, and 12 N HNO_3

HNO_3 (N)	Ce(III) CARRIER (g/liter)	La HOLDBACK (g/liter)	% Eu^{155} ACTIVITY IN PRECIPITATE
2	0.2	0.2	81.8
4	0.2	0.2	93.6
8	0.2	0.2	98.0
10	0.2	0.2	97.8
12	0.2	0.2	95.5

This was accomplished by preparing two sets of duplicate samples of 4 N HNO_3 solution. To one set was added, per liter, 200 mg of Ce(III) carrier, 200 mg of La holdback carrier, Np(IV) tracer, and NaBrO_3 ; to the other, the same except for NaBrO_3 . Both sets were warmed for 20 min on a steam bath prior to the addition of HIO_3 and then allowed to cool before centrifugation. The iodate precipitate was dissolved in HCl in preparation for counting. To eliminate the absorbing effect of the iodate in counting the neptunium activity in the filtrate, 35% NaOH was added to this acidic solution to precipitate out the rare earth hydroxides. These were separated by centrifugation, washed with H_2O , and dissolved in HCl to prepare a relatively solid-free sample for counting. The results (Table 2.3) indicate little or no difference in solubility in a 4 N HNO_3 solution between the Np(IV) and Np(V), although iodate oxidation of Np(IV) may have occurred.

TABLE 2.3

Recovery of Np^{239} (IV) and Np(V) from the Precipitation of Cerium as Ceric Iodate

SAMPLE	CARRIER (mg)		La HOLDBACK (mg)	1 M NaBrO_3 ADDED (ml)	YIELD OF Np^{239} IN FILTRATE (%)
	Ce(III)	Ce(IV)			
Np(IV), No. 1	20	None	20	None	92.3
No. 2	20	None	20	None	92.0
Np(V), No. 3	None	20	20	5	84.5
No. 4	None	20	20	5	88.2

Dense Precipitation of $Ce(IO_3)_4$. It has been demonstrated by Willard⁽²⁾ that when ceric iodate is precipitated slowly by gradual oxidation in a strong HNO_3 solution a $Ce(IO_3)_4$ crystal is formed which has a diameter many times greater than that formed by rapid precipitation. The wet volume of the precipitate is therefore several times smaller. This method of dense precipitation appeared to offer good possibilities as a means of removing the cerium quantitatively without losing the neptunium on an otherwise flocculent precipitate.

While a much more attractive crystalline $Ce(IO_3)_4$ was obtained by the recommended procedure, it is believed that the poor separation obtained is inherent in the very high cerium concentration (1 to 2 g/liter), under which conditions the solubility of $Ce(III)$ iodate is exceeded. The results of this investigation can be seen in Table 2.4.

TABLE 2.4

Recovery of Np^{239} by "Dense Precipitation" of $Ce(IO_3)_4$ Compared with Direct Precipitation of Ceric Cerium from 4 N HNO_3

SAMPLE	Ce(III) CARRIER (g/liter)	La HOLDBACK (g/liter)	H_2O_2 ADDED (ml)	YIELD OF Np^{239} IN FILTRATE (%)
Direct, No. 1	2	0.16	0	83.2
" " No. 2	2	0.16	0	81.6
"Dense" No. 3	2	0.16	2	32.8
" " No. 4	2	0.16	2	32.7

Yield Improvement by Reprecipitation of $Ce(IO_3)_4$. In order to demonstrate that it is possible to recover at least 99% of the neptunium as a result of the ceric iodate precipitation for the removal of cerium, three synthetic product solutions containing 0.5, 1.0, and 2.0 g of cerium per liter were prepared in 4 N HNO_3 solution. These samples were treated with 1 N $NaBrO_3$ to assure complete oxidation of the cerium and a 200-fold excess of HIO_3 reagent to precipitate the cerium. As indicated in Table 2.5, the yield of Np^{239} in the filtrate varied from 84.2 to 91.7% with the first iodate precipitation. Since a single iodate precipitation entailed too great a loss of neptunium,

(2) H. H. Willard, private communication.

the precipitates were dissolved in dilute HCl for a reprecipitation. As an intermediate step the rare earths were precipitated with 35% NaOH to eliminate the iodate. The hydroxides, after thorough washing with H₂O, were again dissolved in a volume of 4 N HNO₃ equivalent to that used in the beginning. The resulting solutions were treated in a manner identical to that used previously to precipitate the iodates the first time; after counting the precipitate and filtrate fractions it was found that 74 to 100% of the neptunium activity remaining from the first precipitation was recovered in the second iodate filtrate. This gave a gross yield with two iodate precipitations of 96 to 100% of the total Np²³⁹.

TABLE 2.5

Total Recovery of Np²³⁹ from Precipitation of 1.0 to 2.0 g of Cerium per Liter as Ceric Iodate from Synthetic Product Solution

Ce (g/liter)	4 N HNO ₃ (ml)	YIELD OF Np ²³⁹ IN 1st IODATE (%)	YIELD OF Np ²³⁹ IN 2nd IODATE (%)	NET YIELD OF Np ²³⁹ WITH TWO IODATE PRECIPITATIONS (%)
1.0	250	86.4	~100	~100
	250	84.2	74	96
2.0	125	89.1	95.8	98.8
	125	85.1	~100	100

Summary. This investigation has shown that the removal of cerium in concentrations of 0.5 to 2.0 g/liter can be satisfactorily accomplished from a mixture of fission rare earths by precipitation of Ce(IO₃)₄ out of a strong HNO₃ solution. When two precipitations are made the loss of trivalent rare earths and Np to the Ce(IO₃)₄ precipitate can be expected to be of the order of 1 to 2%.

3. RADIO-ORGANIC CHEMISTRY

SYNTHESIS OF LOW-MOLECULAR-WEIGHT INTERMEDIATES CONTAINING C¹⁴

E. J. Dowling W. J. Skraba
A. R. Jones T. C. Weeks

Methanol-C¹⁴

One hundred and fifty millicuries of methanol-C¹⁴ has been prepared by the catalytic reduction of carbon dioxide-C¹⁴. Methanol is formed in this process in a yield of 90% and is obtained as a colorless liquid with the refractive index and vapor pressure of pure methanol. However, a comparison of the specific activity of the carbon dioxide with that of the methanol indicates that a dilution of about 15% occurs in the process. Physical methods, applicable for the determination of impurities in the methanol, have indicated high purity. Comparison of the infrared spectrum of this product with that of pure methanol has shown the materials to be qualitatively identical. Mass spectrograms (by Roger Hibbs of the Chemistry Division, Y-12) have also shown that, from mass number 12 to mass number 104, the two substances are qualitatively identical.

Formic Acid-C¹³

By the Tolbert *et al.*⁽¹⁾ modification of the Melville *et al.*⁽²⁾ procedure for the catalytic reduction of potassium bicarbonate, 31.5 mmoles of 30% formic acid-C¹³ has been prepared in good yield.

Glycine-1-C¹⁴, Glycine-2-C¹⁴, Malonic Acid-2-C¹⁴

Several attempts to prepare glycine-1-C¹⁴ by the method of Sakami⁽³⁾ resulted in an impure product.

(1) B. M. Tolbert, P. A. Dans, and R. E. Seliff, unpublished report.

(2) D. B. Melville, J. P. Rachele, and E. B. Keller, "Synthesis of Methionine Containing Radiocarbon in the Methyl Group," *J. Biol. Chem.* 169, 419 (1947).

(3) W. Sakami, W. E. Evans, and S. Gurin, "Synthesis of Organic Compounds Labelled with Isotopic Carbon," *J. Am. Chem. Soc.* 69, 1110 (1947).

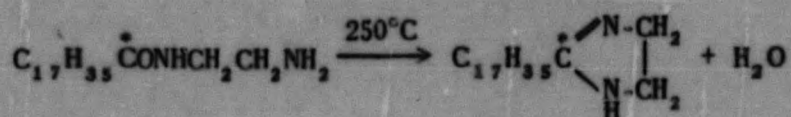
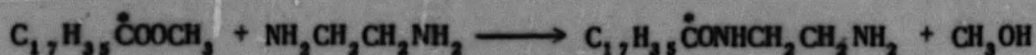
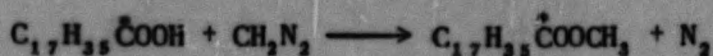
Progress is being made in the preparation of glycine-1-C¹⁴, glycine-2-C¹⁴, and malonic acid-2-C¹⁴ through the intermediate chloroacetic acid.^(4,5) In this method equimolar amounts of chlorine and anhydrous acetic acid are allowed to react at 140°C for 2 hr in the presence of catalytic quantities of phosphorus pentachloride, iodine, phosphorus, and acetyl chloride. The products of chlorination are treated with a mixture of ammonium hydroxide and ammonium carbonate at 60°C for 12 hr. The resulting glycine is separated by crystallization from methanol.

SYNTHESIS OF HIGH-MOLECULAR-WEIGHT COMPOUNDS CONTAINING C¹⁴

Preparation of 2-Heptadecylglyoxalidine-2-C¹⁴

V. F. Raaen and G. A. Ropp

Discussion. Labeled heptadecylglyoxalidine has been prepared on a 1-mmole scale by a modification of a process developed by Carbide and Carbon Chemicals Division. The reactions involved are the following:



Experimental. Stearic acid-1-C¹⁴⁽⁶⁾ (0.284 g or 1 mmole, assaying 987 microcuries per millimole) was methylated with diazomethane. To the resulting methyl stearate was added 0.67 ml (10 mmoles) of ethylene diamine. The mixture was permitted to stand for 15 hr at 70°C. Excess diamine and alcohol were removed at reduced pressure, and the residue was distilled at a pot

(4) B. M. Tolbert and D. M. Hughes, *An Improved Synthesis of Glycine-1-C¹⁴ and Glycine-2-C¹⁴ from C¹⁴-Labeled Acetic Acid*, UCRL-705 (May 16, 1950).

(5) G. A. Ropp, *Preparation of Ethyl Acetate-2-C¹⁴ and n-Butyl Acetate-2-C¹⁴ Using Alkyl Phosphates*, *J. Am. Chem. Soc.* 72, 4459 (1950).

(6) Prepared by U. S. Testing Co., Hoboken, N. J.

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temperature of 250°C at 3 mm Hg, giving 0.248 g or 80.5% of the theoretical amount, m.p. 77 to 79°C. Radioactive assay: 985 microcuries per millimole.

High-Level Synthesis of C¹⁴-Labeled Polynuclear Hydrocarbons

D. N. Hess and C. J. Collins

An apparatus has been constructed for the high-level production of the hydrocarbons phenanthrene, benzanthracene, chrysene, and 3,4-benzphenanthrene, labeled with C¹⁴. Chrysene was prepared successfully from 1,2-benzfluorene⁽⁷⁾ without isolating the intermediate ester or carbinol. Approximately 10 millicuries of chrysene-5,6-C₁¹⁴ has been prepared in an overall yield of 94% based on unrecovered carbon dioxide.

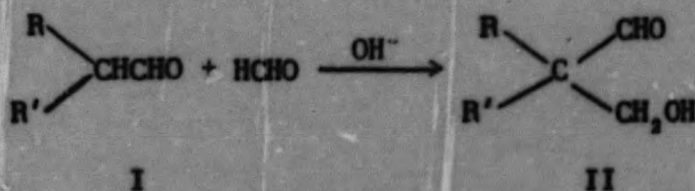
MECHANISM OF ORGANIC REACTIONS

Reaction of Formaldehyde with Aldehydes Containing One Alpha Hydrogen

J. G. Burr, Jr.

As a result of the discovery that 9-formylfluorene-10-C¹⁴ reacted with formaldehyde to give inactive 9-fluorenemethanol (with displacement of the aldehyde group as formic acid),⁽⁸⁾ other similarly constituted aldehydes have been studied in an attempt to clarify this reaction.

In the normal reaction of formaldehyde with aldehydes containing one alpha hydrogen atom, the first step probably involves the aldol addition of formaldehyde to the aldehyde to form an intermediate (II).⁽⁹⁾

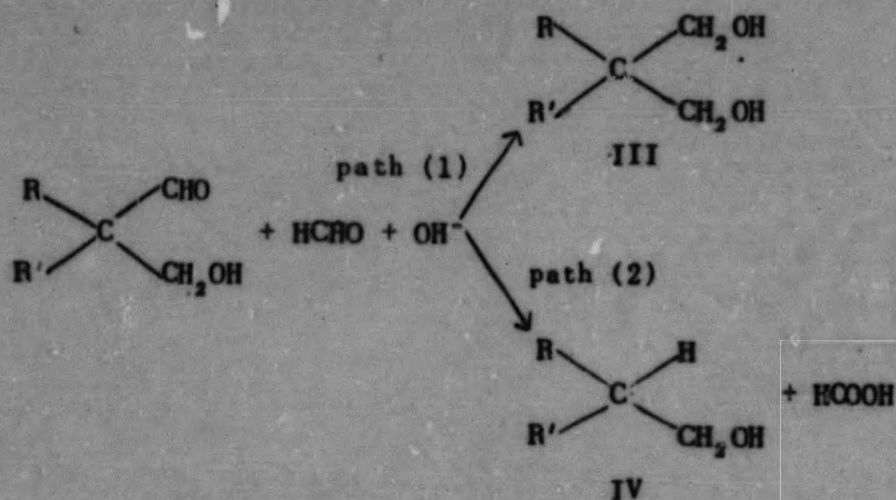


(7) C. J. Collins, A. R. Jones, and G. M. Toffel, in *Chemistry Division Quarterly Progress Report for Period Ending June 30, 1950*, CPNL-795, p. 75 (Oct. 3, 1950).

(8) J. G. Burr, Jr., "The Reaction of 9-Formylfluorene with Formaldehyde," *J. Am. Chem. Soc.* 73, 823 (1951).

(9) R. Adams, *Organic Reactions*, vol. II, p. 100, Wiley, New York, 1949.

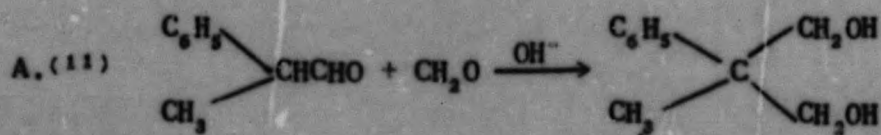
This compound is then presumably reduced by excess formaldehyde to give the glycol (III).



However, in the reaction of 9-formylfluorene with formaldehyde, the intermediate II, if it forms, loses the aldehyde group as formate to form a carbinol as represented by IV.⁽⁸⁾

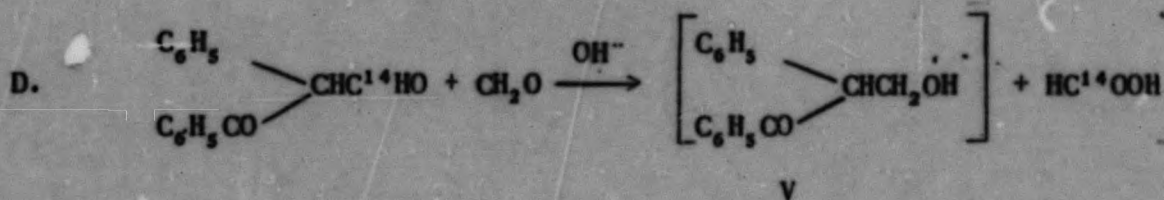
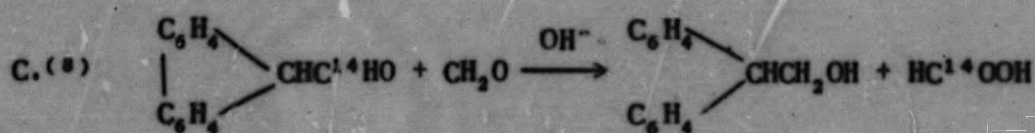
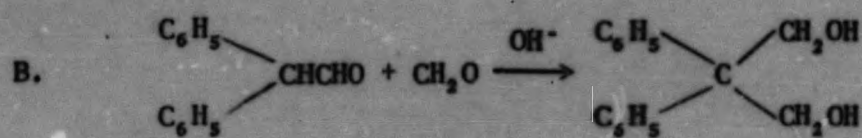
In the scheme below are shown the results of the study of two additional aldehydes, diphenylacetaldehyde and formyldeoxybenzoin, together with two previously reported reactions. The aldehydes are arranged in the order of

ascending basicity of the $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}' \end{array} \text{CH}$ moiety, as reported by Conant and Wheland.⁽¹⁰⁾



(10) J. B. Conant and G. W. Wheland, "The Study of Extremely Weak Acids," *J. Am. Chem. Soc.* 54, 1212, esp. 1215, (1932).

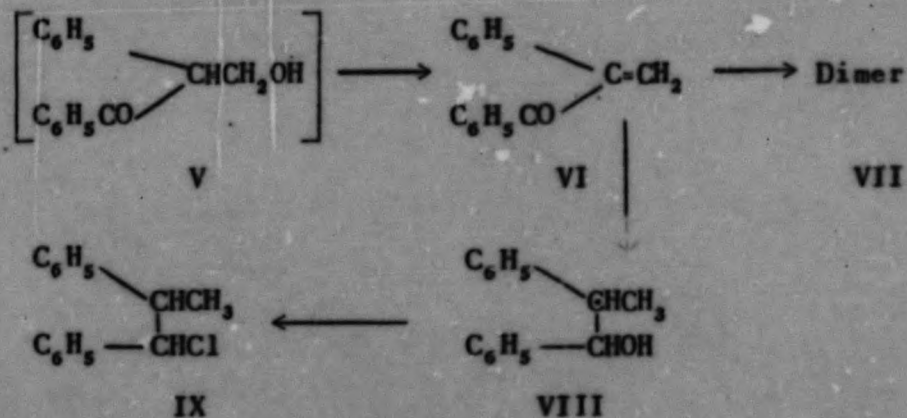
(11) A. Franke, "Abnormal Behavior of Several 1,3-Dibromo- and 1,3-Dihydroxyparaffins," *Monatsch.* 34, 1893, esp. 1904 (1913).



It is evident that the change in the course of the reaction from path 1 to path 2 parallels the increased basicity of this moiety.

An explanation of this may be adduced from a study of the several reaction paths which have been postulated for the Cannizzaro reaction.⁽¹²⁻¹⁵⁾

The carbinol, V, is indicated in brackets because it yields VI spontaneously:



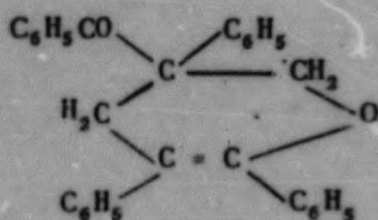
(12) E. R. Alexander, *Principles of Ionic Organic Reactions*, p. 168, Wiley, New York, 1950.

(13) R. Adams, *op. cit.*, p. 96.

(14) E. R. Alexander, *op. cit.*, p. 207.

(15) R. Adams, *op. cit.*, p. 99.

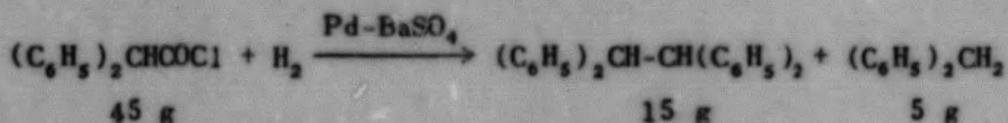
The dehydration product, VI, was identified by determinations of molecular weight, molecular refraction, carbonyl content, uptake of hydrogen, and, finally, by reduction to the carbinol, VIII, which gave a known chloride, IX. It was found that product VI (an oil) upon standing was slowly but completely converted to a white crystalline solid, melting at 108 to 110°C. This solid was shown to have the empirical composition $C_{30}H_{24}O_2$, a dimer of VI. However, it gave no reaction of the carbonyl group, or of the hydroxyl group, and did not show any unsaturation. The structure, X,



X

tentatively proposed to explain these observations, represents the product of a Diels-Alder reaction, and would have both a highly hindered double bond and also a highly hindered carbonyl group. Further investigation of this substance is in progress.

In the effort to prepare diphenylacetaldehyde from diphenylacetyl chloride by a Rosenmund type reduction, an unusual product was obtained, i.e., tetraphenylethane:



An explanation of this anomalous reaction is being sought.

Experimental.* *β,β-Diphenyltrimethylene Glycol.* Diphenylacetaldehyde (9 g), prepared by the rearrangement of either hydrobenzoin or *α,α*-diphenylethylene glycol, was dissolved in 50 ml of 10% sodium hydroxide and treated

*All melting points were taken on a Fisher-Johns block and are uncorrected. C^{14} assays were accomplished by a wet combustion of compounds, and ion-chamber counting of the carbon dioxide was done on a vibrating-reed electrometer. Microassays for carbon and hydrogen were by H. W. Galbraith, Knoxville, Tennessee.

with 10 ml of 37% formalin solution overnight. The oil, which separated and was removed with ether, weighed 9 g. - The product, distilled at 1 mm Hg pressure, partly crystallized. Recrystallization from benzene-pentane gave 2.1 g of colorless microplates which melted at 102 to 103°C.

Anal. Calc. for $C_{15}H_{16}O_2$: C, 78.8; H, 7.07; OH, 14.9%. Found: C, 78.6; H, 6.61; OH, 14.0%.

The compound formed a dibenzoate melting at 107 to 108°C (depressed by admixture with the diol).

Anal. Calc. for $C_{20}H_{24}O_4$: C, 79.8; H, 5.59. Found: C, 79.3; H, 5.52.

Reaction of β -hydroxy- α -phenyl-acrylophenone (Formyldesoxybenzoin) with Formaldehyde. Desoxybenzoin (103 g) was converted to formyldesoxybenzoin with a solution of 33 g of commercial sodium methoxide and 62 ml of ethyl formate in 200 ml of alcohol. The unreacted ketone weighed 30.5 g. The moist enol (91 g) suspended in 200 ml of 37% formalin was treated with a solution of 23 g of potassium hydroxide in a mixture of 150 ml of alcohol and 30 ml of water. After the solution was stirred overnight and poured into water, the insoluble oil was extracted with ether and distilled at less than 1 mm Hg pressure. The distillate, collected in four fractions, weighed 60.7 g. The analytical data obtained for the purest fraction are shown in Table 3.1.

TABLE 3.1

Analytical Data for Compound VI

DETERMINATION	METHOD	FOUND	CALC. FOR $C_{15}H_{12}O$ (XI)
Molecular weight	B.p. elevation in benzene	213	208
Carbonyl	Hydroxylamine hydrochloride ⁽¹⁶⁾	13.0%	13.4%
Molecular refraction		65.0*	63.8
Hydrogenation**	Adams PtO ₂ in alcohol	2.0 moles	2.0 moles

*This is an exaltation of 1.2 units, which is not surprising for a carbonyl group conjugated with a phenyl group and a double bond.

**Normal pressure.

(16) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, p. 17, Wiley, New York, 1949.

Ten grams of compound V was hydrogenated. The product, distilled at 130°C at 1 mm Hg pressure, was converted to the chloride, IX, m.p. 139 to 140°C, by the procedure of Kayser.⁽¹⁷⁾

The liquid product VI, after standing for a week and half, deposited crystals, m.p. 107 to 108°C, from alcohol solution and in a few weeks was almost completely solid.

Anal. Calc. for $C_{30}H_{24}O_2$: mol. wt. 416; C, 86.3; H, 5.82. Found: mol. wt. 420; C, 85.7; H, 6.04.

This dimer did not react with hydroxylamine in the procedure of Siggia,⁽¹⁸⁾ it did not absorb hydrogen at normal pressure in the presence of platinum, and it did not react with phthalic anhydride in the presence of pyridine⁽¹⁹⁾ (showing the absence of hydroxyl function). The ultraviolet spectrum had a single maximum at 241 $m\mu$ ($\log E_M$ 4.22), which is characteristic of a conjugated carbonyl function. The infrared spectrum (paste in Nujol) showed absorption peaks characteristic of carbonyl function, but none where the hydroxyl bonds might be expected.

Preparation of β -Hydroxyl- α -phenyl-(acrylo- β - C^{14})phenone and Its Reaction with Formaldehyde. To a solution of 2.43 g of sodium methoxide in 25 ml of alcohol was added 3.11 g of ethyl formate containing 100 microcuries of C^{14} . To this was added a solution of 7.85 g of desoxybenzoin in 20 ml of alcohol. After this solution was stirred for 36 hr, it was poured into water. The recovered ketone weighed 4.38 g (56%), and was radiochemically inactive. The aqueous layer, upon acidification, deposited 2.70 g (31%) of the labeled formyl-desoxybenzoin, m.p. 109 to 110°C. The benzoate was prepared, m.p. 106 to 107°C (mixture with the enol melted at 90 to 100°C). This substance contained 2.04 microcuries of C^{14} per millimole.

A suspension of 2.43 g of the labeled formyl-desoxybenzoin in 5 ml of formalin solution was treated with 10 ml of 10% alcoholic potassium hydroxide. After the solution was stirred for 18 hr and poured into water, the product was extracted into ether and was distilled at high vacuum in a short-path still to give 1.74 g of a yellow oil, n_D^{24} 1.5730. This substance took up 11

(17) M. F. Kayser, "Contribution à l'étude des réactions dissymétriques," *Ann. chim.* 6, 145, esp. 171 (1936).

(18) S. Siggia, *op. cit.*, p. 7.

(19) *Ibid.*, p. 17.

mmoles (68% of theory) of hydrogen in the presence of platinum. The hydrogenation product when distilled in high vacuum yielded 1.54 g of a colorless oil, n_D^{25} 1.5571. This substance (crude VIII) upon assay showed less than 5% of the starting material molar C^{14} activity. This small residual activity is probably not significant because on such small-scale runs it was not possible to purify the products thoroughly.

The aqueous fraction of the reaction product was diluted with 980 mg of nonradioactive sodium formate. The solution was treated with 10 ml of 20% benzylthiuronium chloride solution. The precipitated salt, m.p. 146 to 147°C, was dried and assayed. It contained 0.456 millicurie of C^{14} per millimole, 57% of the theoretical 0.803 millicurie per mole. This demonstrated that the C^{14} activity had been converted predominantly to formate.

Attempted Rosenmund Reduction of Diphenylacetyl Chloride. A suspension of 4 g of 5% palladium—barium sulfate catalyst poisoned with 0.6 ml of quinoline-S solution in 200 ml of toluene was prepared. To this solution was added 44.6 g of diphenylacetyl chloride, and a stream of hydrogen was passed through the solution as it was refluxed and stirred. The effluent hydrogen chloride was titrated with 5 N sodium hydroxide. After overnight reaction, 28 ml of NaOH had been consumed (75% of theory). The cooled solution was filtered from the catalyst and evaporated under vacuum. The residual solid was heated with aqueous sodium bicarbonate; the undissolved material was filtered off; and the filtrate, after extraction with ether, was acidified to give 5.5 g (13.5%) of unreacted diphenylacetic acid. The neutral organic materials were combined and stirred with ether. The ether extract was evaporated and the residue was distilled. The distillate, 4.4 g (13.5%), b.p. 87 to 89°C, n_D^{28} 1.5788, was diphenylmethane.

The ether-insoluble material weighed 15 g (47% yield) and melted at 209 to 210°C after several crystallizations from benzene. This material conforms in analysis and properties to tetraphenylethane.

Anal. Calc. for $C_{26}H_{22}$: C, 93.3; H, 6.64; mol. wt. 334. Found: C, 92.6; H, 6.29; mol. wt. 320.

A mixture melting point with authentic tetraphenylethane (m.p. 211 to 212°C, from diphenylchloromethane and zinc) showed no depression.

ISOTOPE EFFECT IN DECOMPOSITION OF FORMIC ACID-C¹⁴

G. A. Ropp A. J. Weinberger
O. K. Neville

Experiments previously reported⁽²⁰⁾ have shown that the decomposition of formic acid-C¹⁴ in concentrated sulfuric acid to form carbon monoxide and water involves a measurable isotope effect. Successive samples of evolved gas were found to contain increasing amounts of C¹⁴ radioactivity. Since the kinetics of the decomposition are of the first order, an expression of the following form has been written:

$$\ln S = K + (k_{12} - k_{14})t \quad (1)$$

where

S = the specific activity of the evolved gas sample at time t

K = a constant

k_{12} = rate constant for formation of carbon monoxide-C¹²

k_{14} = rate constant for formation of carbon monoxide-C¹⁴

It is seen that substitution of values for $\ln S$ and for t should permit the plot of a straight line of slope $k_{12} - k_{14}$.

This equation differs from those previously derived⁽²¹⁻²³⁾ in that the specific activity figure used is not an integral of all increments of radioactivity up to time t but rather is the specific activity of one small increment of gas at some time t . Hence the smaller the sample of gas measured as a percentage of the total volume of product, the more nearly will Eq. (1) be expected to be applicable in correlating the experimental results. The present method, involving measurement of the specific activity of successive increments of product, is superior to that of measuring the increase in

(20) G. A. Ropp and A. J. Weinberger, "The Isotope Effect in the Decomposition of Formic Acid-C¹⁴," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1950*, ORNL-870 (Mar. 1, 1951).

(21) P. E. Yankwich, "Isotopic Effects in Some Simple Chemical Compounds," *Isotopic Exchange Reactions and Chemical Kinetics*, p. 44, (BNL-C-8) Brookhaven Conference Report, December 1 - 3, 1948.

(22) J. Bigeleisen, *ibid.*, p. 53.

(23) W. H. Stevens and R. W. Attree, "Effect on Reaction Rates Caused by the Substitution of C¹⁴ for C¹². I. Alkaline Hydrolysis of Carboxyl-Labeled Ethyl Benzoate," *Can. J. Res.* 27B, 807 (1949).

specific activity of the total product up to time t in that a greater difference in radioactivity will be observed between samples collected at any two times, and hence the adverse effect of counting error is smaller.

In order to approach more closely the ideal system of measuring the activity of point samples, a flow system containing a 10-ml ion chamber has been designed and used in recent experiments. The radioactivities of successive 10-ml increments of a total of 1000 ml of gas may thus be measured by means of a vibrating-reed electrometer and recorded continuously on a Brown recorder. The kinetics of the reaction can be studied simultaneously by measurement of the volume of the gas evolved as a function of time. Figure 3.1 shows the apparatus which has been used. In this figure, *A* is the reaction vessel designed to allow the maximum surface for evolution of the gas with a minimum volume for the gas above that surface; *B* is a copper heat exchanger whose function is to bring the gas to room temperature, regardless of the temperature of the reaction vessel; *C* is an ascarite tube to remove formic acid spray which might contaminate the ion chamber, *D*; *E* is a gas-volume measuring device which permits the collection of gas without changing the pressure in the ion chamber; and *F* is a mercury monometer. The reaction vessel contains a magnetic stirring bar and is enclosed in a constant-temperature bath, whose maximum variation is 0.05°C. The entire apparatus is contained in a hood where a fairly constant temperature can be maintained. The vibrating-reed electrometer is so adjusted that the ion current increase due to isotopic effect during an experiment produces one-half to full scale deflection on a Brown recorder. A plot of the logarithm of the recorded specific activity against the time has been found to give a fairly straight line. The slope of this line multiplied by 2.303 is equal to $k_{12} - k_{14}$. This divided by k_{12} from the kinetic observations is one form for the expression of the isotope effect. In Table 3.2 are the data obtained in six experiments at 0°C and five experiments at 24.7°C.

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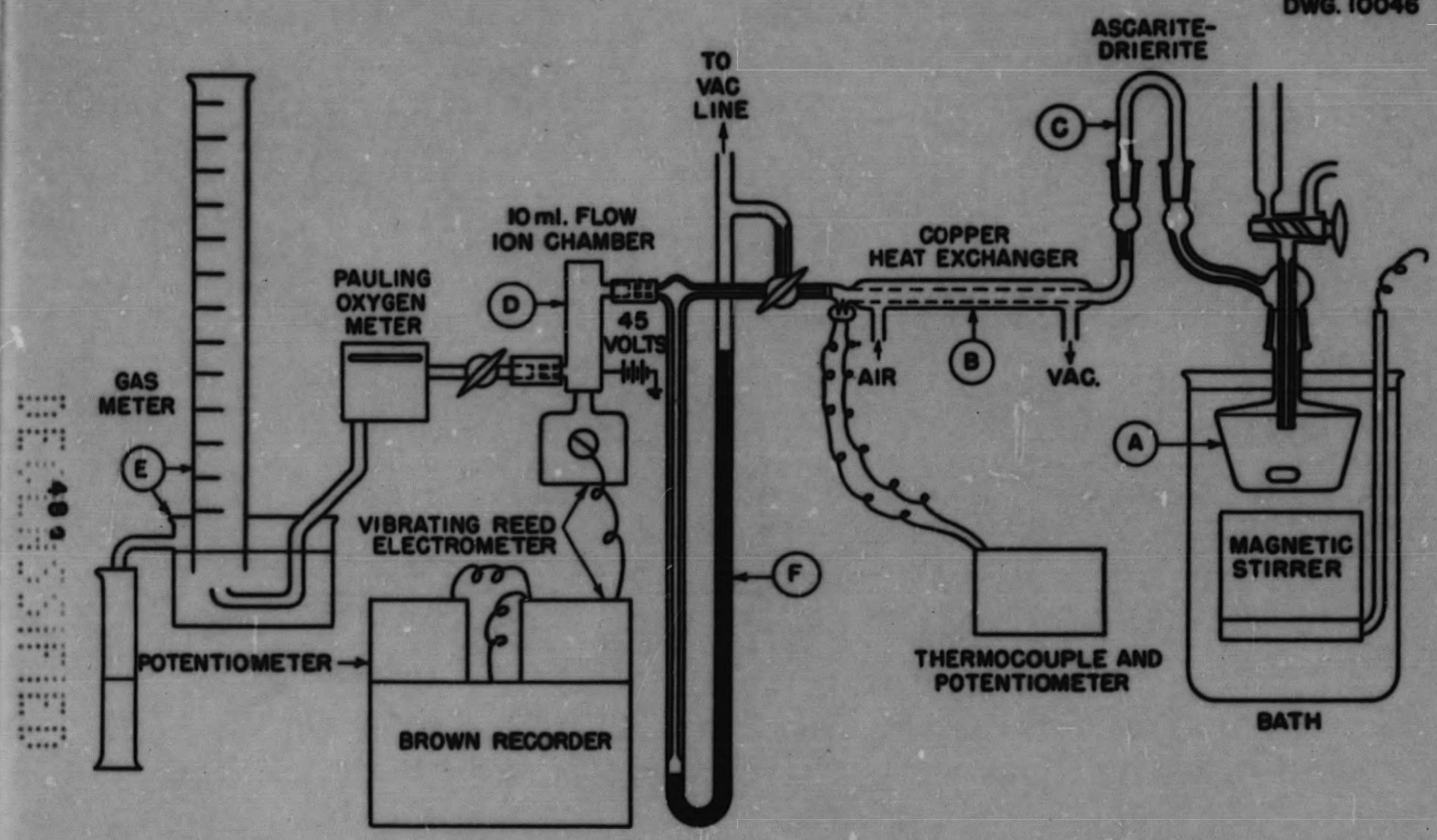


FIG. 3.1

ISOTOPE EFFECT IN FORMIC ACID DEHYDRATION: APPARATUS
USED IN CONTINUOUS MEASUREMENT OF GAS VOLUME AND
SPECIFIC ACTIVITY OF CARBON MONOXIDE EVOLVED

TABLE 3.2

Data for Determination of Isotope Effect in Decomposition of Formic Acid
in Sulfuric Acid Solution

TEMPERATURE (°C)	k_{12} ($\text{min}^{-1} \times 10^3$)	$k_{12} - k_{14}$ ($\text{min}^{-1} \times 10^4$)	$\frac{k_{12} - k_{14}}{k_{12}}$ (%)	ISOTOPE EFFECT (% deviation from avg)
0	3.48	4.23	12.2	+10.9
	3.61	3.35	9.3	-15.5
	3.58	4.01	11.2	+1.8
	3.37	3.59	11.7	+6.4
	3.50	3.51	10.0	-9.1
	3.57	4.10	11.5	+4.5
Avg.	3.52	3.80	11.0	9.6
24.7	76.5	65.4	8.55	-0.1
	75.0	67.1	8.95	+4.6
	74.5	63.0	8.46	-1.2
	81.4	62.3	7.66	-10.5
	80.1	73.7	9.20	+7.5
	77.5	66.3	8.56	4.8
Avg.	77.5	66.3	8.56	4.8

The difference in activation energy for formic acid- C^{12} and formic acid- C^{14} can be calculated as follows: From the Arrhenius equations for the activation energies of active and inactive formic acid at temperature T_1 ,

$$\left(\frac{k_{14}}{k_{12}}\right)_{T_1} = \left(\frac{A_{14}}{A_{12}}\right)_{T_1} \frac{\exp(-E_{14}/RT_1)}{\exp(-E_{12}/RT_1)} \quad (2)$$

where

k_{12} and k_{14} are the rate constants for the C^{12} and the C^{14} compound, respectively.

A_{12} and A_{14} are the respective collision numbers (including steric factors).

E_{12} and E_{14} are the respective activation energies.

An expression similar to Eq. (2) can be derived at temperature T_2 . Dividing the equation for T_1 by the equation for T_2 ,

$$\frac{(k_{14}/k_{12})_{T_1}}{(k_{14}/k_{12})_{T_2}} = \frac{(A_{14}/A_{12})_{T_1}}{(A_{14}/A_{12})_{T_2}} \exp \frac{\Delta E}{R} \left[\frac{T_1 - T_2}{T_1 T_2} \right] \quad (3)$$

since $\Delta E = E_{14} - E_{12}$. Although A_{14} may be somewhat different from A_{12} , the ratio of the two should be practically temperature-independent.

Putting Eq. (3) into logarithm form, it becomes

$$\Delta E = 2.303R \left[\frac{T_1 T_2}{T_1 - T_2} \right] \log \frac{(k_{14}/k_{12})_{T_1}}{(k_{14}/k_{12})_{T_2}}$$

Now

$$\frac{k_{14}}{k_{12}} = 1 - \left[\frac{k_{12} - k_{14}}{k_{12}} \right]$$

Then for $T_1 = 298.0^\circ\text{K}$ and $T_2 = 273.2^\circ\text{K}$,

$$\left[\frac{k_{12} - k_{14}}{k_{12}} \right]_{298.0^\circ\text{K}} = 0.08 \left[\frac{k_{12} - k_{14}}{k_{12}} \right]_{273.2^\circ\text{K}} = 0.10$$

$$\Delta E \approx 180 \text{ cal/mole}$$

In 90.5% H_2SO_4 ,

$$\text{Avg. } k_{12} \text{ at } 298.0^\circ\text{K} = 77.5 \times 10^{-3}/\text{min}$$

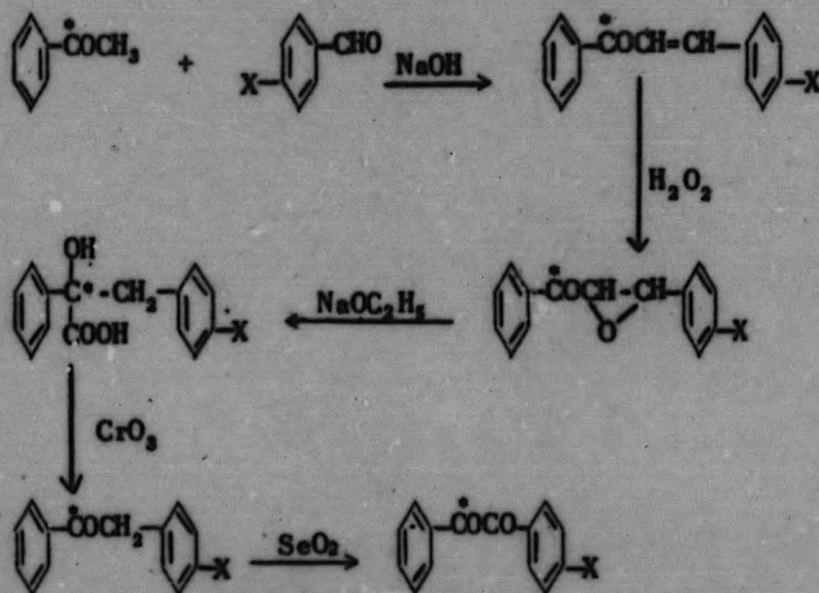
$$\text{Avg. } k_{12} \text{ at } 273.2^\circ\text{K} = 3.52 \times 10^{-3}/\text{min}$$

In addition to the experiments listed in Table 3.2, one special run was made using the apparatus described previously except that the ascarite trap, the heat exchanger, and the manometer were removed from the flow system. Removal of these parts and the redesigning of the reaction vessel eliminated about 95% of the free volume of the system between the surface of the sulfuric acid and the ion chamber. At 0°C, using this modified apparatus, a value of 10.0% was obtained for the isotope effect. Since this value is not significantly different from the average value of 11.0 for the previous experiments, it was concluded that movement of the carbon monoxide through the system was essentially "plug flow" and that the temperature coefficient of the isotope effect was probably not due to difference in the degree of mixing within the free volume of the system, i.e., to difference between the rates of elution.

**C¹⁴ TRACE STUDIES IN THE REARRANGEMENTS OF α -DIKETONES:
UNSYMMETRICAL BENZILS**

E. C. Hendley* O. K. Neville
C. J. Collins

An investigation of a new method for the preparation of carbonyl-labeled unsymmetrical benzils has been undertaken. The method involves the reactions indicated in the equations below:



*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.

In the present case, the unsymmetrically substituted group, X, is the *p*-methoxy group. In the following section the preparations involving the first four of the reactions in the scheme are described.

Experimental. (1) *Phenyl p-Methoxystyryl Ketone*. To a stirred mixture of 25.8 g of acetophenone, 11 g of sodium hydroxide, 62 ml of alcohol, and 98 ml of water, at room temperature, was added 29.2 g of anisaldehyde. The mixture was then heated at 30°C for 3 hr, allowed to stand overnight in a refrigerator, and filtered while cold. The yellow solid residue was washed free of alkali with water and finally with cold alcohol. After crystallization from four times its weight in alcohol, the product melted at 73 to 75°C and weighed 42.84 g (84% of the theoretical yield).

(2) *Phenyl p-Methoxystyryl Ketone Oxide*. The phenyl *p*-methoxystyryl ketone was converted to phenyl *p*-methoxystyryl ketone oxide by adding 3 ml of 30% hydrogen peroxide to a mixture of 1 g of the ketone, 2.5 ml of 2 *N* sodium hydroxide, and 30 ml of alcohol and stirring for 20 min at room temperature. The precipitate which resulted from adding 15 ml of water and cooling weighed 730 mg. After the product had been dried over phosphorus pentoxide in a vacuum desiccator, the yield was 69.4% of the theoretical amount, m.p. 81 to 83°C.

(3) *Phenyl p-Methoxybenzyl Glycolic Acid*. A mixture of 730 mg of the epoxy compound formed in (2) above, 2.2 ml of 2 *N* sodium hydroxide, and 8 ml of alcohol was refluxed for 1.5 hr. After 28 ml of water had been added and the mixture saturated with carbon dioxide (dry ice), the impurities were extracted with ether. Acidification of the water layer produced 660 mg of the acid. The yield was 84.5% of the theoretical amount, m.p. 185 to 187°C.

(4) *Phenyl p-Methoxybenzyl Ketone*. A mixture of 520 mg of the acid from (3), 46 ml of glacial acetic acid, and 125 mg of chromic acid was stirred overnight, after which 118 ml of water was added. The product was extracted continuously into ether, and the ether extract was washed with sodium bicarbonate solution. Crystallization from alcohol yielded 170 mg of the substituted desoxybenzoin melting at 95 to 97°C.⁽²⁴⁾ The yield was 39.3% of the theoretical amount.

(24) Cf. S. S. Jenkins, "Benzoin Reduction. I. The Mechanism of Ketone Formation. The Case of Benzoin," *J. Am. Chem. Soc.*, 54, 1155, esp. p. 1157 (1932).

4. CHEMISTRY OF SEPARATIONS PROCESSES



SOLVENT EXTRACTION

The Organic Chemistry of Solvents (W. H. Baldwin and C. E. Higgins).
Sulfones. Work on these compounds has been temporarily discontinued to allow full effort to be devoted to the study of phosphates.

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Esters of Phosphoric Acid. Several preparations of tri-*n*-butyl phosphate (P^{32}) have been made by the reaction between Ag_3PO_4 and *n*-butyl bromide. Samples of this radioactive material have been supplied to research and development groups at HEW and KAPL. The labeled TBP is being used in our laboratory for the study of the distribution of TBP between aqueous nitric acid solutions and nonpolar solvents.

ELECTRODEPOSITION BEHAVIOR OF SILVER

J. C. Griess, Jr. (in conjunction with L. B. Rogers
and J. T. Byrne of M.I.T.)

Studies during the past quarter have embraced a wide variety of topics, all of which have been considered to be variables affecting the electrodeposition behavior of fractional monolayers of silver on inert surfaces. It has been known for some time that the past history, as well as the type of electrode material, is an important variable, but it has just been demonstrated that although the behavior can be changed by igniting an electrode, the pre-ignition behavior will be regained by repeated anodic polarizations of the electrode. Thus, if the treatment of a set of electrodes is consistent, the data will be internally consistent. With one or two minor exceptions, a person in another laboratory reproduced the behavior using another electrode of the same material, provided the treatment of the electrode, particularly the cleaning procedure, is the same.

Heretofore it has been a question whether or not other elements such as platinum, palladium, or copper, which might be present in solutions of the radioactive tracer, influence the behavior of the silver. During the past quarter, the behavior of traces of silver was found to remain unaffected in the presence of amounts of these elements as great as $10^{-2} M$.

Earlier studies have shown that the deposition behavior of traces is often considerably different from that predicted from the Nernst equation whenever fractional monolayers are deposited. However, during the past quarter a successful attempt has been made to study changes that occur in the transition region of concentrations between pure "trace" behavior and "macro" behavior. A comparison of the transition behavior on gold, platinum, and palladium electrodes indicated that distinct differences exist which are

characteristic for all electrodes of the same material. Although small differences were observed between different electrodes of the same material, the behavior for a particular electrode appeared to be completely reproducible.

These studies with silver have made it possible to modify and to extend current hypotheses concerning the electrodeposition behavior of trace quantities of other elements on inert electrodes. In general, the shapes of the deposition curves confirm the suggestion by Haissinsky that the deposition behavior of fractional monolayers is strongly influenced by the heterogeneity of the surface. However, using a rigorous thermodynamic treatment, it has been possible to give a more comprehensive description of the experimental phenomena than has heretofore been available.

The experimental work at this laboratory has been completed and the work at M.I.T. will be completed within a few weeks. A complete report will be issued in the near future, as a paper in the *Journal of the Electrochemical Society*.

VOLATILITY

P. A. Agron and E. G. Bohlmann

Introduction. The study of the effects of the phosphorus fluoride gases on thorium fluoride was extended to higher pressures in sealed quartz tubes. Evidence for a possible complex which is unstable at room temperature and at reduced pressures had been obtained in previous work; therefore it seemed desirable to make visual observations on these gas-solid systems under varying pressure and temperature conditions.

Experimental Results. Thorium fluoride salt was subjected to $\text{PF}_3(\text{g})$, $\text{PF}_5(\text{g})$, and $\text{POF}_3(\text{g})$ at various pressures in sealed 4-mm quartz tubes. These tubes were then heated in a tubular quartz furnace under the conditions given in Table 4.1 to a series of temperatures ranging from 300 to 450°C. At 300°C the gas pressures are roughly twice the initial pressures; however, the dissociation pressures of the hypothetical complex may be greater than the gas pressures attained at the elevated temperatures in these experiments. Therefore the $\text{ThF}_4(\text{s})$ in tubes 2, 3, and 5 was also examined at temperatures below the temperature of the gas (major portion) by lowering the portion of the tube containing the solid below the furnace windings.

TABLE 4.1
**Conditions for Heating Thorium Fluoride with Phosphorus
 Fluoride Gases in Quartz Tubes**

TUBE NO.	VOLUME OF TUBE (ml)	GAS	CALCULATED PRESSURE AT ROOM TEMPERATURE (atm)	MOLES OF GAS PER MOLE OF SOLID
1	1.4	PF ₃	11.3	1.4
2	1.4	PF ₃	16.7	2.1
3	2.5	PF ₃	26.8	9.6
4	1.4	PF ₅	15.0	1.9
5	2.5	PF ₅	21.0	5.0
6	1.4	POF ₃	10.0	1.2

In none of the above experiments was any liquid phase observed. The solid in tube 3 showed a tendency to cake when it was kept at a temperature lower than that of the gas as described above. The white thorium fluoride became gray in all tubes except tube 6; in tube 6 it was unchanged. The color change was observed when the tubes were heated above 300°C. After a number of cyclic heatings tube 5 exploded when the upper portion was heated to 490°C in the furnace.

As in previous studies, electron micrographs of the treated materials in tubes 1, 2, 4, and 6 show an apparent particle breakdown. The effect seems to be more prevalent in samples 1 and 2. The product from tube 3 has not been examined to date. It is hoped that electron diffraction patterns of the treated samples may soon be obtained to establish the identity of the very fine particles that appear in the electron microscope plates.

Future Work. A metal system has been set up for passing the phosphorus fluoride gases over irradiated ThF₄(s) at elevated temperatures and pressures. An attempt will be made to see whether these treatments will facilitate the removal of protactinium and uranium from their lattice sites in the irradiated solid. At present, test runs using UF₄(s) as a stand-in are being carried out.

5. CHEMICAL PHYSICS

MICROWAVE SPECTROSCOPY

R. Livingston

I¹³¹ Studies. The amount of foreign salt present in the radioactive sodium iodide solution, the starting solution used in the previous runs, was found to be too large. This caused a low chemical yield of methyl iodide and the formation of considerable amounts of foreign gas, which prevented successful microwave observations. Studies have been made on the use of hydrazine solution as a take-up liquid in the distillation of iodine. A number of experiments have been done on a semimicro scale with natural I¹²⁷, and tracer experiments have been done with I¹³¹. If iodine is dissolved in a hydrazine solution and the solution is evaporated to dryness by evacuating (not heating), a dry residue is obtained which loses no iodine on prolonged pumping. Chemical assay indicates the residue to be a hydrazine salt, N₂H₄·HI or perhaps more correctly N₂H₅I. The salt will undergo violent thermal decomposition somewhat below 200°C but is safe up to at least 100°C.

A test experiment with the microwave equipment showed this salt to be a suitable starting material for preparing methyl iodide. However, slightly more foreign gas seems to form than when pure sodium iodide is used. If sodium hydroxide is added to the solution of iodine in excess hydrazine and the solution is taken to dryness, the dry residue contains more hydrazine than a similar solution dried without the sodium hydroxide. It was hoped that the dry residue in this case would contain no hydrazine and would be essentially sodium iodide. The use of hydrazine as a take-up liquid for elemental iodine has several advantages over the use of sulfurous acid. A very large excess of hydrazine can be used. This will allow sufficient reserve of reducing agent to be present so that the iodine will always be present as iodide even though the solution is stored for a few days and considerable hydrogen peroxide forms by radiation decomposition of the solution. When the solution is pumped to dryness the excess hydrazine volatilizes away. In the case of a sulfurous acid take-up liquid, the practice has been to neutralize the solution with sodium hydroxide after the iodine has been absorbed. This prevents loss of iodine as HI when the solution is taken to dryness. Any excess

sulfurous acid then contributes to the total salt residue. However, some excess sulfurous acid must be present to assure an effective take-up liquid and as a reserve against future peroxide formation by radiation.

One hot experiment has been carried out using the hydrazine method. It was not successful because of too much salt being present, but in this case the source of the salt could only have been spray-formed in the final iodine distillation process. As a result of this experience it has been decided to purify the normal I^{131} product produced by the Operations Division by a solvent extraction step. A small extraction apparatus that can easily be operated by remote control has been built, and several tracer experiments have been carried out. The extraction of 1-curie amounts of carrier-free I^{131} appears practical, but the chemical yield will not be very good. The method has been to convert the starting material to elemental iodine, extract it into carbon tetrachloride, and then back-extract it into a dilute hydrazine solution. More complete details of the method will be presented in a later report.

Magnetic Moment of I^{129} . The magnetic moment of I^{129} is being determined by the nuclear induction method in a cooperative program with Harold Walchli of the Isotope Physics Division at Y-12 and Gordon Hebert of the Chemistry Division at this Laboratory. The sample was 33 mg of iodine in hydrazine solution with some heavy water added. Both the I^{127} and I^{129} resonances, as well as deuterium, have been seen in the sample. The I^{127} resonance was very weak. Measurements were therefore made on a separate solution of similar chemical composition. In addition, I^{127} was measured in sodium iodide solution to check on possible chemical shift effects. This was considered desirable since published measurements on I^{127} were carried out in sodium and potassium iodide solutions. The measurements are nearly complete. The results presented below are preliminary.

It is estimated that our 33-mg sample contained about 75% I^{129} , the remainder being I^{127} .

Frequency measurements of iodine relative to deuterium were made at fixed-reference magnetic fields, giving

$$\frac{\nu_{I^{129}}}{\nu_D} = 0.86744 \pm 0.0001$$

$$\frac{\nu_{I^{127}}}{\nu_D} = 1.30337 \pm 0.0002$$

The results of less extensive measurements of I^{127} in sodium iodide solution, $\nu_{I^{127}}/\nu_D = 1.30345$, were not sufficiently different from the above to state that a chemical shift was observed. Using Levinthal's⁽¹⁾ deuteron-to-proton frequency ratio of 0.1535059, the above ratios become

$$\frac{\nu_{I^{129}}}{\nu_H} = 0.13316$$

$$\frac{\nu_{I^{127}}}{\nu_H} = 0.20007$$

Using a spin of $5/2$ for I^{127} and of $7/2$ for I^{129} ,⁽²⁾ a diamagnetic correction of 0.545% for iodine,⁽³⁾ and a value of 2.79268 nuclear magnetons for the proton moment,⁽⁴⁾ the final magnetic moment values in nuclear magnetons are:

$$\mu_{I^{129}} = 2.6173 \pm 0.0003$$

$$\mu_{I^{127}} = 2.8089 \pm 0.0004$$

and

$$\frac{\mu_{I^{127}}}{\mu_{I^{129}}} = 1.0732$$

- (1) E. C. Levinthal, "Relative Nuclear Moments of H^1 and H^2 ," *Phys. Rev.* 78, 204 (1950).
- (2) R. Livingston, O. R. Gilliam, and W. Gordy, "The Nuclear Spin and Quadrupole Moment of I^{129} ," *Phys. Rev.* 76, 149 (1949).
- (3) W. C. Dickinson, "Hartree Computation of the Internal Diamagnetic Field for Atoms," *Phys. Rev.* 80, 563 (1950).
- (4) H. Sommer, H. A. Thomas, and J. A. Hipple, "Values of μ_p , F , and M_p/m_1 Using the Omegatron," *Phys. Rev.* 80, 487 (1950).

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The estimated accuracies do not include uncertainties in the diamagnetic correction. The only previous measurement on I^{129} (5) was done by microwave spectroscopy and resulted in a value of $2.74 \pm 5\%$ nuclear magnetons. Our new value is within the estimated error of the older value. The I^{127} value can best be compared with published values as the frequency ratio to the proton. Pound (6) found 0.75664 ± 0.0002 relative to Na^{23} , which is listed below after conversion with Bitter's (7) Na^{23} to proton ratio of $0.26450 \pm 0.01\%$. Zimmerman and Williams (8) measurement and ours are also listed.

$$\frac{\nu_{I^{127}}}{\nu_H} = 0.20013 \pm 0.00005 \text{ (Pound)}$$

$$\frac{\nu_{I^{127}}}{\nu_H} = 0.20003 \pm 0.00007 \text{ (Zimmerman and Williams)}$$

$$\frac{\nu_{I^{127}}}{\nu_H} = 0.20007 \pm 0.00003 \text{ (ours)}$$

CALORIMETRY OF RADIOACTIVITY

G. H. Jenks and F. H. Sweeton

Calorimetric determinations of the heat liberated by the weighed samples of C^{14} described in a previous quarterly report (ORNL-685, p. 129) have been completed. However, the power generated by decay of the samples is still uncertain because of the possibility that an appreciable fraction of the decay energy may have been stored in the charcoal on which the $C^{14}O_2$ making up the samples was adsorbed and in which the beta particles were absorbed. Measurements designed to establish whether such a storage of energy occurred are now

- (5) W. Gordy, O. R. Gilliam, and R. Livingston, "Nuclear Magnetic Moments from Microwave Spectra: I^{127} and I^{129} ," *Phys. Rev.* 76, 443 (1949).
 (6) R. V. Pound, "On the Nuclear Moments of I^{127} , Ga^{69} , Ga^{71} , and P^{31} ," *Phys. Rev.* 73, 1112 (1948).
 (7) F. Bitter, "Magnetic Resonance Frequencies for Several Nuclei," *Phys. Rev.* 75, 1326 (1949).
 (8) J. R. Zimmerman and D. Williams, "Determination of Nuclear Gyromagnetic Ratios I," *Phys. Rev.* 76, 350 (1949).

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underway. In case a storage is detected, the fraction stored can also be found from the measurements.

The calorimetric determinations which have been completed consisted of two separate measurements on one sample and of a single measurement on the other. A calibration measurement was also made. The results of the two measurements on the one sample differed by less than 0.5%. The results for the two different samples (in terms of heat per unit amount of the original batch from which the samples were aliquoted) differed by 1.3%. The calibration measurement demonstrated that the calorimeter was operating as expected and showed that the heat leakage during the measurements was 4×10^{-9} watts or about 0.5% of the power generated by the samples.

During the time the above measurements were being made the performance of the calorimeter was excellent. Before that time, however, a number of measurements on one of the samples had been attempted but, in each case, had failed because of a poor vacuum in the calorimeter jacket. The poor vacuum resulted from leaks which apparently developed when the calorimeter was cooled, since the jacket appeared tight when tested at room temperature. The source of the leaks was found to be in the Cerrolow solder, a low-melting alloy of indium used instead of normal soft solder to seal the jacket because the calorimetric samples could not safely be heated much above room temperature. Other means were therefore taken to prevent heating of the sample and the Cerrolow was replaced with lead-tin solder. There was no further trouble with leaks.

6. RADIATION CHEMISTRY

RADIATION DECOMPOSITION OF WATER AND AQUEOUS SOLUTIONS

C. J. Hochanadel

Recent work using Co^{60} gamma radiation is being written up for presentation at the April meeting of the American Chemical Society. A summary of the paper will appear in the next quarterly report.

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

J. A. Ghormley

This work will be presented at the April meeting, of the American Chemical Society, and a summary of the paper will be in the next quarterly report.

EFFECTS OF IONIZING RADIATION UPON HETEROGENEOUS CATALYSTS

J. A. Wethington and E. H. Taylor

A decrease in the activity of a ZnO catalyst for ethylene hydrogenation has been observed as a result of irradiation with Co^{60} gamma rays. A sample of reagent-grade ZnO was activated by evacuating for 16 hr at about 360°C . The half-time of the hydrogenation of ethylene at 0°C ($\text{H}_2/\text{C}_2\text{H}_4 = 2/1$) was then 21 hr. Successive 2-hr evacuations at 100°C increased the half-time to a constant 29 hr. Thirteen days of exposure to gamma rays at about 15,000 r/min increased the half-time to 36 hr.

It is hoped that this reflects a direct effect upon the catalyst itself, but other possibilities exist. The principal alternative hypotheses involve either radiation decomposition of adsorbed reactants or products with resulting poisoning, or radiation release of adsorbed water or oxygen from the glass with stronger adsorption upon the ZnO. These possibilities are being investigated.

RADIATION STABILITY AND IN-PILE CORROSION STUDIES FOR THE HRE

J. W. Boyle	D. M. Richardson
F. J. Fitch	C. H. Secoy
J. F. Manneschildt	M. D. Silverman
H. F. McDuffie	A. W. Smith
A. R. Olsen*	F. H. Sweeton

Twenty-two in-pile corrosion-irradiation tests of aqueous uranyl sulfate solutions in contact with only type 347 stainless steel surfaces were carried out in the X-10 graphite reactor during the past quarter. This work is described in detail in the *Homogeneous Reactor Experiment Quarterly Progress Report for Period Ending November 30, 1950* (ORNL-925) and will be only summarized here. The stainless steel surfaces had been either pretreated with 1% HNO₃ or 2% CrO₃, or had been simply cleaned and etched prior to the experiments. Thirteen of the tests were classed as giving encouraging or successful results, seven as giving inconclusive results because of some abnormality during the run, and two as failures. Classification as being successful or having failed was on the basis of pressure-temperature-flux data recorded throughout the run; a successful run showed normal responses to temperature and flux changes and maintained appreciable pressures of hydrogen and oxygen in excess of steam pressure throughout the run; an unsuccessful run failed to maintain pressure in excess of steam pressure, suggesting that the uranium had been removed from solution. There is some evidence suggesting that the failures were associated with reactor shut-downs. Available analytical data indicate that only very small amounts of tetravalent uranium and reduced sulfur are present at the end of a run.

Improvements in apparatus and technique during the past quarter now permit experiments to be carried out with greater safety and less loss of experimental data than previously. Additional facilities for radiation studies have been made available at hole 60 of the X-10 reactor and placed in service.

In anticipation of the plans to carry out experiments at higher neutron flux in the MTR mock-up, a high-pressure testing area has been constructed. All experiments so far have been carried out at fluxes which, while not so high as those for which the HRE is designed, are considerably higher than those at which the HRE will operate until the system has been thoroughly

*Reactor Technology Division.

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tested. It is therefore unlikely that deleterious radiation effects, the absence of which may be demonstrated in the present study, will be manifested at the low power levels which will characterize early operations of the HRE.

Ampoule experiments are underway in which the effects of different levels of uranium concentration, pH, temperature, and neutron flux upon the precipitation of uranium peroxide are being studied. This work is considered to be of interest in connection with problems of start-up and shut-down as well as the prevention of precipitation during operation at a steady level.

DETERMINATION OF HYDROGEN PEROXIDE IN THE PRESENCE OF URANIUM IONS

E. J. Dowling W. J. Skraba
A. R. Jones T. C. Weeks

As an important part of the study of radiation effects on aqueous uranyl sulfate solutions, several methods for the determination of hydrogen peroxide at concentrations of 10^{-4} M have been investigated. The photometric method reported by Allen *et al.*⁽¹⁾ failed to give sufficient accuracy owing to interference in the light absorption by uranyl ion. Potentiometric titration with ceric ion and ferrous *o*-phenanthroline indicator failed at high dilution. At present, a polarographic method for the determination of hydrogen peroxide is being investigated.

(1) 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*, ORO-130 (Oct. 11, 1949).

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7.1 INSTRUMENTATION

A DIFFERENTIAL AND INTEGRAL PULSE-HEIGHT SELECTOR FOR THE A-1 AMPLIFIER

E. Fairstein

Introduction. The increased use of scintillation counters for the measurement of beta- and gamma-ray energy spectra has emphasized the need for an inexpensive differential pulse-height selector. Because of the wide use of the A-1 amplifier at this Laboratory, a unit small enough to replace the integral pulse-height selector now incorporated in it is most desirable. Such a unit should require a minimum of amplifier circuit change without appreciably sacrificing speed of operation or reliability.

A circuit which meets these requirements has been designed and built. There has been insufficient time for extensive reliability tests, but there appears to be no reason for early failure in the present unit.

Description of Circuit. The basic differential pulse-height selector consists of a pair of gate circuits followed by an anticoincidence circuit (Fig. 7.1). The difference in triggering level of the two gate circuits constitutes the slit width. The sensitivity of both gate circuits is varied simultaneously by the pulse-height selector control. The anticoincidence circuit accepts only those amplifier pulses whose peak amplitudes fall within the slit. Larger pulses are prevented from passing through.

Because of the finite rise and fall time of the signal pulse from the amplifier, the lower gate is triggered before the upper, and the upper gate recovers before the lower. It becomes necessary for proper operation of the anticoincidence circuit to delay the signal from the lower gate until the upper has triggered, and to store the signal from the upper gate until the lower has recovered. The delay is accomplished by using the differentiated trailing edge of the lower gate signal. Storage is accomplished by charging a small condenser through a diode.

T_1 through T_4 are the gate circuits. Western Electric 404A tubes are used because of their high figure of merit and reported long life. To get positive triggering on the fast pulses from the A-1, it is necessary to provide inductive compensation in the plate circuits of T_1 and T_3 . Overcompensation

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is used for two reasons: (1) An increase in speed of triggering of nearly a factor of 2 results, and (2) the minimum recovery time is fixed at approximately $0.3 \mu\text{sec}$. Ringing is prevented by the diode clamps.

The gate circuits are followed by two halves of a 12AT7 tube, each half being used as an impedance transformer and phase inverter. This tube is represented by T_{5a} and T_{5b} on the diagram. Both halves are biased to complete cutoff to conserve tube life and power drain.

The storage circuit is driven by one-half of a 6AL5 twin diode. The remaining half is used as a clamp to discharge the storage circuit at the end of a signal pulse. The clamp is driven by the plate circuit of T_{5b} , whose plate load is an open-end delay line. The clamp is opened by the leading edge of the signal from the lower gate circuit. It is not closed until after the lower gate has recovered and the differentiating circuit has been discharged.

T_7 is a combined anticoincidence circuit and pulse shaper. The pulse shaping is accomplished by connecting the tube as a univibrator. Its output pulse has an amplitude of about 30 volts and a duration of $0.6 \mu\text{sec}$. It is triggered (in the absence of an inhibiting signal) by the trailing edge of the differentiated signal from the lower gate circuit. It is prevented from triggering by the inhibiting signal from the storage circuit.

T_8 is an impedance transformer used as the output stage for the circuit. It will feed a 13-volt $0.5\text{-}\mu\text{sec}$ pulse of either positive or negative polarity to an external circuit. Its source impedance is 680 ohms.

The grid-to-cathode capacity of the 404A tube results in a small signal being transmitted through the gate circuits even without triggering action taking place. The amplitude of the signal is dependent upon the rise time and amplitude of the output pulse from the A-1. This spurious signal is easily neutralized by feeding a negative signal equal in magnitude and shape to that of the normal output signal from the A-1 into the cathode circuits of the 404A. A coupling capacity equal to the grid-to-cathode capacity of the 404A must be used.

This negative signal can be obtained from the plate circuit of the output tube of the last feedback loop in the amplifier (see Fig. 7.1). This change and the replacement of the power transformer with one of higher power-handling capacity are the only changes needed in the wiring of the remainder of the A-1.

Miscellaneous Information. After the initial adjustments of the zero positions of the slit width and pulse-height-selector controls, no additional adjustments are necessary when it is used on the three available bandwidths. The maximum setting of the pulse-height-selector dial represents an actual pulse amplitude of about 85 volts. The maximum setting of the slit-width dial represents 10% of this value. The output of the pulse-height selector will drive an external scaler or count-rate meter. The minimum dead time of the circuit is about 1 μ sec. Under no condition of operation will it limit the maximum counting rate which the A-1 can now tolerate. The minimum actual pulse amplitude it will accept is 2.4 volts. The linearity of the circuit is as good as that of the best obtainable helipot. Unfortunately, when the A-1 is set for the 2-megacycle bandwidth, the amplifier itself begins to saturate at about 60 volts. At full scale on the pulse-height-selector dial the error is 12%. The maximum errors for the 0.5- and 0.1-megacycle settings are 0.5 and 0.1%, respectively. The linearity is degraded with aging of the 6AG7 tubes in the amplifier.

FIELD-FORMING ELECTRODES IN CYLINDRICAL PROPORTIONAL COUNTERS

R. S. Stone and C. J. Borkowski

In energy measurements with proportional counters it is essential that ionizing events with equal energies should give rise to identical voltage pulses, regardless of location of the ionizing event within the active volume of the chamber. This means that the gas multiplication, and hence the electric field, must be constant for the entire length of the collection wire. It is proposed to investigate methods of achieving this in the case of the usual cylindrical counter.

An infinitely long cylinder with a uniform coaxial center wire would have a constant field of the type sought, but when end walls, sample holders, or other discontinuities are inserted, the field is found to be distorted. For example, an end wall which is at the same potential as the side walls will reduce the field in its vicinity by an amount proportional to $\exp -kz/b$, where z is the distance from the end wall and b is the radius of the chamber.⁽¹⁾

The usual means of dealing with this problem is to record only the events occurring in the uniform-field portion of the counter (one chamber radius or more from the ends). This is accomplished in various ways, one of the most

(1) N. M. Blachman, "The Counting Volume of a Cylindrical Ionization Chamber," *Rev. Sci. Instruments* 20, 477 (1949).

common of which is to increase the wire diameter near the ends so as to make the field there too low for gas multiplication to take place. This change in wire diameter will, of course, itself create a distortion in the field, but of a lesser degree and in a direction opposite to that introduced by the end wall. For the measurement of energies of gaseous radioactive nuclides such as H^3 , C^{14} , I^{129} , and S^{35} it is important to maintain a uniform field throughout the chamber volume if possible.

An approach to this ideal could be obtained by making the end wall in the form of a number of concentric insulated rings, each held at the potential which would exist at that radius if the cylinder were infinite in length. This potential is

$$V = V_r \frac{\ln r/a}{\ln b/a}$$

where V_r is the total potential across the chamber and b , a , and r are the radii of the chamber, center wire, and point in question, respectively. With an infinitely large number of rings this device could duplicate perfectly the field of a chamber with no end walls, a finite number of rings giving a field only approximately uniform.

Another source of field distortion is a sample holder which projects into the chamber. Such a holder is useful in energy measurements of soft electrons, in which cases we wish the electrons from the sample to give up all their energy in the counter gas. To make this possible the source must be held a sufficient distance from the walls to ensure that no particles reach them. The same type of construction may be employed here as in the case of the end walls. The holder can be made in insulated sections and each held at roughly the correct potential for its position in the chamber.

In order to investigate the behavior of these devices, an electrolytic bath analogy was set up; the results are plotted in Figs. 7.2 through 7.6. Figure 7.2 shows the effect on the field of the conventional type of guard sleeve. It is seen that this type of correction straightens out the field considerably; moreover, pulses collected within this region have such low gas multiplication that they are not usually counted. To hold field distortion to a minimum, the wire enlargement should be no more than is necessary to cut the

FIG. 7.2
FIELD PATTERNS FOR END WALL CORRECTING SLEEVES IN CYLINDRICAL
COUNTER; AS DEDUCED FROM MEASUREMENTS IN ELECTROLYTIC TANK

SECRET
70

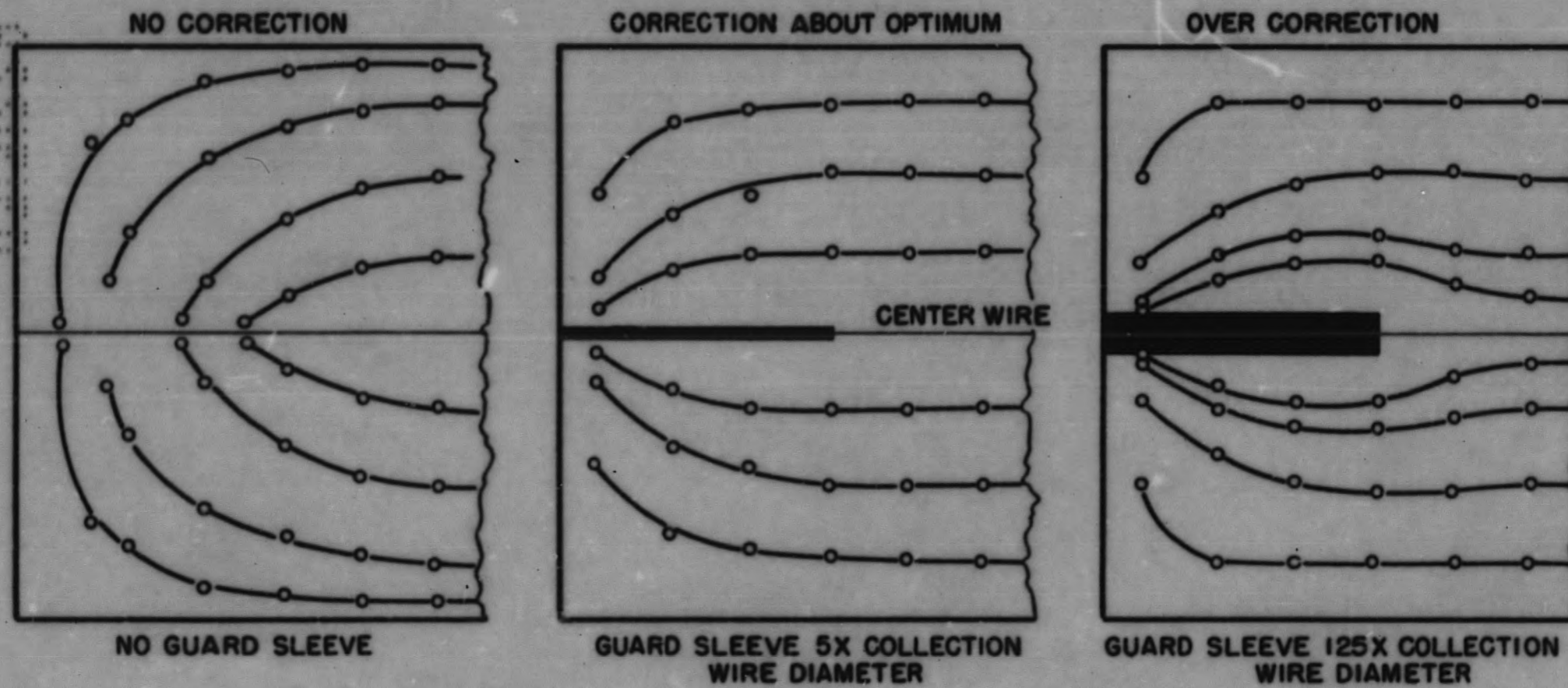


FIG. 7.3

FIELD PATTERNS FOR END WALL EFFECTS IN CYLINDRICAL
COUNTER WITH AND WITHOUT RING-TYPE CORRECTION;
AS READ FROM ELECTROLYTIC BATH MEASUREMENTS

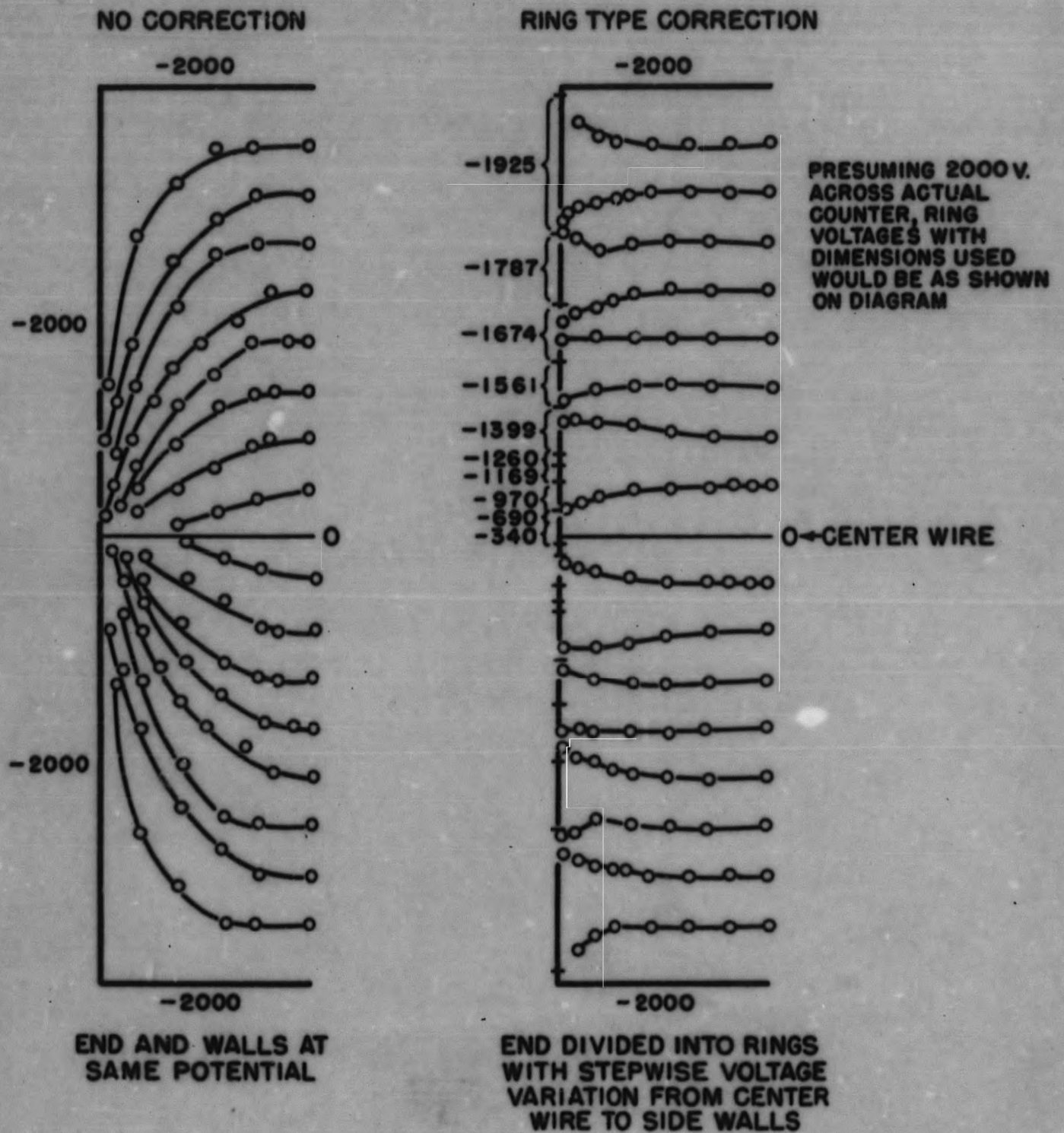


FIG. 7.4

FIELD PATTERN FOR DISTORTION DUE TO INTERNAL SAMPLE
HOLDER AT SAME POTENTIAL AS WALL-AS READ IN ELECTROLYTIC BATH

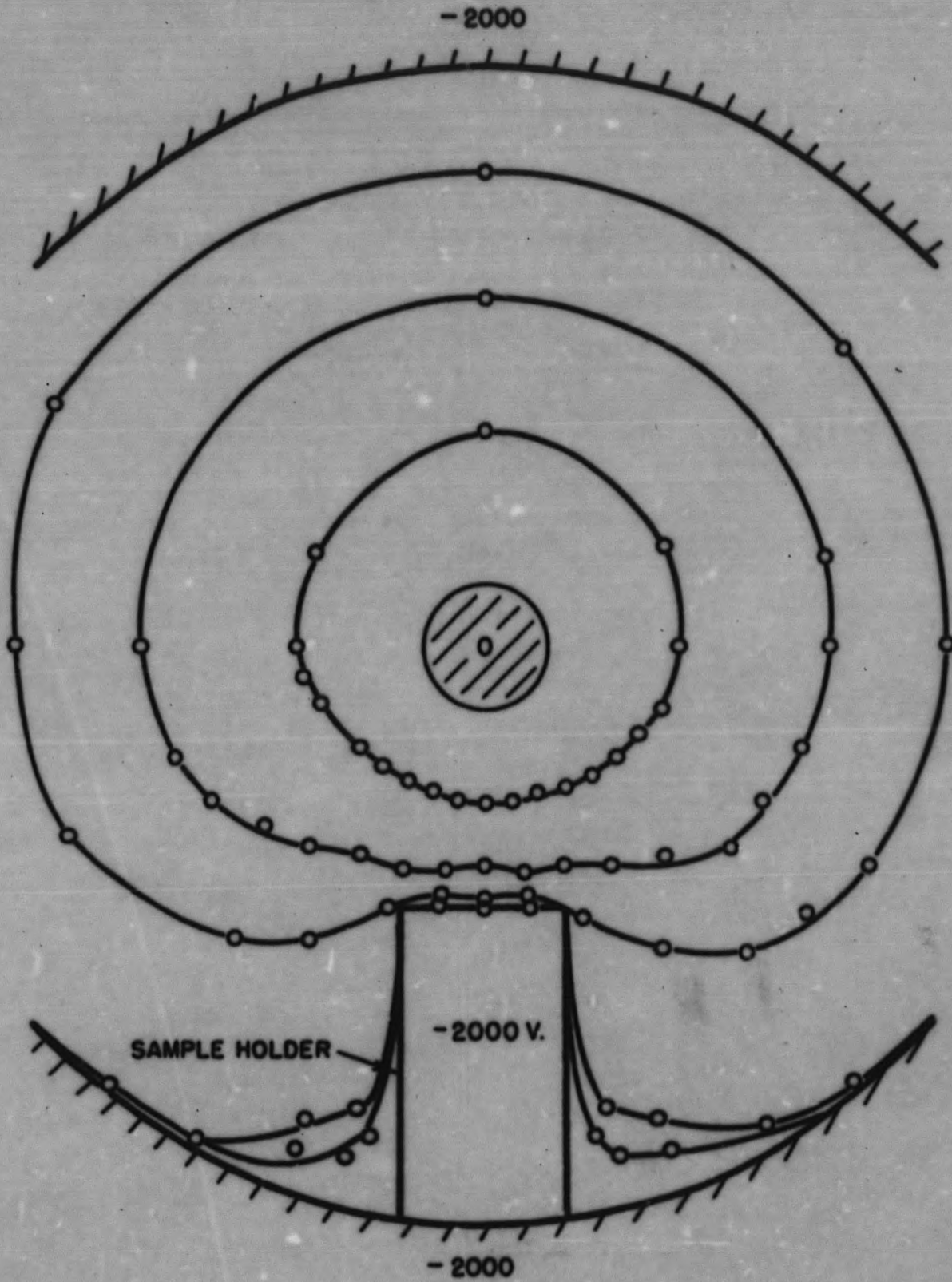
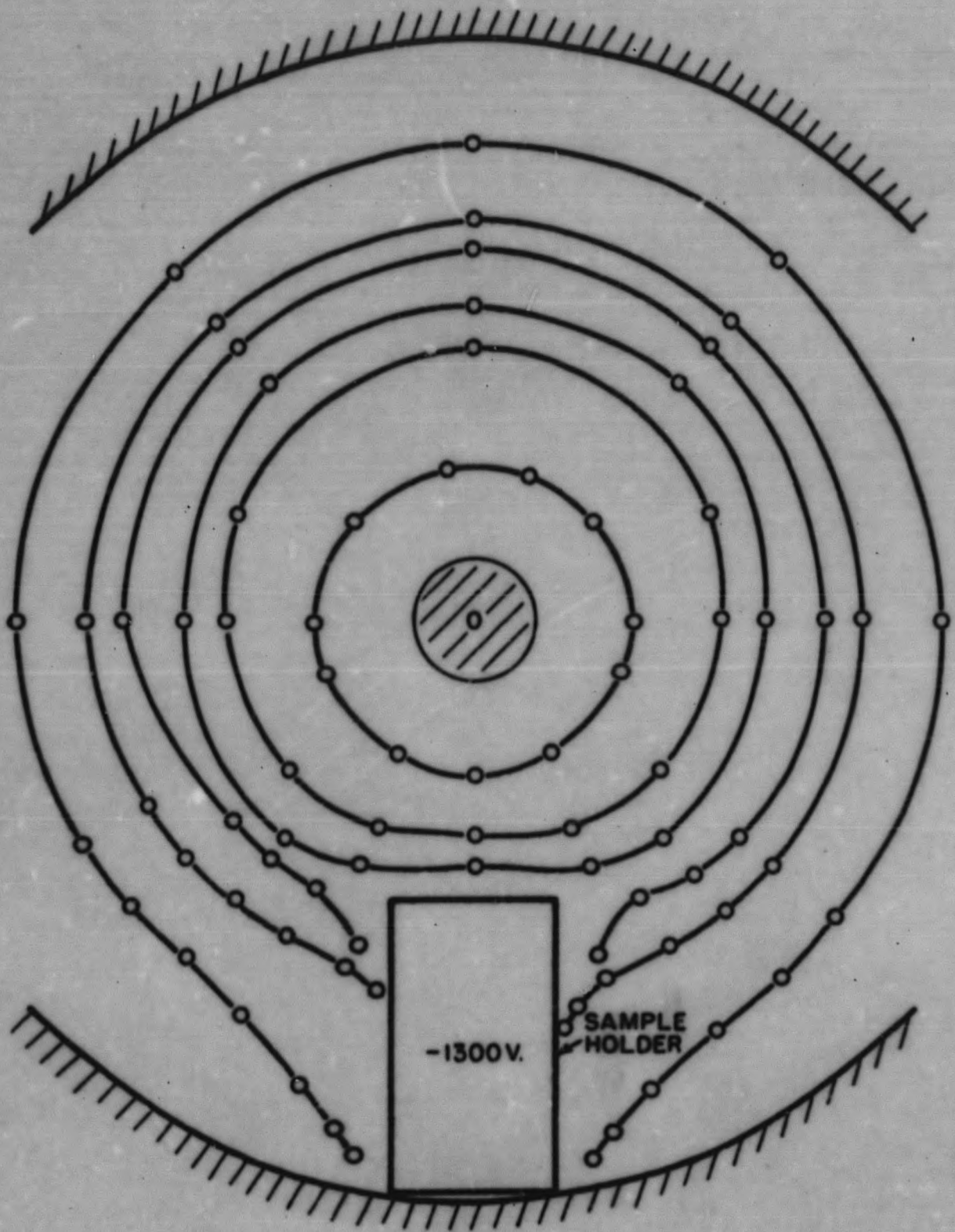


FIG. 7.5

FIELD PATTERN FOR DISTORTION DUE TO INTERNAL SAMPLE
HOLDER WHOSE VOLTAGE IS HELD AT VALUE CORRECT FOR
ITS INNERMOST POINT-AS READ IN ELECTROLYTIC BATH

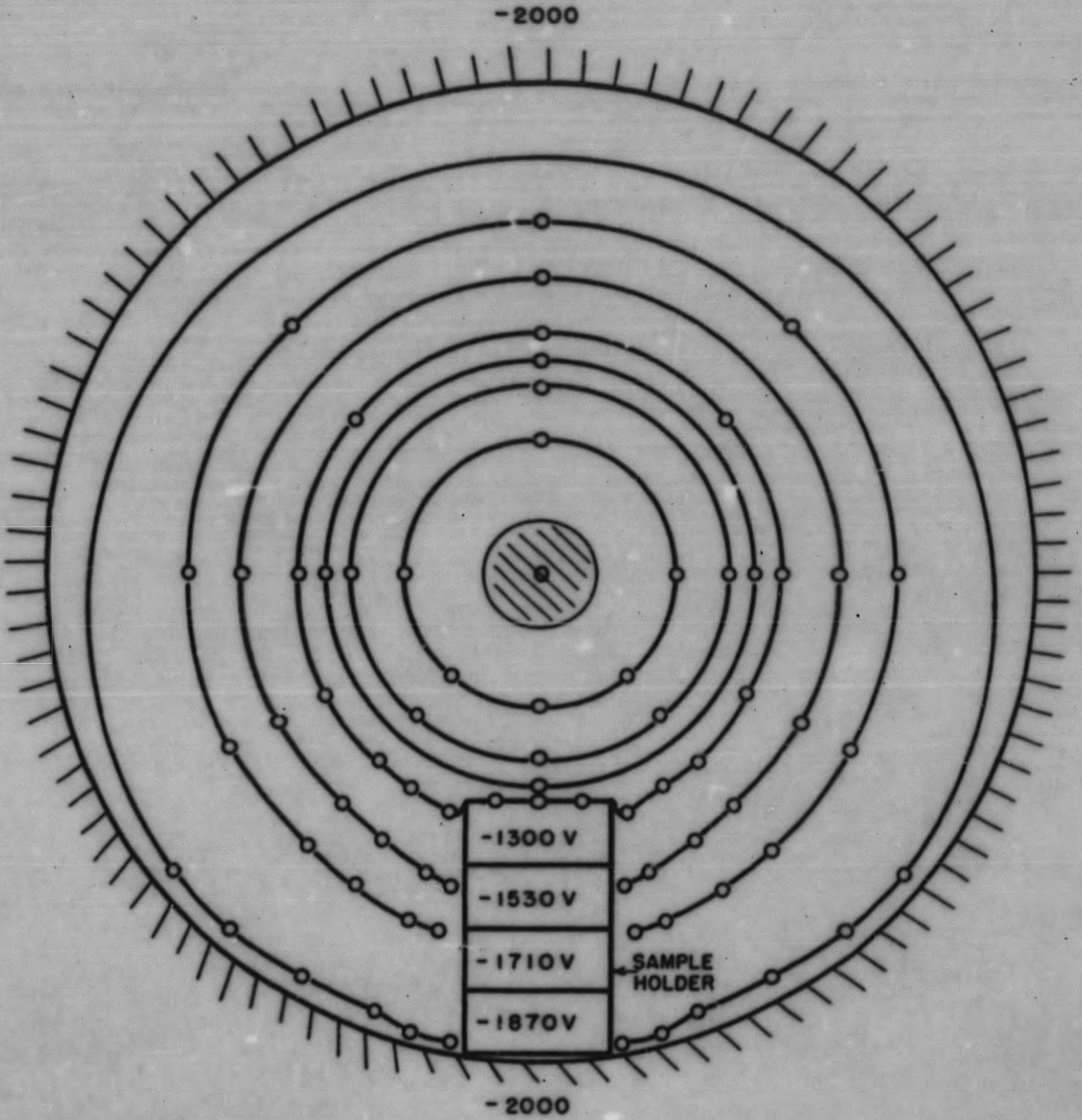
- 2000



-1300V.

SAMPLE
HOLDER

FIG. 7.6
FIELD PATTERN FOR DISTORTION DUE TO INTERNAL SAMPLE HOLDER
WITH FOUR VOLTAGE STEPS - AS READ IN ELECTROLYTIC BATH



gas amplification to a negligible value. Figure 7.3 indicates that the postulated ring type of end construction is capable of much better field correction than guard sleeves, permitting use of the entire counter volume. It is seen that more rings are needed near the center wire than further out, since the potential gradient is much greater near the center than in the vicinity of the side walls. This is as expected.

Figures 7.4 through 7.6 show the effect of sample holders held at various potentials. It is seen that an internal sample holder held at wall potential introduces bad field distortion (Fig. 7.4), but that by insulating the holder and applying proper voltages to it, either as a whole or in part (Figs. 7.5 and 7.6), its disturbing influence may be minimized. While segment type construction gives the best field smoothing (Fig. 7.6), it is seen that simply holding the whole structure at the potential correct for its deepest penetration into the chamber gives what is probably quite adequate correction (Fig. 7.5).

These investigations are felt to be encouraging enough to justify constructing a chamber with the above type of correction for end effects. In one scheme the end rings could be mounted on an insulating disk and connected by dropping resistors of the proper values; the whole assembly could then be mounted inside an overall gastight chamber envelope. It should be noted that to avoid introducing resistor noise into the output of the chamber, separate high-voltage supplies should probably be used for this correcting system and for the chamber potential source proper.

END