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ORNL 795
Progress Report

CHEMISTRY DIVISION
QUARTERLY PROGRESS REPORT
FOR PERIOD ENDING JUNE 30,1950

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ORNL 795
Progress Report

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CHEMISTRY DIVISION

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QUARTERLY PROGRESS REPORT

for Period Ending June 30, 1950

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ABSTRACT

CHEMISTRY OF SOURCE, FISSIONABLE AND STRUCTURAL ELEMENTS

Solution Chemistry. A much improved anion exchange column separation of Pa(V) and U(VI) has been devised using a mixture of HF and HCl as an eluent. A separation of tetravalent uranium and Pa(V), however, was not effected in this instance.

A study of the hydrolytic behavior of Th(IV) has been completed and will appear in report ORNL-765. The initial stages of the hydrolysis of thorium tetrachloride $HClO_4$-$NaClO_4$ solutions could be described quantitatively.

A method for the isolation of millicurie quantities of UX_1 from uranium hexafluoride feed-tank concentrates has been developed and is described. Further studies of the chloride complexing of thorium up to an ionic strength of four have demonstrated the applicability of the same two parameter equation previously shown valid to $\mu = 2.0$. Initial studies of thiocyanate complexing of thorium in aqueous solutions have yielded data which fit an equation of the same form as for chloride systems. Formation constants for the mono- and trithiocyanato thorium ions were obtained.

Phase Rule Studies—Fuel Media for Homogeneous Reactors. A phase study of the uranyl fluoride-water system from the ice eutectic (-13°C) up to the critical point for water (~377°) has been completed excepting for a few details upon which work will continue. Because a two liquid phase region forms above 313°, it appears that this system may not be of practical value above roughly 300°.

The aqueous UO_2F_2 solutions also were found to manifest abnormally small freezing point depressions. Accordingly, a special study of these was made and mean thermodynamic activity coefficients were computed. The low values found suggest either an incomplete dissociation of the salt, or polymerization.

A program has been initiated for the measurement of the solubilities of fission product element salts in the sulfate systems at elevated temperatures and pressures. Such information should be of value in anticipating changes in the character of homogeneous reactor solutions with operation and in determining the feasibility of various decontamination and recovery processes. The solubility of lanthanum sulfate will be measured first.

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NUCLEAR CHEMISTRY

Elements in the Fission Product Region. Investigations on the tin radionuclides have continued. The assignment of the 9.7 day period to mass 125 has been made more definite. The radiations from a long-lived activity in Sn^{121} have been measured on the magnetic lens spectrometer and a maximum beta energy of 0.42 ± .02 Mev was found. A preliminary half-life for Sn^{119m} of 270 ± 20 d has been determined. This, and the measured K/L ratio of 0.35 are consistent with the shell theory prediction of a $h^{-}_{11/2}$ state. The abnormal fission yields of 136 d Sn^{123} and 9.7 d Sn^{125} can be explained by branching in their In^{123} and In^{125} parents.

Lens and scintillation spectrometer measurements on 22 h Cb^{96} have given a maximum beta energy of 0.75 ± 0.01 and a gamma ray of 0.85 ± 0.10 Mev. Coincidence absorption studies indicate a simple spectrum with the gamma ray following the beta transition.

Further quantitative measurements on the previously known 9.4 y Kr^{85} have revealed a beta branching of 0.65 ± 0.15% in the decay of this isotope. The branching was shown to consist of a 0.15 Mev maximum energy beta particle followed by 0.54 Mev gamma. This discovery was made possible because of the extremely high purity of Kr obtained in the rare gas chromatographic studies described previously.

A new radioactive isotope of argon, presumably A^{39}, has been found. This nuclide appears to decay with a half-life greater than 15 years and with a maximum beta energy of 0.565 Mev and no gamma. Both the Kr^{85} and A^{39} beta spectra indicate a forbidden transition.

High Level Fission Product Separations. Testing operations using the flow sheet previously described for the recovery of Np, Tc, Pm and other fission product rare earths from CR-1AW raffinates have been continued. A number of mechanical difficulties were discovered and minor alterations in the process have been made. Studies of the radiation reduction of Cr(VI) and of the carrying of Np(IV) by cerous hydroxide were made.

Szilard-Chalmers Reactions in the Chain Reacting Pile. A detailed investigation of the origins of the radiation decomposition of $KBrO_3$ in the ORNL pile has indicated that roughly one-half of this is caused by gamma rays.

Shielding with lead therefore gives a two-fold increase in specific activity of 35.9 h Br^{82} over that for an unshielded recoil reaction with $KBrO_3$. Shielding with Cd in an attempt to reduce the decomposition caused by slow neutrons actually gave a four-fold increase, presumably owing to the abundant capture gamma radiation from the cadmium. Exact quantitative data on the enrichment do not conform to expectations based on a simple production-decomposition rate theory.

RADIO-ORGANIC CHEMISTRY

Preparation of C-14 Labeled Compounds. Organic compounds prepared during the past quarter include: (1) 36 mc of potassium acetate-2-C^{14}, (2) 4.66 mc of acetic acid-2-C^{14}, (3) 2.54 mc of sublimed malonic acid-2-C^{14} from acetic acid-2-C^{14} in 55% yield, and (4) 56 mc of potassium cyanide-C^{14} by the modified Loftfield procedure. An attempt to prepare methylene labeled maleic anhydride from dibromoacetic acid anhydride by reaction with zinc failed because of polymerization.

Reaction Studies. The rearrangement of 11-benz(b)fluorene-11-methanol-12-C^{14} by the action of phosphorus pentoxide in boiling xylene gave benzanthracene-5,6-C_1^{14} in 93% yield. The relative proportions of C^{14} in the 5 and 6 positions were shown to be 45:55. The distribution of C^{14} in the 5 and 6 positions of chrysene-5,6-C_1^{14}, synthesized from 1,2-benzofluorene-9-methanol-10-C^{14} through the Wagner rearrangement, was found to be 60:40.

Because of the importance and widespread use of decolorizing carbon, chromatographic adsorption and fractional distillation for the purification of organic compounds obtained by the technique of isotopic dilution, it was found necessary to determine whether isotope effects occurred during the use of these procedures in order to validate the technique. During the use of decolorizing carbon, no isotope effect was observed within the limits of error of the procedure.

Radiation Effects. A program was initiated on the effects of radiation on organic compounds.

Instruments and Standards. In a study of materials for scintillation counters, three lithium boralkoxides were prepared and suitable solvents from which to grow large crystals were investigated. A gas sampling apparatus was

devised to permit determination of the radioactivity of vapors having high specific activity. A very simple and inexpensive instrument for measuring the ion current produced by C^{14} beta disintegration was developed by combining a Borkowski ionization chamber with a Lauritsen electroscope. Progress was made in the absolute calibration of the vibrating reed electrometer for measurement of C^{14}.

CHEMISTRY OF SEPARATIONS PROCESSES

Volatility Studies. Studies on the interaction of thorium fluoride and the phosphorus fluorides have continued. Thus far no definite evidence for the formation of a complex compound stable above room temperature has been obtained although the occurrence of some interaction has been indicated in the treatment of thorium fluoride with liquid or gaseous phosphorous fluorides.

Solvent Extraction Principles and Applications. Further investigations of the mechanism operative in TBP solvent extraction processes have been concerned with those factors governing the distribution of nitric acid between aqueous and organic phases. Evidence for 1:1 HNO_3:TBP in the organic phase seems good. The partition coefficient was found to decrease with temperature for nitric acid of concentrations lying between 0.005 and 5 f in water. The quantity of acid extracted was dependent strongly on the nature of the organic solvent for the TBP solution.

Electrochemistry. Measurements of the electrodeposition of traces of ruthenium have shown that fractions unplatable on bright Pt electrodes may be deposited completely on mercury cathodes at sufficiently negative potentials. Essentially complete deposition of ruthenium from very dilute ruthenium solutions can also be effected by Pt black electrodes at potentials as low as - 0.40 v (vs. SCE). Perhaps in this latter case a surface catalyzed hydrogen reduction is operative.

Ion Exchange. An enrichment of Li^7 up to 94.397 ± .021% from its natural abundance of 92.476% was observed in the first 0.05% of a Li band eluted through a 146 cm bed of standard Dowex 50 (*i.e.*, ca. 10% cross-linked). Enrichment extended surprisingly far into the band. A fraction taken at 26.8% of the total lithium showed 92.796 ± .010% Li^7. A second bed of 16% cross-linked Dowex 50 128 cm deep showed only a very slight enrichment when operated under the same conditions.

Basic studies on the equilibrium and rate processes governing the performance of ion exchangers have continued. Further evidence that an osmotic membrane type equilibrium must hold was found. Rate studies have shown the great importance of ion charge and exchanger cross-linking in determining the velocity of approach to equilibrium. The occurrence of a practical degree of cation-exchange from a variety of organic solvents was demonstrated. A variety of inorganic ion separations using anion exchangers has been effected

CHEMICAL PHYSICS

The group working on calorimetry of radioactivity has measured calorimetrically the energy absorbed in graphite in Hole 12 of the ORNL Reactor and compared it with the value computed from ion chamber measurements at the same position. The values agreed closely, and constitute the desired absolute calibration of the ion chamber for use in the MTR.

The new neutron spectrometer has been completed, and is being tested and calibrated.

RADIATION CHEMISTRY

The work for the Homogeneous Reactor Experiment has been summarized in the feasibility report for that project. The principal radiation chemical problem appears to be the effect of radiation on corrosion.

The decomposition of water and aqueous solutions is being studied with the radiation from the new cobalt gamma ray source. A good deal of auxiliary equipment has been developed to make possible highly precise measurements.

A spectroradiometer has been built for studying the spectral distribution of the light emitted from irradiated alkali halide crystals. It consists of a Beckmann spectrophotometer as a monochromator and a photomultiplier and count-rate meter as detector and is sensitive enough to measure the fluorescence spectra of such crystals under gamma irradiation.

INSTRUMENTATION

Some faults which have appeared in the alpha energy analyzer after a year's use have been corrected.

Preliminary work has been done on a method of energy analysis in which electronic pulses from a counter are displayed on an oscilloscope, photographed, and analyzed for energy distribution by subsequent examination of the photograph.

A highly precise and stable pulse generator has been built for testing high-gain wide-band amplifiers and differential discriminators.

CHEMISTRY OF SOURCE, FISSIONABLE AND STRUCTURAL ELEMENTS

SOLUTION CHEMISTRY

ANION EXCHANGE STUDIES OF URANIUM (VI) IN HCl-HF MIXTURES. SEPARATION OF Pa(V) AND U(VI).

George E. Moore Kurt A. Kraus

Uranium (VI) had previously been shown[1] to be strongly taken up from hydrochloric acid solutions by the anion exchange resin Dowex-1. Its exchange has been studied in some detail throughout the HCl concentration range 0.25 - 9 *M*, and was found to increase very rapidly with increasing HCl concentration. The adsorbable species, though not yet uniquely identified appears to be either $UO_2Cl_3^-$ or $HUO_2Cl_4^-$, with the latter ion being somewhat more probable.

Addition of 0.01 *M* HF to the chloride solutions causes no significant change in the adsorbability of U(VI). Some decrease in distribution coefficients, however, is noted on addition of 0.1 *M* HF particularly at HCl concentrations of the order of 1 to 5 *M*. Based on these data the preliminary estimate of the stability constant of the uranium (VI) fluoride complex $K_f = 15$ was obtained for the assumed reaction

$$UO_2^{++} + HF + H_2O \rightleftharpoons UO_2F^+ + H_3O^+.$$

Since the absorbability of protactinium in HCl solutions is dramatically decreased through addition of small amounts of HF[2] and uranium (VI) is not, it appeared that separation of these two elements could be greatly improved through use of HCl-HF mixtures, rather than HCl alone.[3] Further equilibration studies of Pa(V) in HCl-HF mixtures (0.01 to 0.1 *M* HF and 1 to 9 *M* HCl) showed that in these media adsorption of Pa(V) is consistently poor ($K_d \leq 1$) permitting thus a wide choice of conditions for the separation of Pa(V) and U(VI). For example excellent separation was achieved with a 6 cm column of 0.023 cm^2 cross section using tracer Pa^{233} and tracer (6γ) U^{233}, absorbing from 9 *M* HCl, eluting Pa^{233} with 7 *M* HCl - 0.11 *M* HF, in a very sharp band and

(1) Kraus, K. A. and Moore, G. E., *Chemistry of Protactinium. V. Separation of Thorium, Protactinium and Uranium with Anion Exchange Columns in HCl Solutions*, ORNL 330 (April 27, 1949).

(2) Kraus, K. A. and Moore, G. E., *Anion Exchange Studies III. Protactinium in Some HCl-HF Mixtures. Separation of Niobium, Tantalum and Protactinium*, ORNL 673 (June 1, 1950).

(3) Kraus, K. A. and Moore, G. E., *op. cit.*, ORNL 330.

then U^{233} with 0.5 *M* HCl, again in a very sharp band. A small amount of α-activity was found in the 9 *M* HCl fraction, which through α-range analyses (carried out by Mr. E. Fairstein) was identified as the U^{232} decay series, and another small amount of α-activity (ca. 0.25% of total) was found in the main Pa^{233} fraction. The latter was found by Mr. Fairstein to have the range of U^{233} and was probably a small amount of uranium (IV), which was found to be strongly absorbed from 9 *M* HCl and rapidly eluted by 7 *M* HCl - 0.11 *M* HF. For comparison it may be recalled that thorium (IV) is not absorbed from 9 *M* HCl and that hence there must be considerable differences in the stability constants of the Th(IV) and U(IV) chloride complexes.

Details of this work have been written up and will be issued soon as report ORNL-759.

HYDROLYTIC BEHAVIOR OF THORIUM (IV)

R. W. Holmberg K. A. Kraus

The study of the acid liberation on dissolution of thorium tetrachloride in $HClO_4$-$NaClO_4$ solutions of known initial acidity have been completed. The work is being written up and will be issued as report ORNL 765. It was found that the initial stages of the hydrolysis [up to ca. 0.5 moles OH^- per mole of Th(IV)] can be represented by the equations

$$Th^{+4} + 4H_2O \rightleftharpoons ThO^{+2} + 2H_3O^+ \qquad (1)$$

and

$$2Th^{+4} + 4H_2O \rightleftharpoons Th_2O^{+6} + 2H_3O^+ \qquad (2)$$

and the constants K_1 = ca. 3×10^{-8} and K_2 = ca. 3×10^{-5}, respectively. The data are now being analysed in greater detail to obtain more precise values of the constants.

ISOLATION OF Th^{234} (UX_1) ACTIVITY FROM URANIUM HEXAFLUORIDE FEED-TANK CONCENTRATES

W. C. Waggener R. W. Stoughton

The most generally suitable thorium isotope for use as a radioactive tracer is Th^{234} (UX_1). This isotope is a weak beta emitter (0.20 Mev) of 24.1 day half-life, but its 1.14 minute daughter, Pa^{234} (UX_2), provides a 2.32 Mev beta with low γ-background (5% 0.8 Mev γ). By using an aluminum absorber of ca. 25 mg/cm^2 essentially only the UX_2 beta is counted.

The steady state concentration of Th^{234} activity in natural uranium is ca. 0.33 mc/kg. This activity is non-volatile (ThF_4), and accumulates in the uranium hexafluoride feed tanks. These empty feed tanks therefore are a convenient source of quantities of Th^{234} activity.

The following procedure has worked satisfactorily for processing millicurie quantities of Th^{234} from UF_6 tank washings:

Step 1. Activity is removed from empty feed tanks by slurring with two-three liters of distilled water. The green colored solution so obtained (probably UO_2F_2 and UF_4 with $Th^{234}F_4$) is allowed to settle at least 48 hours in a well paraffined[4] glass bottle.

Step 2. The clear supernatant solution which is virtually inactive is decanted and discarded, and the green precipitate is washed as a fine slurry into a 1000 ml platinum dish.

Step 3. The slurry is dissolved by first reducing its volume to ca. 200 ml, adding an equal volume of nitric acid, then adding solid sodium bromate in small portions with frequent stirring while hot until a clear solution is obtained. This generally requires the order of two hours and 25 g $NaBrO_3$; the resulting solution is dark orange with a small amount of aggregated black solid present.

Step 4. The solution volume is reduced to 200 ml under a heat lamp, cooled, and then centrifuged in 100 ml Lusteroid tubes. The supernatant

---

(4) Intermixture of colloidal silica with LaF_3 gives an insoluble residue which is impervious to repeated evaporations with HF and $HClO_4$. Sources of silica therefore must be scrupulously avoided prior to elimination of fluoride.

solution is transferred to clean Lusteroid tubes with a pipette improvised from large diameter polyethylene tubing. The black insolubles removed contain a negligible fraction of the total activity and are discarded.

Step 5. Fluoride coprecipitation of Th^{234} with La used as carrier is performed in the 100 ml Lusteroid tubes. The solution from Step 4 is adjusted to 3 *M* HF with 48% HF, after which $La(NO_3)_3$ is added (0.1 mg La/ml of solution). The solution is stirred and allowed to stand 10-15 minutes, centrifuged, and the UO_2F_2 solution decanted and discarded. The precipitate then is washed three times with a solution 1 *M* in both HNO_3 and HF.

Step 6. The La carrier and Th activity are dissolved by conversion of fluoride to perchlorate. The fluoride precipitate is washed into a platinum dish with 6 *M* HNO_3 and the liquid evaporated with $HClO_4$ added. Complete elimination of fluoride is assured by several evaporations with 3-4 ml of $HClO_4$ using care to wash down the upper surfaces of the dish. At this point the precipitate is brown in color due to iron contamination.

Step 7. The iron contaminant is conveniently removed by transferring the residue from the preceding step to a 100 ml glass stoppered cylinder using hot 8.0 *M* HCl (ca. 40 ml). After cooling, this solution is extracted three times with 30-40 ml volumes of diisopropyl ether. The aqueous layer should be colorless after this extraction.

Step 8. Benzene-TTA extraction is used to separate Th^{234} activity from the La carrier. The aqueous extract from Step 7 is transferred to a quartz dish and evaporated to dryness with 5 ml of $HClO_4$ under a heat lamp. This residue is taken up in ca. 40 ml of 0.10 *M* $HClO_4$ and equilibrated 15 minutes with an equal volume of 0.257 *M* benzene-TTA solution in a 100 ml glass cylinder. The relatively inactive aqueous phase is removed, and the thorium activity stripped into an equal volume of 1.79 *M* $HClO_4$ by equilibrating 10-15 minutes (strip-ratio = 100:1).

Step 9. The aqueous layer containing activity is transferred to a quartz dish and taken to dryness two times with $HClO_4$ to remove traces of organic matter. After a second evaporation with $HClO_4$ there should be no color or visible material in the dish, and the radiation level directly above the dish should be the order of 100-200 R/hr.

Step 10. The carrier-free Th^{234} activity may be taken up with several drops of hot 2 *M* $HClO_4$ or HCl and washed into a small glass stoppered flask

with hot 0.01 *M* acid to a convenient dilution (*e.g.* 0.1 *M*). Samples giving an estimated 100-200 R/hr in Step 9 yield 10-20 mc of Th^{234}. Perchlorate solutions containing Th^{234} at the mc level show some decomposition, developing a slight yellow color over a period of several weeks.

Acknowledgement is due R. L. Macklin and A. S. Goldin for their thorough cooperation and aid in obtaining the feed tank concentrates of Th^{234} for this work.

STUDIES OF CHLORIDE AND THIOCYANATE COMPLEXING OF AQUEOUS THORIUM BY SOLVENT - TTA EXTRACTION METHOD

W. C. Waggener R. W. Stoughton

Summary. The chloride complexing studies with aqueous thorium reported last quarter[5] have been extended to 4 *M* chloride and an ionic strength of four. The data at $\mu = 4.0$ can be fitted satisfactorily to a two-parameter equation similar in form to that applied to data at $\mu = 2.0$. Assuming two species, mono- and thrichloro- thorium ions, the formation constants (concentration) are 1.85 and 0.16, respectively. These values are compared with 1.20 and 0.25 obtained at $\mu = 2.0$.

Initial studies of thiocyanate complexing of aqueous thorium have been made in the concentration range, 0 - 0.5 *M* NCS^-, and at $\mu = 1.0$. From a single series of experiments completed at this time it appears that the data fit an equation of the same form as the chloride data. Assuming the two species, mono- and trithiocyanate thorium ions, the formation constants (concentration) obtained are 12.1 and 60, respectively.

Future Work. It is planned to confirm the minimum found for k_n (for $Th^{+4}+Cl^- = ThCl^{+3}$) versus μ which apparently occurs between $\mu = 1.0$ and $\mu = 4.0$ by a more critical series of experiments in the low chloride-high ionic strength region.

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(5) Waggener, W. C. and Stoughton, R. W., "Studies of Chloride Complexing of Aqueous Thorium by TTA-Benzene Extraction Method," *Chemistry Division Quarterly Report for Period Ending March 31, 1950*, ORNL-685, 24-30 (June 16, 1950).

Study of thorium complexing by thiocyanate is continuing, and an aqueous solution of hydrazoic acid has been prepared for an exploratory experiment with this weak acid and its anion, NNN^-.

The thiocyanate radical is the anion of a strong acid, and interacts with thorium ion more strongly than chloride. For this reason the thiocyanate-thorium system should be more convenient than the chloride-thorium system for continuing investigation of the influence of temperature as well as ionic strength upon both aqueous thorium complexing and solvent-TTA extraction equilibria.

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PHASE RULE STUDIES

THE URANYL FLUORIDE-WATER SYSTEM

W. L. Marshall J. S. Gill
C. H. Secoy

A phase study of the system uranyl fluoride-water has been completed up to the critical temperature except for a few details. The identities of the solid phases have not been established with surety and a phenomenon occurs above 200° in solutions of less than about 25% UO_2F_2 which has not as yet been explained.

No solubility data for this system are in the open literature. In fact, very little was known concerning uranyl fluoride solutions prior to 1941. A few solubility values in the temperature range from 0° to 100° have been reported in the project literature.[6,7] These data do not agree and, consequently, it seemed advisable to repeat measurements in this region as well as to extend the study of higher and lower temperatures.

The ice curve has been determined from 0° to the eutectic point at -13° and 64.25% UO_2F_2. The solubility curve for the solid has been determined all the way to the critical temperature of the saturated solution, 377°. A solid phase transition (an incongruent melting point) occurs at 150° and a second transition occurs at 240°. At 347° an invariant system is found consisting of the four phases, solid—liquid I—liquid II—vapor. At temperatures below 347° and in solutions not saturated with respect to the solid, a two liquid phase region occurs. This two liquid phase region is similar to that found by Secoy[8] for the uranyl sulfate-water system except that its upper limit is the temperature of solidification of the salt-rich liquid phase rather than the critical temperature of the water-rich liquid phase.

Experimental. Anhydrous uranyl fluoride obtained from the Harshaw Chemical Company was used in these experiments. A spectrographic analysis of the Harshaw material showed no impurities other than faint traces of a few metals. Analysis by ignition at 900° to U_3O_8 gave 99.5% UO_2F_2. By potentiometric

(6) Dean, G. R., *Properties of Uranyl Fluoride*, CC-2092 (September, 1944).

(7) Kunin, R., *The System UO_2F_2-HF-H_2O*, A-3255 (May, 1945).

(8) Secoy, C. H., *The System Uranyl Sulfate-Water*, ORNL-98 (July 7, 1948).

analysis, this value was 99.3%. Fluoride was determined by conversion to SiF_4 gas and subsequent titration with standard $Th(NO_3)_4$ to give 11.8% fluoride (theoretical = 12.07) which is in the range of experimental accuracy for this method. Direct measurement of *p*H and titration curve determinations[9] indicated no detectable amount of excess uranium trioxide (*i.e.* as UO_2^{++} in solution); therefore, the low determination by conversion to U_3O_8 might be due to a slight amount of moisture.

Solubility data for the phase study were obtained by four different methods depending on the particular region of the system.

All solubility points below 0° were obtained by standard methods of cooling and warming curve determinations. A copper-constantin thermocouple was used for temperature measurements. Analytical solubility determinations were made from 0° to 90°. The solutions were stirred in a thermostat from four to twenty-four hours. Samples taken after four hours stirring time agreed in most cases with later samples. These samples were analyzed by ignition at 900° to U_3O_8, the precision of duplicates being within ± 0.10%.

All work above 100° was done in sealed quartz capillary tubes as described by Secoy.[10] An aluminum cylinder containing a therocouple well and observation slit was substituted for the stainless steel cylinder used previously. Four and five millimeter inside diameter quartz tubing was used from 100° to 250°; however, above 250° two millimeter capillary tubing was required. With the exception of data between 150° and 240° points were obtained by slowly heating the cylindrical block (wrapped with michrome resistance tape and rocked in a special mechanism) containing a known solution in the quartz tube and observing through a slit any phenomena occurring. These solubility points were checked to ± 1° or better by raising and lowering the tube temperature. Owing to the rather vertical portion of the curve in the range 150° to 240°, this latter synthetic method was not effective. Therefore, an analytical approach was used in which a saturated solution and excess solid were rocked in the aluminum cylinder for 24 to 48 hours at a constant temperature, the variation in temperature being of the order of ± 1°. The rocker was then stopped and the tube allowed to cool about an hour before analysis. Above

(9) Marshall, W. L. and Gill, J. S., "The Uranyl Fluoride-Water System," *Chemistry Division Quarterly Report for Period Ending March 31, 1950, Part I, Chemical Research*, ORNL-685, 36 (June 16, 1950).

(10) Secoy, C. H., *op. cit.*, ORNL 98.

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150° the saturated solution is very viscous but will still flow in five millimeter (I.D.) tubing; whereas, below this temperature, if it is not shaken on cooling, the solution forms a translucent gel. It appears unlikely that the solubility equilibrium is changed to any extent. After cooling, the tube was broken and the gel-solid and crystalline-solid separately analyzed for uranium.

The *p*H measurements were made on prepared solutions using a Beckman *p*H meter. No effect on the glass electrode was noted.

The Data and Discussion. The data are given in Tables I and II and are shown graphically in Figs. 1, 2, and 3.

Table I and Figs. 1 and 2 show the variation of density and *p*H with concentration at room temperature. The condensed phase diagram for the system is shown in Fig. 3, the data being given in Table II.

Region *J* of Fig. 3 represents unsaturated solution for the system uranyl fluoride-water. The ice curve is represented by line *AB* down to the eutectic point *B*. Any mixture of the two components in region *ABK* will consist of ice and saturated solution represented on the ice curve. Below line *KBL*, there will be two solid phases, ice and $UO_2F_2 \cdot XH_2O$. Line *BC* corresponds to the $UO_2F_2 \cdot XH_2O$ solubility concentration in contact with solid $UO_2F_2 \cdot XH_2O$. This hydrate is probably $UO_2F_2 \cdot 2H_2O$ based on analytical determinations of the solid phase; however, more work must be done to fix precisely the hydrate composition.

Point *C* corresponds to either a hydrate or allotropic transition to $UO_2F_2 \cdot YH_2O$ in which Y may not equal X. A preliminary analysis of the solid phase at 195° gave 98.5% $UO_2F_2 \cdot 2H_2O$, uranyl fluoride dihydrate. (Theoretical 100% if correct hydrate.) The solid phase below 150° appears as very fine, silky needles which mix throughout the solution, whereas in the region 150 - 240° the solid phase is more clearly defined and of a definite crystal structure. An attempt was made to determine the structural system of the crystals formed in the 150 - 240° temperature range. No success was attained using a polarizing microscope. It appeared that the individual crystal units (metastable at room temperatures) had rearranged within the macro-crystal system to produce a pseudomorphic form. By visual observation the crystal structure is probably either in the hexagonal or cubic system.

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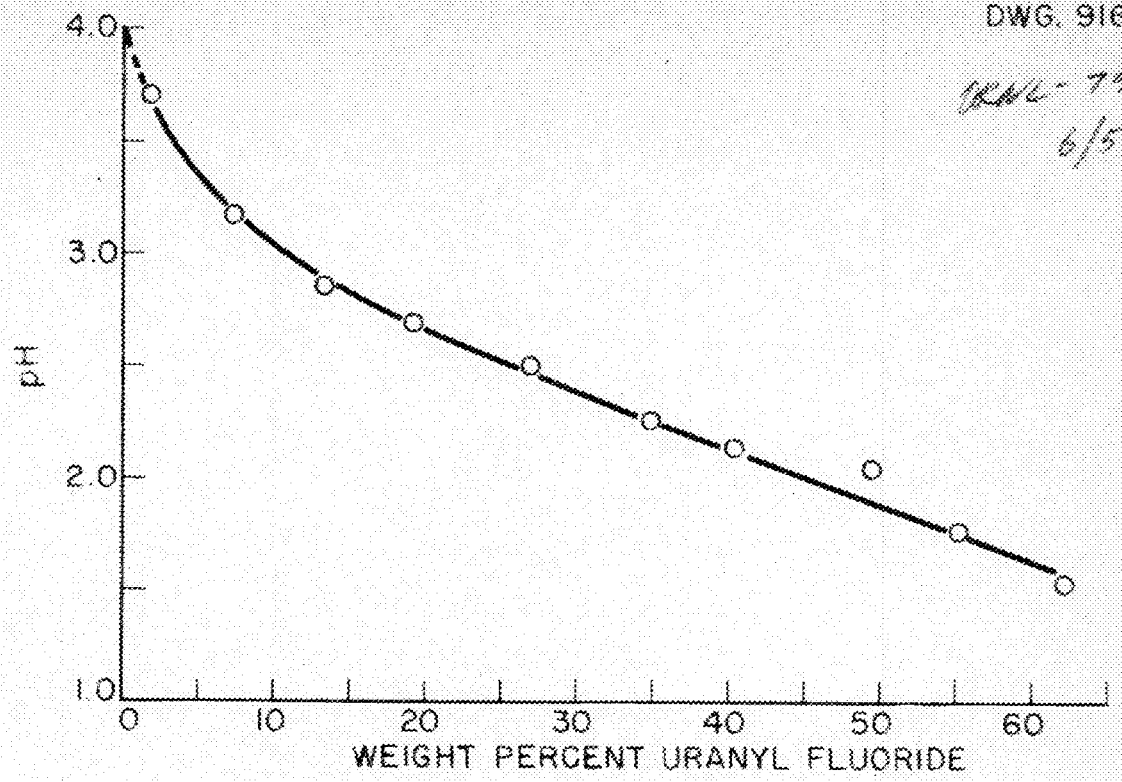

FIG. 1
THE pH OF AQUEOUS URANYL FLUORIDE AT 25° C

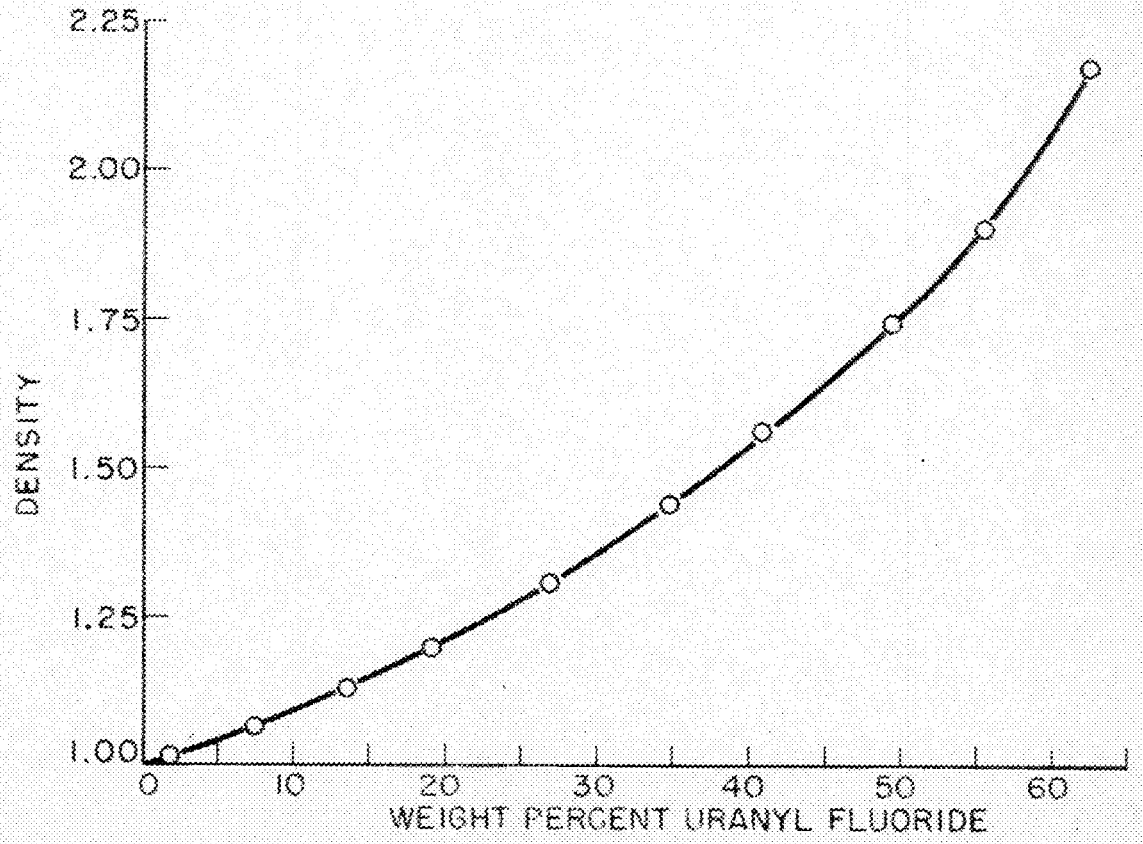

FIG. 2
THE DENSITY OF AQUEOUS URANYL FLUORIDE AT 25° C

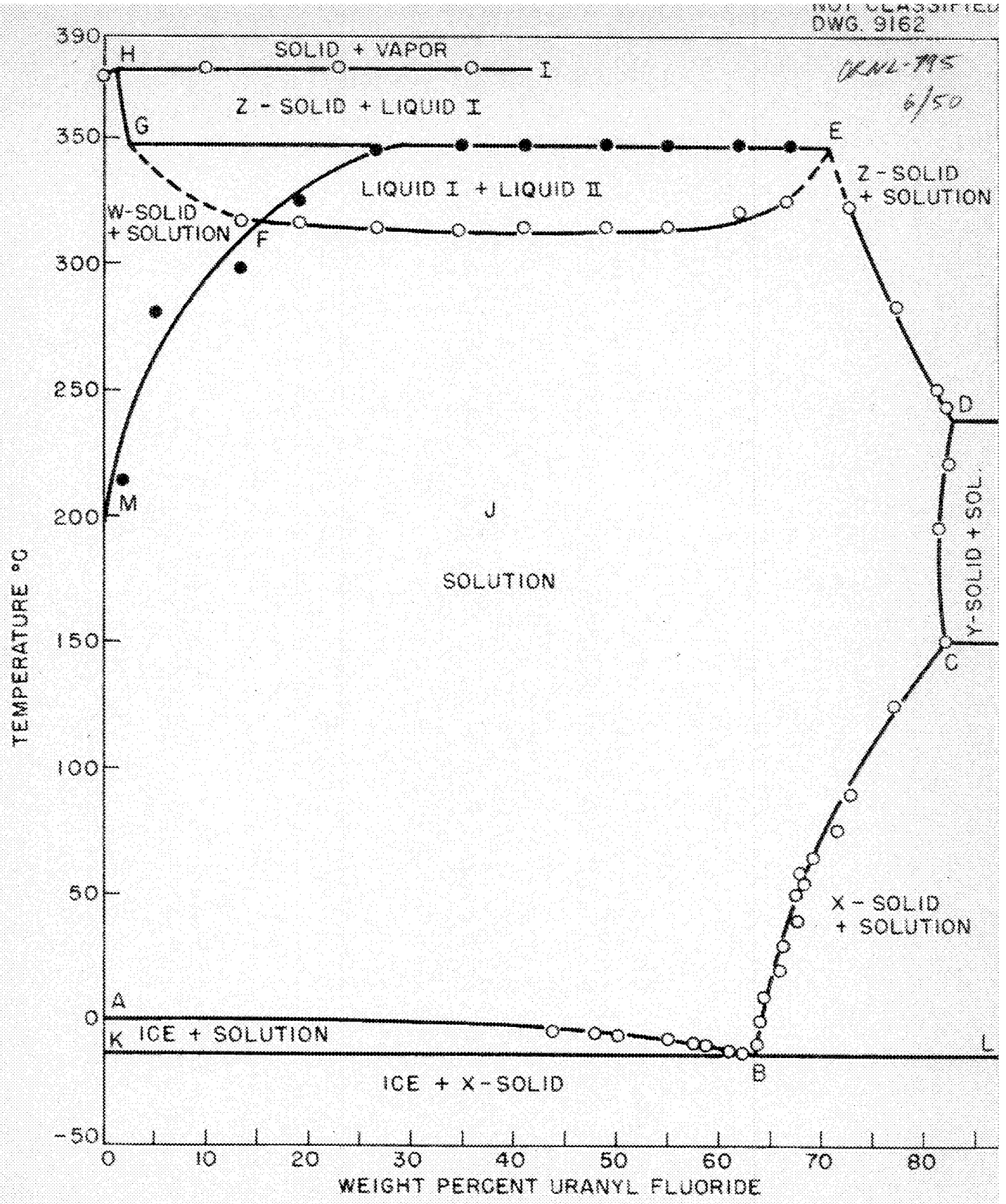

FIG. 3
THE SYSTEM, URANYL FLUORIDE - WATER

At 240° another transition occurs to give $UO_2F_2 \cdot ZH_2O$ (where Z may or may not equal Y) and also to give a negative solubility-temperature relationship. Points along line *DE* were rather difficult to obtain because of tube explosions upon reaching the solid phase temperature. In the few runs that were successful, the solid phase appeared to liberate bubbles, possibly due to the liberation of water vapor. Point *E* represents an invariant point at which temperature and composition, a solid ($UO_2F_2 \cdot ZH_2O$), and two liquid phases are in equilibrium in the condensed system. Seven attempts to get a point near the apex met with failure due to tube explosion just before the apex temperature (347°) was reached.

The invariant point temperature was fixed by the solidification points for the uranyl fluoride rich liquid phase, at which temperature this liquid loses water to the water-rich liquid phase and solid $UO_2F_2 \cdot ZH_2O$ is deposited.

Area *GFE* represents a two-liquid phase region. The minimum critical point lies between 49.24 and 55.13 percent uranyl fluoride and at 313°. In the region above *GE* and below *HI*, there are two phases in the condensed system, water-rich liquid and solid $UO_2F_2 \cdot ZH_2O$. The critical temperature of the saturated solution is represented along line *HI*. Above this line, there is a gaseous phase and the $UO_2F_2 \cdot ZH_2O$ solid. The critical point for pure water (374.4°) does not appear to have been elevated more than three or four degrees, thus indicating that the solubility of the Z solid has reached a low value.

Along *FM* a crystal formation appeared to some extent. These crystals had a light yellow to white appearance in the yellow uranyl fluoride solution. The crystals originated at two or three positions along the tube wall and grew out from the center as elongated needles. Upon lowering the temperature the crystals would redissolve; however, after remaining in the 200-300° range for five to twenty hours, irreversible decomposition occurred. These crystal formations are unexplainable on the basis of a two component system. There might be some reaction with quartz tubing in the low concentration region and at appropriate temperatures. Because of the crystal formations, attempts to complete the two liquid phase curve in this concentration region were not successful.

The system appears thermally unstable at all concentrations above 300°. Though equilibrium points were obtained above this temperature, there was some irreversible decomposition to a yellow gel type precipitate and also to black solid particles presumably U_3O_8. This decomposition did not appear to increase with time but rather occurred in the first few hours.

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Future Work. Further attempts to clear up the crystallization phenomena along *FM* and to determine the identity of all solid phases will be continued.

Summary. The uranyl fluoride-water system has been studied from the ice eutectic to the critical points of water. Density and *p*H data are given at room temperature. (Tables I and II).

Further work is necessary to clear up questionable features.

TABLE I

The Density and *p*H of Aqueous Uranyl Fluoride Solutions at 25°C

WEIGHT PERCENT UO_2F_2	DENSITY	*p*H
2.112	1.0136	3.70
7.565	1.0699	3.18
13.86	1.1349	2.86
19.39	1.2005	2.69
26.75	1.3016	2.50
34.76	1.4411	2.25
40.98	1.5754	2.13
49.24	1.7511	2.05
55.13	1.9212	1.76
61.98	2.1764	1.52

THE MEAN ACTIVITY COEFFICIENTS OF URANYL FLUORIDE IN WATER SOLUTIONS AT 25°

C. H. Secoy

In the determination of the ice-curve for the system uranyl fluoride-water as described in the preceding section of this report, it was noted that the depression of the freezing point of water was much less than one would expect from a salt capable of forming three ions per mole. This indicates a

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TABLE II

The Solubility of Uranyl Fluoride in Water

WEIGHT (Percent UO_2F_2)	TEMPERATURE (°C)	PHASE DISAPPEARING OR APPEARING	SOLIDIFICATION POINT - UO_2F_2 IN LIQUID PHASE	CRITICAL POINT
44.23	-4.2	Ice		
47.72	-5.0	Ice		
50.76	-5.9	Ice		
55.49	-7.8	Ice		
57.28	-8.1	Ice		
58.54	-9.2	Ice		
61.20	-10.9	Ice		
62.58	-11.9	Ice		
(64.25	-13.)	Ice + $UO_2F_2 \cdot XH_2O$		
64.28	-10.7	$UO_2F_2 \cdot XH_2O$		
64.30	0.0	$UO_2F_2 \cdot XH_2O$		
64.40	10.1	$UO_2F_2 \cdot XH_2O$		
66.09	19.7	$UO_2F_2 \cdot XH_2O$		
66.50	30.5	$UO_2F_2 \cdot XH_2O$		
67.78	39.8	$UO_2F_2 \cdot XH_2O$		
67.25	51.2	$UO_2F_2 \cdot XH_2O$		
68.45	54.3	$UO_2F_2 \cdot XH_2O$		
68.42	60.1	$UO_2F_2 \cdot XH_2O$		
69.37	65.8	$UO_2F_2 \cdot XH_2O$		
71.73	75.0	$UO_2F_2 \cdot XH_2O$		
73.02	89.8	$UO_2F_2 \cdot XH_2O$		
76.98	125	$UO_2F_2 \cdot XH_2O$		
81.72	150	$UO_2F_2 \cdot XH_2O$ + $UO_3F_2 \cdot YH_2O$		
81.40	195	$UO_2F_2 \cdot ZH_2O$		

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Table II (Cont'd)

WEIGHT (Percent UO_2F_2)	TEMPERATURE (°C)	PHASE DISAPPEARING OR APPEARING	SOLIDIFICATION POINT - UO_2F_2 IN LIQUID PHASE	CRITICAL POINT
82.61	219	$UO_2F_2 \cdot ZH_2O$		
-	240	$UO_2F_2 \cdot YH_2O + UO_2F_2 \cdot ZH_2O$		
82.53	243	$UO_2F_2 \cdot ZH_2O$		
81.22	252	$UO_2F_2 \cdot ZH_2O$		
77.05	283	$UO_2F_2 \cdot ZH_2O$		
72.31	322	$UO_2F_2 \cdot ZH_2O$		
70.5 (extrapolated)	347	$UO_2F_2 \cdot ZH_2O$ + liquid salt + aqueous		
66.46	324	Aqueous	344	
61.98	320	Aqueous		
55.13	314	Aqueous	347	
49.24	314	Liquid Salt	347	
40.98	313	Liquid Salt	347	
36.1				Preliminary Data 376
34.76	313	Liquid Salt	347	
26.75	313	Liquid Salt	344	
23.				Preliminary Data 378
19.36	314	Liquid Salt	325 (?)	
13.86	313	Liquid Salt (Immediately crystallizes) metastable		
13.86	298	Solid W		
10.85				Preliminary Data 377
7.56	277	Solid W		
2.11	215	Solid W		

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high degree of complexing and perhaps polymerization. It seemed worthwhile to extend the freezing point data to very dilute solutions so that a calculation could be made of the mean activity coefficients of the solute.

It has been shown[11] that, if one neglects the effect of the heat of dilution and its temperature coefficient, the logarithm of the mean activity coefficient is given by

$$\log \gamma' = \int_0^m -j \, d \log m - j/2.303 + \frac{0.00025}{\gamma} \int_0^m \frac{\theta}{m} d\theta. \qquad (1)$$

In this equation θ is the observed freezing point lowering in a solution containing m moles of solute per 1000 g of water and γ is the number of ions into which one molecule of salt would be expected to dissociate. The quantity, j, is defined by

$$j = 1 - \frac{\theta}{\gamma \lambda m},$$

where λ is the molal lowering of the freezing point at infinite dilution.

Experimental Data. In addition to the data from the preceding section, several points were obtained in very dilute solutions using a differential thermometer to obtain the freezing temperatures. The solutions were made by adding a weighed amount of dry UO_2F_2 to a known weight of water (40,000 g) in a double walled vessel equipped with the thermometer and a ring stirrer. The vessel was immersed in a salt-ice cooling bath which was maintained at a temperature of approximately -4°C. In all cases the solutions supercooled about one degree. The data so obtained, along with values from the preceding section of this report, are given in Table III.

Calculations and Discussion. The values of the quantities under the integral signs in equation (1) were obtained by graphical integration. In order to evaluate the first of these it was necessary to employ the Lewis - Linhart[12] equation for the concentrations below 0.01 m.

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(11) Lewis and Randall, *Thermodynamics*, p. 347, McGraw-Hill Book Company (1923).
(12) *Ibid.*

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TABLE III

Freezing Point Depression in Uranyl Fluoride Solutions

m	θ, °C	m	θ, °C
0.0012	0.005	0.5209	0.724
.0044	.015	2.57	4.2
.0129	.030	2.96	5.0
.0189	.041	3.35	5.9
.0274	.056	4.05	7.8
.0377	.072	4.35	8.1
.0586	.108	4.59	9.2
.1172	.195	5.12	10.9
.2344	.352	5.43	11.9

Table IV gives the calculated values for γ' as a function of m and the data are shown graphically in Fig. 4. For compairson, curves are also shown

TABLE IV

The Mean Activity Coefficients of Uranyl Fluoride at 25 °

m	γ'	m	γ'
0.01	0.1297	1.00	0.0045
.02	.0814	2.00	.0028
.05	.0426	3.00	.0021
.10	.0253	4.00	.0018
.20	.0152	5.00	.0016
.50	.0075		

for cadmium iodide[13] and for uranyl sulfate.[14] Cadmium iodide is known to be highly complexed, the ionization constant for $(CdI)^+$ being given as 0.004 by Bates and Vosburgh.[15] The much lower activity coefficient of

(13) Bates, R. G., "The Thermodynamics of Bi-univalent Electrolytes VI. Solutions of Cadmium Iodide from 5 to 40°," *Am. Chem. Soc. J.* 63, 399 (Feb., 1941).

(14) Sesoy, C. H., "The System Uranyl Sulfate-Water. I. Temperature-Concentration Relationship Below 300°," *Am. Chem. Soc. J.* 70, 3450 (Oct., 1948).

(15) Bates, R. G. and Vosburgh, W. C., "Equilibria in Cadmium Iodide Solutions," *Am. Chem. Soc. J.* 60, 137 (Jan., 1938).

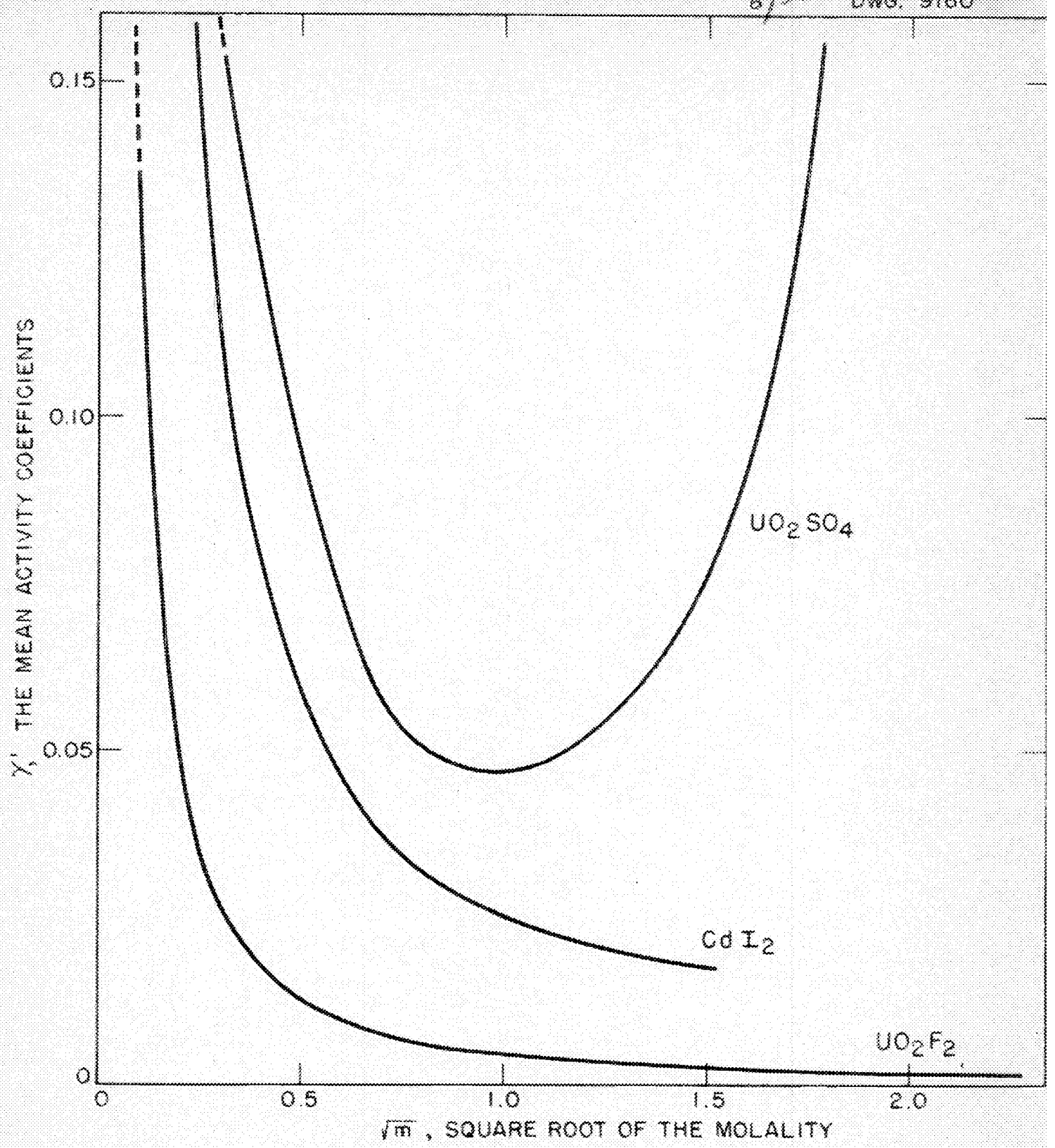

FIG. 4
MEAN ACTIVITY COEFFICIENTS OF URANYL FLUORIDE

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UO_2F_2 indicates an extremely high stability of the $(UO_2F)^+$ ion and the persistence of this stability into very dilute solutions. Of course, it is possible that, at least in part, the low activity of UO_2F_2 is due to some other phenomena such as polymerization.

THE MEASUREMENT OF THE SOLUBILITY OF FISSION PRODUCT SALTS AT HIGH TEMPERATURES AND PRESSURES

M. H. Lietzke B. Zemel

During the operation of a homogeneous solution reactor the fission products will "grow into" the reactor solution. Eventually the solubility products of some of the fission product salts may be exceeded resulting in the precipitation of solid material in the solution. The amount of precipitate may be quite significant, especially in the operation of homogeneous reactors of high power ratings, and may have to be considered both during the operation of the reactor and in the solution decontamination process. Hence it is of interest to determine the solubilities of the various fission product salts under the conditions existing in the reactor. Since contemplated homogeneous reactors will operate at high temperatures and pressures, it is necessary to determine the solubilities of the fission product salts at elevated temperatures and pressures. In the experiments planned, the solubilities of the fission product sulfates will be measured since a sulfate solution will be used in the X-10 homogeneous reactor. No attempt will be made to regulate the pressure on the solution. It will be assumed that the pressure coefficient of solubility of the fission product sulfates will be small.

The bomb shown in Fig. 5 has been constructed. With a bomb of this type it is possible to take several small samples from the same initial solution. It is also unnecessary to cool the bomb to room temperature for each sample. The experimental method will be to equilibrate an excess of salt with water (ca. 150-200 ml) at a given temperature and then to take several samples (ca. 10 ml each) of the solution. The samples will be cooled to room temperature and analyzed quantitatively for the salt in question. During the equilibration process the bomb will be rocked through an angle of 120° from the vertical to ensure complete mixing of the salt and water.

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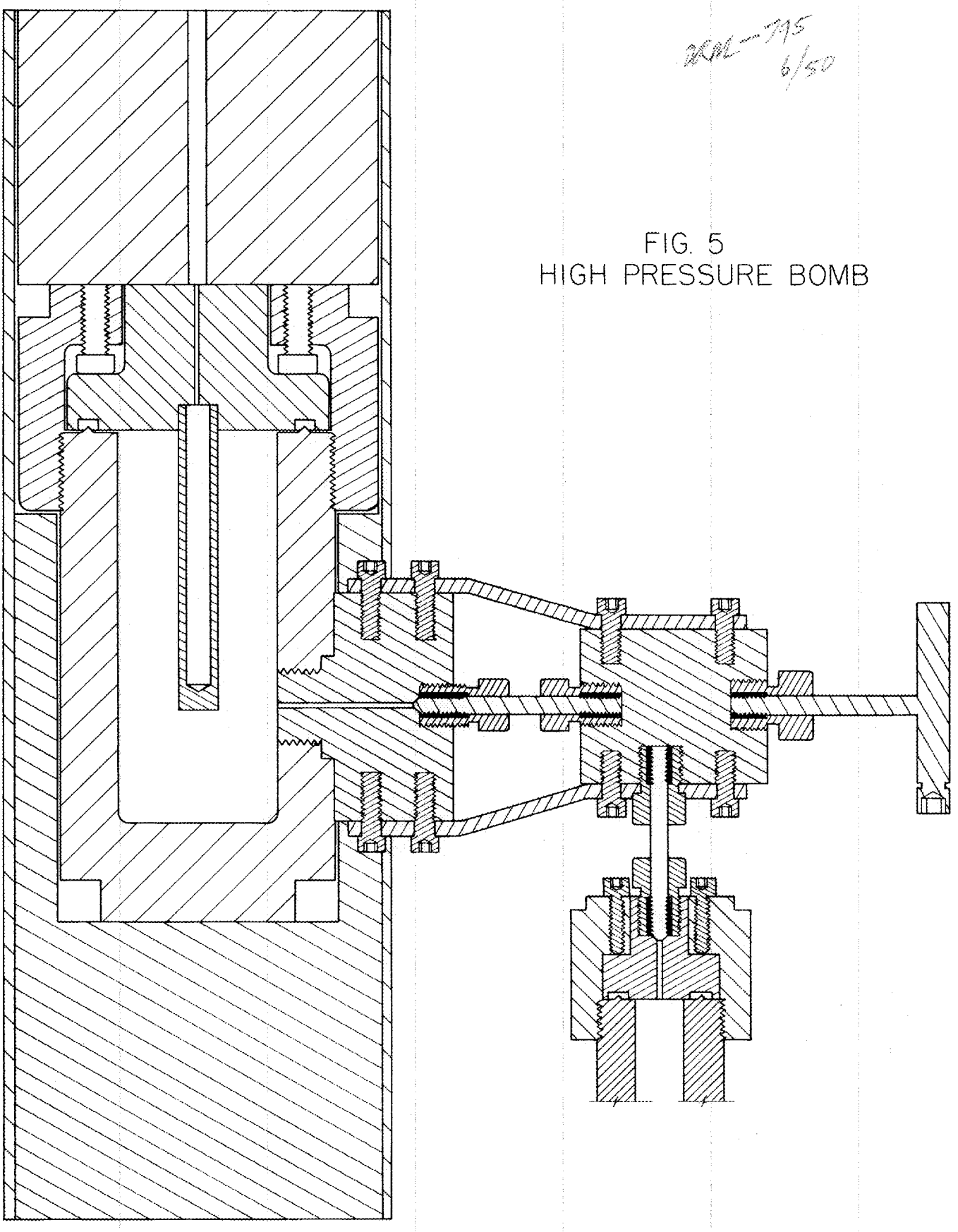

FIG. 5
HIGH PRESSURE BOMB

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Since the temperatures of interest (200°C to 370°C) result in pressures of 2000 to 3000 psi, the bomb was constructed to handle these pressures with a 10X safety factor. The system of valves used in the initial assembly leaked at these pressures and was replaced with the single American Instrument Company valve shown in the figure. This bomb is now undergoing final pressure and temperature tests.

As a check and also as an exploratory guide the quartz tube method[16] will also be used to determine high temperature solubilities. The necessary equipment has been borrowed from C. H. Secoy and W. L. Marshall. This equipment has been calibrated and preliminary runs are being made using freshly prepared and purified $La_2(SO_4)_3$.

(16) Bengath, A. *et al.*, "Solubilities of Salts and Salt Mixtures in Water at Temperatures above 100°C," *Z anorg. u. allgem. Chemie* 231, 285 (1937).

NUCLEAR CHEMISTRY

ELEMENTS IN THE FISSION PRODUCT REGION

RADIONUCLIDES OF TIN

C. M. Nelson B. H. Ketelle
G. E. Boyd

The results of present and past work on the tin activities will be given in a report to be issued soon. Most of this quarter has been spent checking on some points and organizing the work to be given in the report.

9.7 d Sn^{125}. It seems definite now that the 9.7 d Sn activity must belong to mass 125. Newton and McDonell[1] have assigned this activity to mass 123 from their deuteron bombardments of Sn^{124} by a (d, t) reaction. They base their mass assignment to a large extent on their failure to find the 2.7 y Sn^{125} daughter. On the other hand in the present experiments, the 2.7 y Sb^{125} was observed to grow from the 9.7 d Sn activity. In addition, the 58 d Te^{125} also was seen to grow into the Sb fraction after its separation from the Sn. Aluminum absorption curves indicate the identity of the Sb activity. The 9.7 d Sn activity was not observed in the Sn^{122} sample after bombardment with thermal neutrons while it was found in very good yield in the Sn^{124} sample. In order for it to be at the mass 123 position, the nuclear reaction would have to be (n, 2n) which is not very probable for slow neutrons and certainly of lower cross section than a (n, γ) reaction. Lee and Pool[2] have assigned this activity to the mass 125 position, also, on the basis of the yield from deuteron bombardments on enriched tin isotopes.

Long-lived Sn^{121}. There seems to be good evidence for a long-lived beta emitter Sn^{121}. In the spectrometer sample of the Sn^{120} preparation (95% Sn^{120}), a beta distribution was found between the conversion lines due to the Sn^{117m} and In^{113m}. After about five months decay (so that the 14 d Sn^{117m} could disappear) the results shown in Fig. 6 were obtained. This beta distribution has not decayed appreciably whereas the conversion line due to Sn^{117m} disappeared with its corresponding half-life. Unfortunately the In^{113m} is a 105 m daughter of the 112 d Sn^{113}, so that this conversion peak will remain in our source for

(1) Newton, A. S. and McDonell, W. R., *Beta Emitting Isotopes of Tin*, UCRL 395 (July 11, 1949).

(2) Lee, J. C. and Pool, M. L., "Radioactive Tin 121, 123, 125," *Phys. Rev.* 76, 606 (1949).

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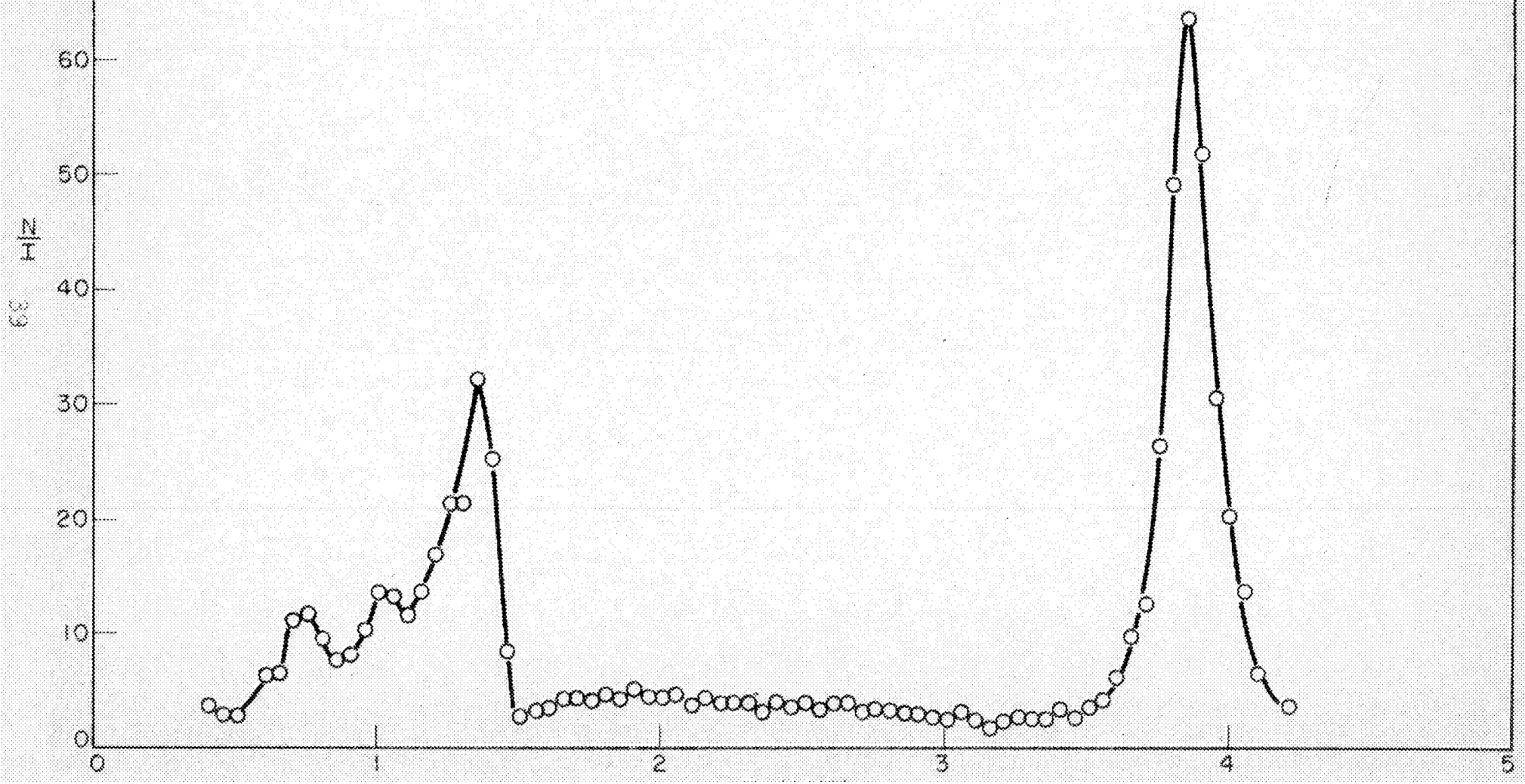
FIG. 6

MOMENTUM PLOT LONG LIVED Sn^{121}



some time. The amount of activity in this region was larger than could be accounted for from the breadth of the conversion lines of this height. Furthermore, since no beta activity at greater energies than the In^{113m} peak was seen, it was concluded that the activity in the region below the In^{113m} peak could not arise from the presence of any Sn^{123} or Sn^{125}. It seems probable then that a long-lived beta emitter can be assigned to the 121 mass position. Upon plotting the data as for an allowed transition, the Kurie plot (Fig. 7) gives a maximum beta energy of about 0.42 ± 0.02 Mev. An attempt is being made to obtain an approximate value of the half-life from the sample in spectrometer. A decay scheme for the mass 121 isomers is given in Fig. 8.

270 d Sn^{119}. The *K* and *L* conversion lines from the gamma ray associated with this activity were measured on the lens spectrometer using a flow type G-M counter with a supported window (6 $\mu g/cm^2$). Essentially the same energy, 64 Kev, as was given in the previous quarterly report[3] was found for the gamma ray. However this value may be slightly low due to electron peak shift caused by source thickness. This isomeric gamma transition has been reported by Mihelich and Hill[4] as having an energy of 69 Kev. The value for the *K/L* ratio as determined from the average of the peak heights and the areas under the peaks is 0.35. This is subject to considerable error because of the source thickness which was about 1 mg/cm^2. Since accurate values of the *L* conversion coefficients are not yet computed, it is not possible to determine the angular momentum change from the *K/L* ratio. The half life value of 270 ± 20 d was obtained from the decay of the *L* conversion line over a period of 70 days. An attempt to see the unconverted gamma ray using a proportional counter spectrometer failed although the source which was used had a high disintegration rate.

According to the Mayer shell theory the excited state of Sn^{119} should be $h^-_{11/2}$ and the ground state is known to be an $s^+_{1/2}$ state. Thus the prediction would be that the transition involves a spin change of five units and a change of parity. If this is true then the radiation would be 2^5 pole electric and the conversion coefficient obtained from the extrapolated α_5 curve computed by M. E. Rose *et al.*, would be 2000. Therefore it is not surprising that the unconverted gamma ray was not detected since it would be present in only 0.05% of the disintegrations. The half-life for this transition as obtained from

(3) Nelson, C. M., Ketelle, B. H., and Boyd, G. E., "The Radionuclides of Tin," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950. Part I. Chemical Research*, ORNL 685, 41, ff. (June 16, 1950).

(4) Mihelich, J. W. and Hill, R. D., "Radiations from Long-Lived Tin Isotopes," *Bull. Phys. Soc.* 24 (7), Paper B-9 (Nov. 25-26, 1949).

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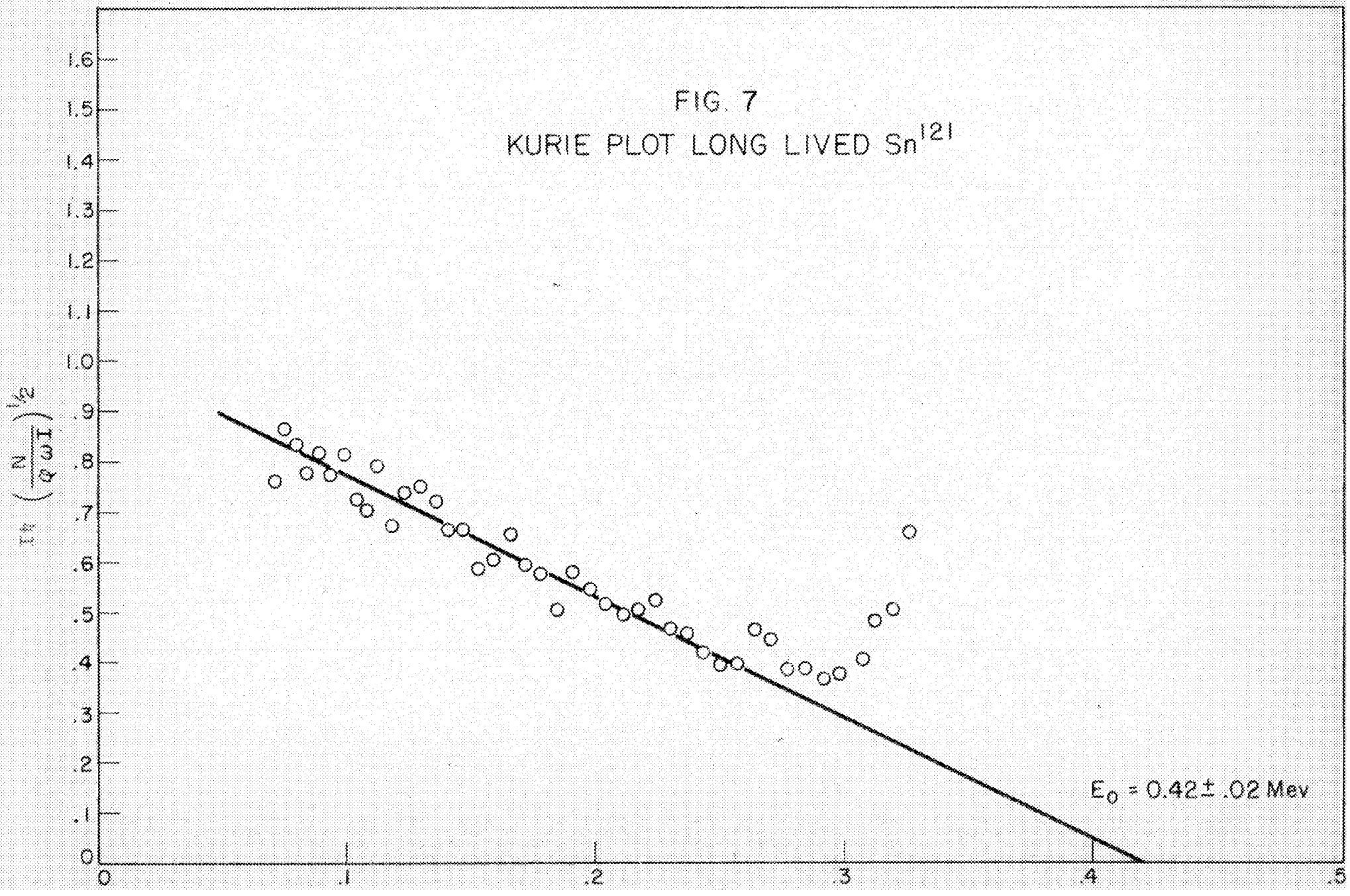
FIG. 7
KURIE PLOT LONG LIVED Sn^{121}



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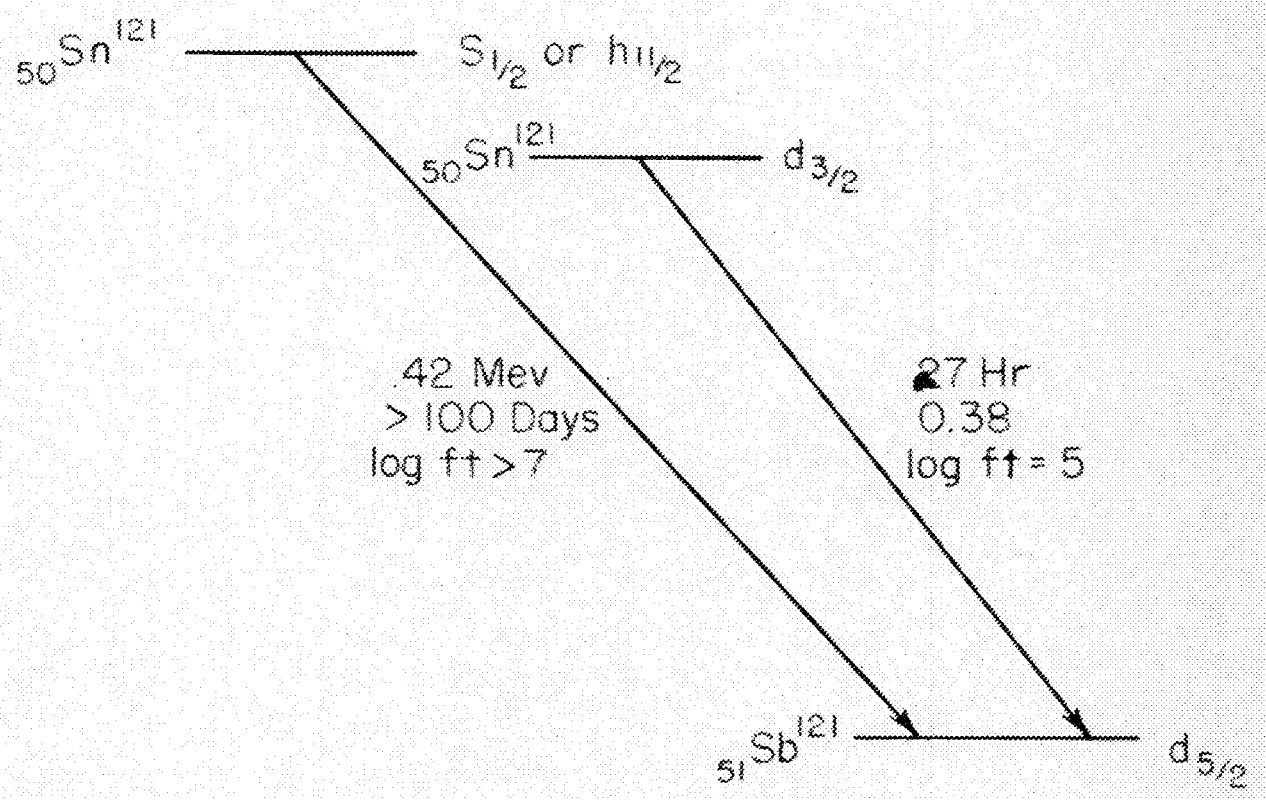

FIG. 8
DECAY SCHEME OF Sn^{121} ACTIVITIES

the plot of half-life vs. gamma energy published by Axel and Dancoff[5] is about 400 days. Since this is in good agreement with the observed half-life, one is inclined to believe that the shell theory prediction is correct.

Sn^{115}. Whereas no definite evidence has been found for an activity at the mass 115 position, the existence of isomerism in each of the other isotopes of odd mass and the prediction by the shell theory of closely spaced levels in each case leads one to expect isomerism in this position also. Cd^{115} is expected to be similar to Sn^{115} since they each have 65 neutrons. It is known that Cd^{115} has isomers which decay by independent beta decay. The fact that a gamma transition between the 43 day Cd and the 2.3 day Cd does not occur in an appreciable fraction of the disintegrations in spite of the considerable energy difference between the levels would indicate that there is a large spin difference between the levels. In Sn^{115} the ground level is known to be $s_{1/2}$ so if the excited level were the $h_{11/2}$ level as in the heavier tin isotopes of odd mass number then the high spin change involved in a transition would make the half-life long as in the cases of Sn^{117} and Sn^{119}. However, if the excited level were the $d_{3/2}$ level then the spin change would be unity and the half-life would be exceedingly short. Further efforts are being made to determine if isomerism occurs in this isotope.

Branching Ratios in the Decay of In^{123} and In^{125}. The results of the mass assignments of the 9.7 d Sn^{125} and the 136 d Sn^{123} can be used to calculate the branching ratio for the formation of the isomers at 123 and 125 in the fission chains from their In parents. Thus, if the fission yields for the 9.7 d and 136 d Sn activities are subtracted from the corresponding total fission yields for these mass positions taken from the smooth fission yield curve[6] in order to obtain the apparent fission yields of the 9.5 m and 40 m Sn activities, the branching ratios are easily calculated. For mass 125 using 0.043% for the total fission yield and 0.0044% for the 9.7 d Sn activity, the branching ratio is about 10% by this path and 90% by the 9.5 m Sn^{125} activity path. Similarly, for mass 123 using 0.015% for the total fission yield and 0.0012% for the 136 d Sn activity, the branching ratio is about 10% by this path and 90% by the 40 m Sn^{123} activity path from the In^{123} parent.

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(5) Axel, P. and Dancoff, S. M., "Classification of Nuclear Isomers," *Phys. Rev.* 76, 893 (1949).

(6) "Nuclei Formed in Fission: Decay Characteristics, Fission Yields, and Chain Relationships," Plutonium Project, *Am. Chem. Soc. J.* 68, 2411 (1946).

CHARACTERIZATION OF Cb^{96}

G. E. Boyd and B. H. Ketelle

A further characterization of the radiations of 22 ± 2 h Cb^{96} produced by Mo^{98} (d, α) was accomplished by lens spectrometer measurements which gave a maximum value for the beta ray energy of 0.75 ± .01 Mev. A Kurie plot assuming an allowed transition gave a straight line. Coincidence absorption measurements showed the beta spectrum to be simple with the beta ray being followed by a 0.85 ± 0.10 Mev gamma ray. Measurements of the gamma ray spectrum were made using a scintillation spectrometer (Tl activated NaI). Complete details together with results for the yield of this isotope in U^{235} fission will be given in the next quarterly report.

FURTHER INVESTIGATIONS ON THE RADIATIONS FROM Tc^{98}

G. E. Boyd and Q. V. Larson

For some time there has been reason to doubt our earlier findings on the Tc^{98} activity produced by Mo^{98} (d, 2n) with 15 Mev deuterons. Thus, whereas a 2.7 d period was seen in the Tc fractions separated from Mo^{98} irradiated at the DTM 60 inch cyclotron, no such period was seen in the fraction from the same Mo isotope bombarded at the UCRL 60 inch cyclotron. Further, the radiations from the 2.7 d activity resembled those of the known 67 h Mo^{99} suggesting that in actuality, owing to a high Mo^{98} (d, p) yield, that the supposed Tc activity was Mo contamination. Accordingly during the elapsed quarter a new search was made. Although as yet these studies are not completed, it can be said that the "2.7 d" Tc^{98} is almost certainly incorrect. Further, if the true period of Tc^{98} is short, it must be less than one minute in half-life. There is, however, considerable evidence that its half-period is very long. This will be presented in the forthcoming quarterly reports.

MISCELLANEOUS RADIOACTIVITY STUDIES

J. W. Cobble

Calibration of a 4 π High Pressure Ionization Chamber. A 4 π geometry ion chamber filled with argon at 40 atmospheres has been calibrated for the

rapid determination of absolute disintegration rates of gamma emitters. The method of calibration followed that of Jones and Overman,[7] although the absolute calibration is somewhat more certain in the low energy region because of the availability of more recent nuclear data. The efficiency curve for various isotopes relative to Co^{60} is given in Fig. 9. This curve has been adjusted for two gammas emitted per disintegration.[8]

The Precision Determination of Half-Lives. The stability and wide range of the high pressure ion chamber has provided an excellent method for determining precision half-lives of gamma emitting isotopes. The output of the instrument was fed into a continuously recording Brown potentiometer thus giving an instantaneous record of the activity of the isotope as a function of time. The following half-lives have been determined for isotopes purified by ion-exchange techniques after bombardment.

TABLE I

ISOTOPE	PREVIOUSLY REPORTED $T_{1/2}$[9]	THIS RESEARCH	INITIAL ACTIVITY	N/N^0 FINAL
Na^{24}	14.8 hrs	15.1 ± 0.1	3 Rd	10^{-3}
Cl^{38}	37 min	37.3 ± 0.1	5 Rd	10^{-4}
Br^{82}	34; 36.0 hrs	35.9 ± 0.1	3 Rd	10^{-3}

The Activation Cross Section of Br^{81} for Pile Neutrons. The cross section of stable Br^{81} for the capture of pile neutrons has been determined in connection with the studies on the Szilard-Chalmers reaction of $KBrO_3$. Samples of $KBrO_3$ irradiated in the pile were measured in the high pressure ion chamber after allowing the 4.4 hour Br^{80} activity to decay out. The following data were used in calculating the cross section: Half-life of Br^{82}, 35.9 hrs; efficiency of Br^{82} relative to Co^{60} in the ion chamber, 1.10; flux (by Co

(7) Jones, J. W. and Overman, R. T., *The Use and Calibration of a 100% Geometry Ion Chamber*, AECD 2367 (Mar. 28, 1948).

(8) Copies of the memo describing this work in detail are available through the author, J. W. Cobble. *Calibration of the 4th High Pressure Ion Chamber*, CF 50-6-114 (June 21, 1950).

(9) Seaborg, G. T. and Perlman, I., *Rev. Mod Phys.* 20, 585 (1948).

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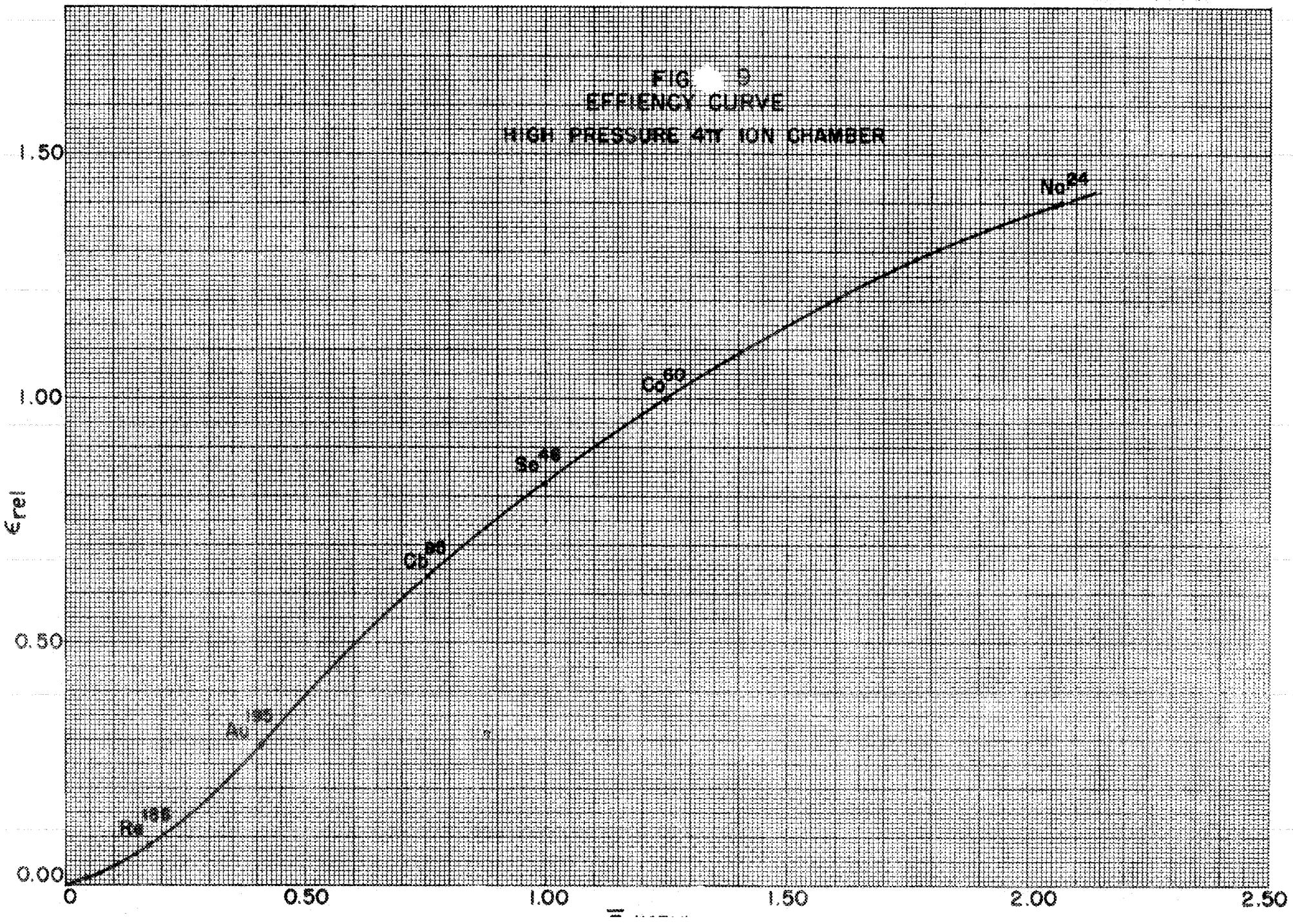

monitoring); 6.7×10^{11} n/cm^2-sec; half-life of Co^{60}, 5.3 yrs; cross section for Co^{59}, 22 barns. The cross-section values obtained were:

Atomic	1.4 barns
Isotopic	2.8 barns

These values are somewhat higher than those reported by Seren *et al.*[10] (Atomic = 1.1 barns).

The Decay Scheme of Cl^{38}. Preliminary measurements by coincidence techniques and absolute gamma counting in the 4π geometry pressure ion chamber cannot be reconciled with the branching ratios given in the decay scheme for 37 m Cl^{38} by Hole and Siegbahn.[11] The high pressure ion chamber is particularly well suited to the determination of the branching ratio in the case of Cl^{38}, and does not involve any uncertainty as does the Fermi plot analysis for three components performed by Hole and Siegbahn. Using the well established ratio of 43/57 for low energy betas, the following preliminary values for the branching ratios were obtained:

TABLE II

ENERGY (Mev)	BRANCHING (Percent)	BRANCHING (Percent) (Hole and Siegbahn)
1.19	12.3	36
2.79	3.7	11
5.0	84	53

This isotope is being studied further and will be reported on more completely in a future report.

(10) Seren, L. *et al.*, "Thermal Neutron Activation Cross Sections," *Phys. Rev.* 72, 888 (1947).

(11) Hole, N. and Siegbahn, K., "The Disintegration of Cl^{38}," *Ar Kiv. f. Math, Astron O. Fysik* 33A (9), (1947).

RADIATIONS OF LONG-LIVED Kr^{85} AND A^{39}

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

Introduction. A long-lived Kr activity was found in fission by Hoagland and Sugarman.[12] From absorption measurements they concluded that this Kr decayed with a maximum beta energy of 0.74 Mev and no gamma radiation. Later Thode[13] using mass spectrometer measurements assigned this Kr to mass 85 and determined the half-life as 9.4 years.

A portion of the fission rare gas sample collected by Parker and co-workers[14] has been purified by the method described in the last quarterly report.[15] In the course of this work gamma radiation was found associated with the long-lived Kr. A more detailed study of the radiations of Kr^{85} was therefore made which is reported below.

A long-lived argon activity has been removed from several different potassium salts after pile bombardment. This is presumably A^{39} formed by an n,p reaction on K^{39}. An attempt to find the 4 min activity previously assigned to this mass number was unsuccessful. A study of the beta spectrum of this long-lived argon is also reported.

Thin Lens Spectrometer Measurements. In measuring the beta spectra of gaseous activities the chief problem is in mounting the source in such a way that scattering and absorption are minimized. In this work the gas was contained in a 6 mm diameter quartz bulb with a thickness of 0.7 mg/cm^2 which was blown on the end of a 0.8 mm O.D. and 0.4 mm I.D. tube. The data indicate that there is very little distortion of the spectra at energies above 150 Kev.

The beta energy distribution of Kr^{85} is shown in Fig. 10 as a Kurie plot for an allowed transition. Because of the curvature the data have been replotted in Fig. 11 on the assumption that the transition is first-forbidden with a spin change of two with a parity change. On this assumption the maximum

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(12) Hoagland, E. J. and Sugarman, N., NNES-PPR Vol. 9B, Paper No. 7.6.1 (1945).

(13) Thode, H. G., *Progress Report for September and October 1946* (National Research Council of Canada Division of Atomic Energy), CR-PRG-37 (Nov., 1946).

(14) Parker, G. W., et al., "Feasibility Test of the Large Scale Collection of Fission Rare Gases," *Chemistry Division Quarterly Progress Report for Period Ending September 30, 1949*, ORNL 499, 52 (Dec. 6, 1949).

(15) Zeldes, H. and Brosi, A. R., "Adsorption Column for the Separation of Radioactive Gases," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950. Part I. Chemical Research*, ORNL 685, 53 (June 16, 1950).

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FIG. 10
ALLOWED KURIE PLOT OF K^{85} BETA SPECTRUM

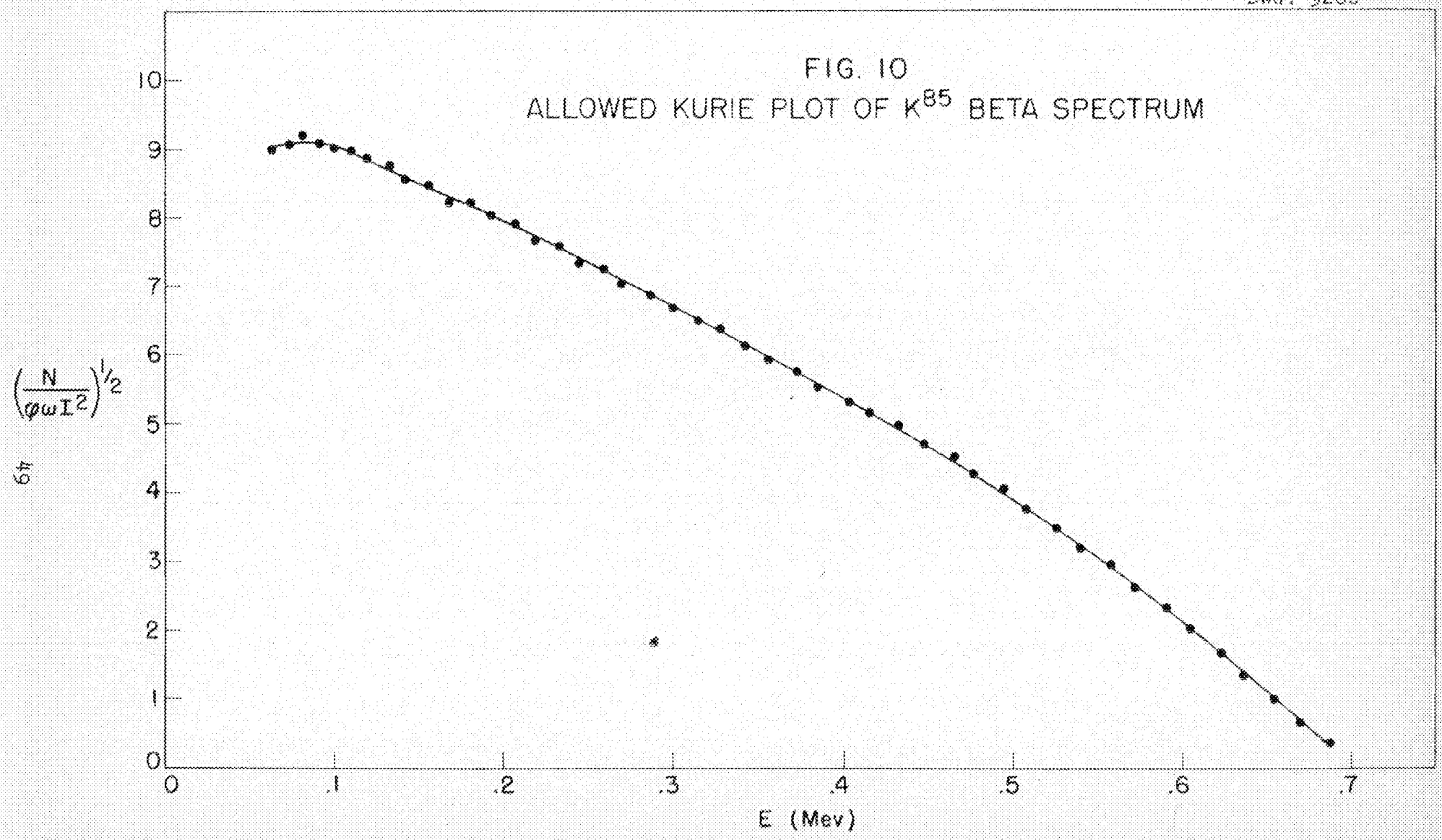

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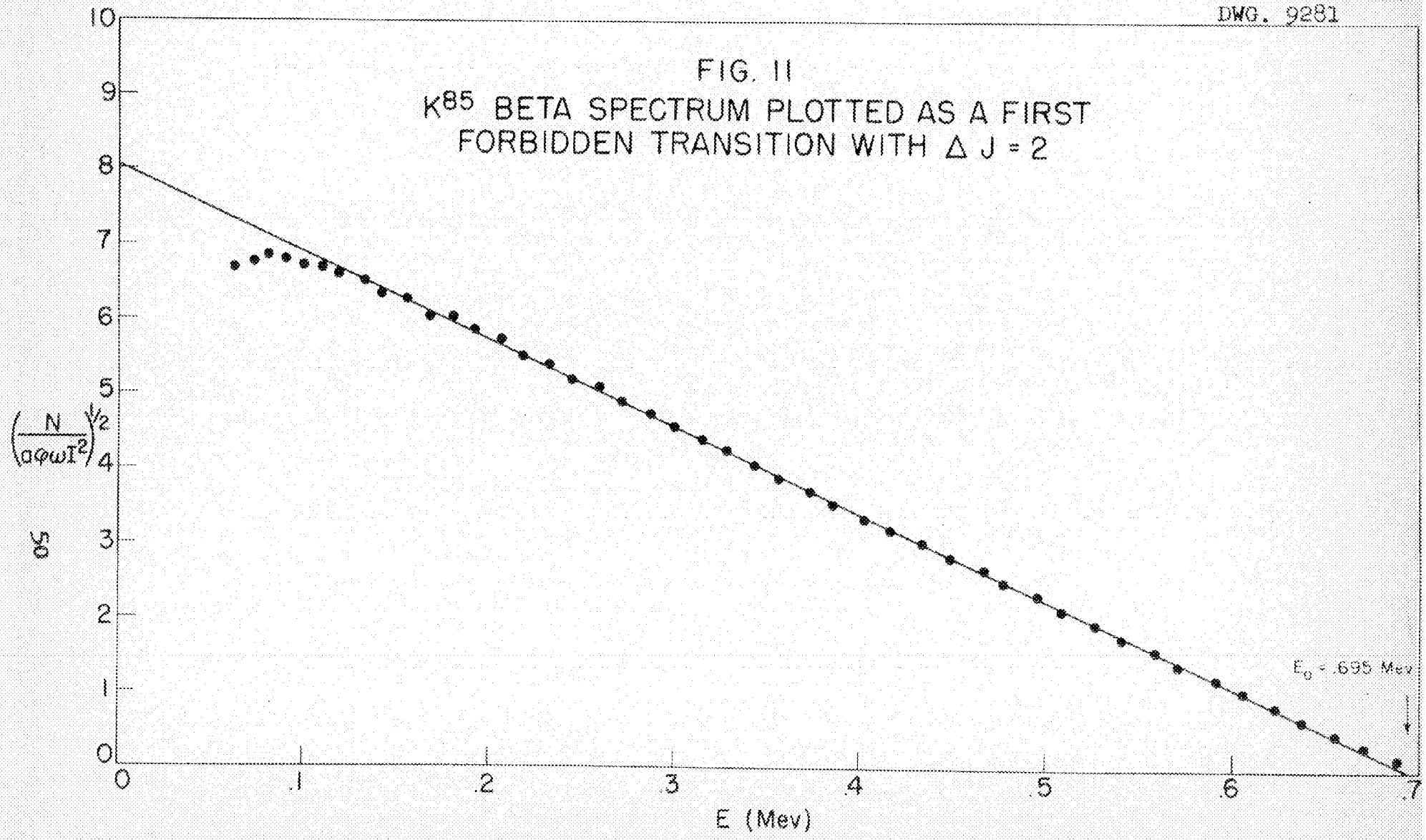
FIG. 11
K^{85} BETA SPECTRUM PLOTTED AS A FIRST FORBIDDEN TRANSITION WITH $\Delta J = 2$



energy of the transition is 0.695 Mev. The log of the *ft* value is nine which is in agreement with the *ft* values found for other first forbidden transitions with a spin change of two.

The beta energy distribution of A^{39} was also found to be that of a forbidden transition. Kurie plots for an allowed and for a first forbidden transition with a spin change of two are shown in Figs. 12 and 13, respectively. On the assumption of a first forbidden transition the maximum energy is 0.565 Mev. Decay measurements indicate that the half-life of this activity is greater than 15 years. The log of the minimum *ft* value is 8.7 which is in the region expected for a transition of this type.

Kr^{85} Gamma Radiation. As stated previously gamma radiation was found associated with the long-lived krypton collected from a Hanford slug. Scintillation spectrometer measurements and lead absorption curves both indicate that the energy of this gamma ray is 0.54 Mev.

Coincidence absorption measurements have been made which show that the gamma ray is in coincidence with a 0.15 Mev beta ray. Since the sum of the energies of the coincident beta and gamma rays is the same within experimental error as the energy of the more abundant beta group of Kr^{85}, these radiations are almost certainly associated with Kr^{85}.

The branching ratio in the decay of Kr^{85} has been calculated from the coincidence data and the calibrated detection efficiency of the gamma counter. It was found that Kr^{85} decays by emission of a 0.15 Mev beta ray in coincidence with a 0.54 Mev gamma ray in 0.65 ± 0.15% of the disintegrations.

Summary. Both Kr^{85} and A^{39} have been found to have forbidden type beta spectra. The maximum energy in Kr^{85} decay is 0.695 Mev. In 0.65% of the disintegrations a 0.15 Mev beta ray in coincidence with a 0.54 Mev gamma ray is emitted. In the decay of A^{39} the maximum beta energy was found to be 0.565 Mev. No gamma radiation was detected.

RECOVERY OF FISSION PRODUCTS AND NEPTUNIUM FROM ORNL REDOX PILOT PLANT CR WASTES

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

Final Cell Plan and Process for Cr Separations.

Summary. Since the proposal of a tentative flow plan[16] for the recovery of fission product radioisotopes and synthetic elements from Special

(16) Parker, G. W., *et al.*, "New Hot Laboratory Facilities and Flow Plan for the Recovery of Fission Products and Neptunium from ORNL Redox Pilot Plant CR Wastes," *op. cit.*, ORNL 685, 62-73.

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FIG. 12

ALLOWED KURIE PLOT OF A^{39} BETA SPECTRUM

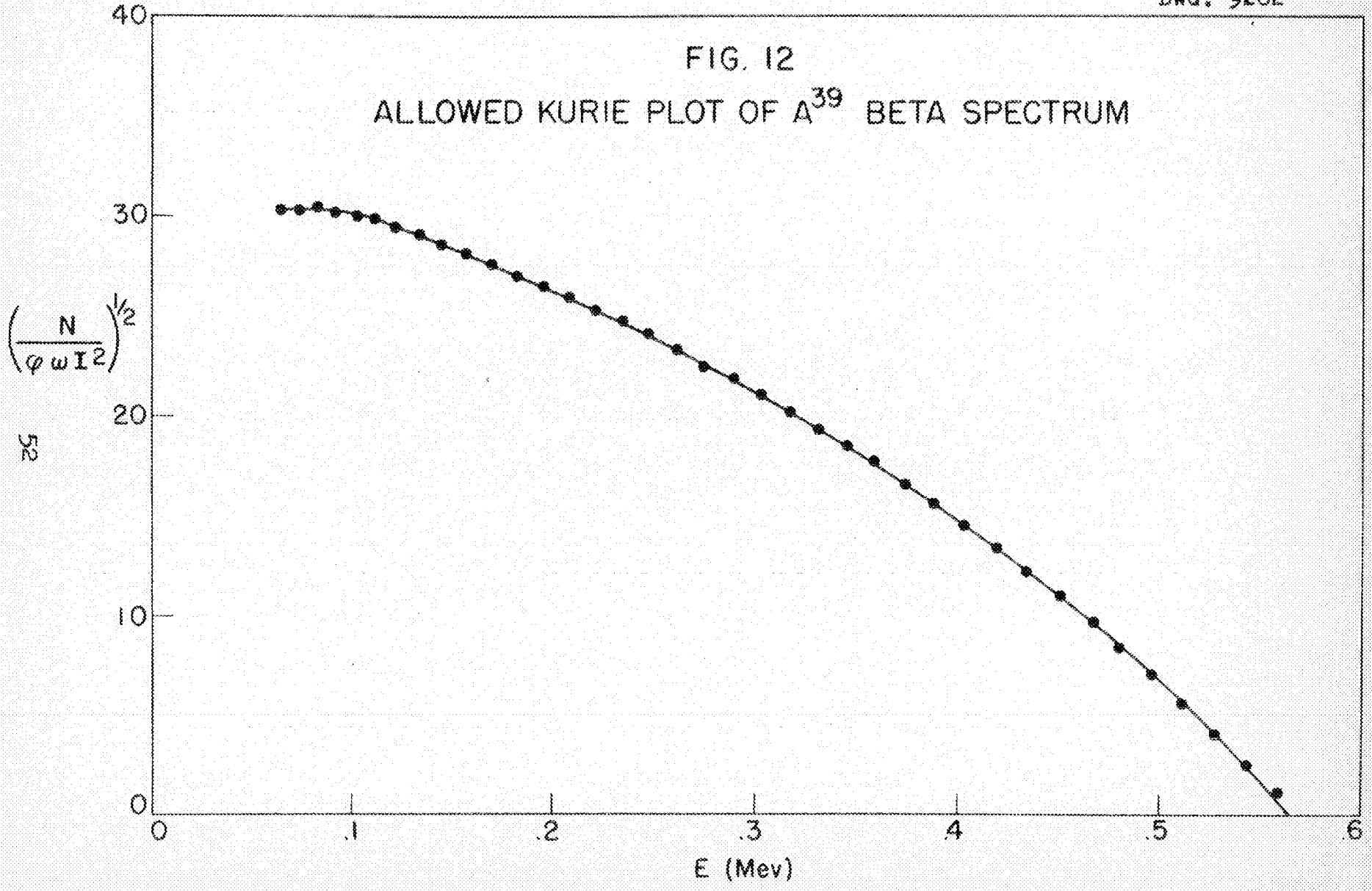

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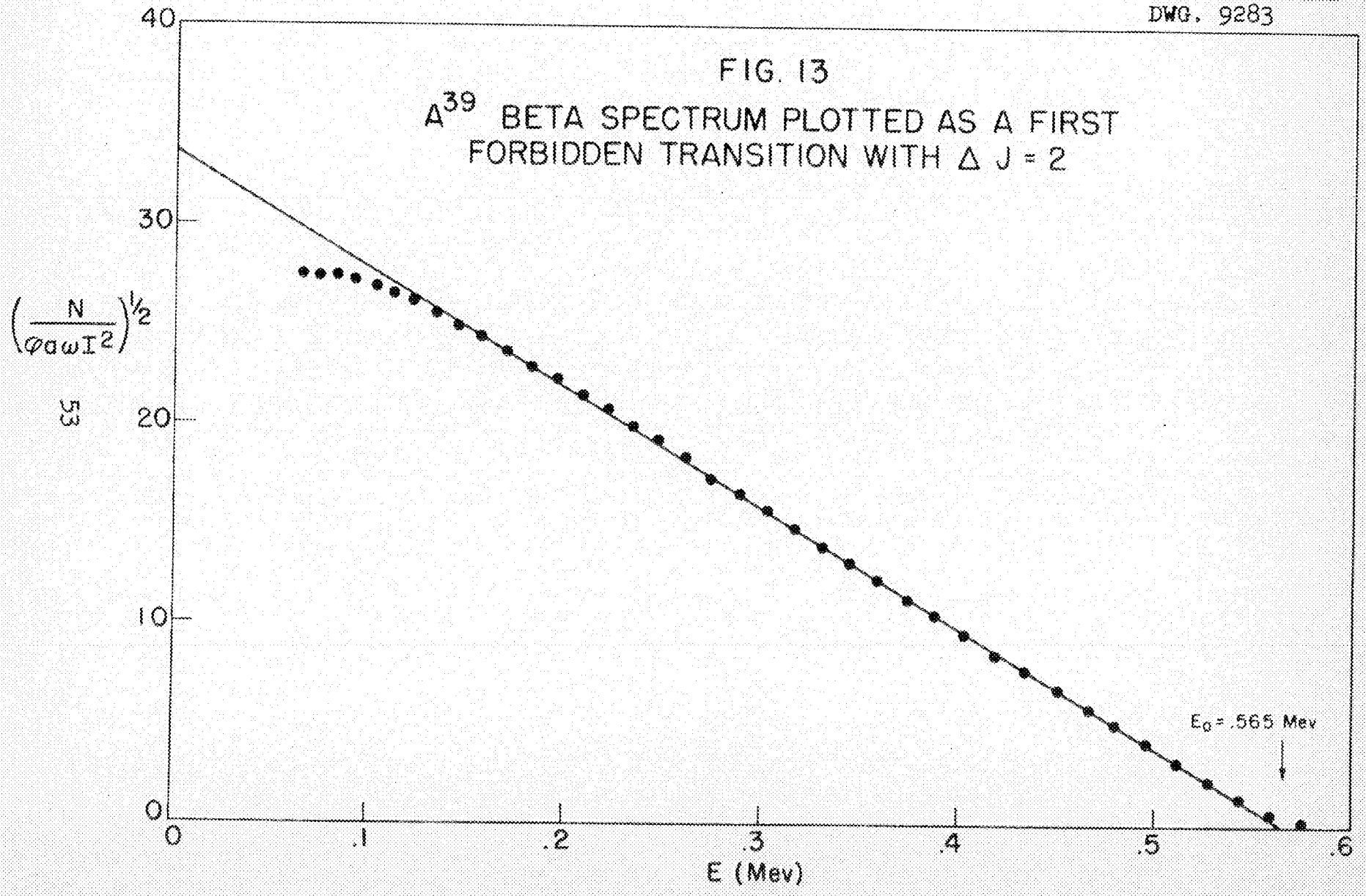
FIG. 13

A^{39} BETA SPECTRUM PLOTTED AS A FIRST FORBIDDEN TRANSITION WITH $\Delta J = 2$



Redox wastes, an intensive testing procedure has indicated the usual number of mechanical difficulties, the necessity for a moderate amount of reconsideration of the process, and in some instances, a few revisions. While making a number of cold runs, equipment performance and yield characteristics have been determined.

While it was originally planned to make hot runs concurrently with those in the Pilot Plant in order to preserve the identity of the batches from different sections of the rods, this was finally conceded as impossible because of many complications which delayed the completion of the necessary tracer runs.

At the present time all of the CR 1AW raffinates from the Pilot Plant have been sampled, analyzed and stored in three holding tanks. These contain the batches No. 1 and 2 (low-level CR), No. 3, 4, 5 and 6 (highest MWD CR), and batch No. 7 (Hanford), respectively.

A number of unanticipated variations in the ratios of Cr(III) and Cr(VI), the uranium content, as well as the expected rise in activity level (Table III) as the batches approached the center sections of the rods, have been observed.

An attempt has been made to obtain a tentative material balance of the alpha emitting transuranics in order to establish the presence and concentration of Np^{237}. The results are tentative but, as such, check the calculated quantities.

Studies on the rate of reduction of chromium (VI) by radiation show a linearity with the specific activity and an average reduction for this level of about 2% per day. There seems to be little effect due to the hexone, normally present to the extent of about 2% by volume.

Additional work on the identification of states associated with the chemical reduction of Np(V) to Np(IV) and its carrying on $Ce(OH)_3$ has been continued. A summary of the data is tabulated.

Cell 1, Bank 1: The *A* series of reactors, filters, and settling tanks, etc., shown in Fig. 14 comprise the complete series of steps for the prior chromium removal and the precipitation of anions from the Redox raffinates.

Tank A-1 is a partly double walled vessel containing a heating coil and sparger and a 40 gallon hold-up pre-filter for the rough filtrations of large

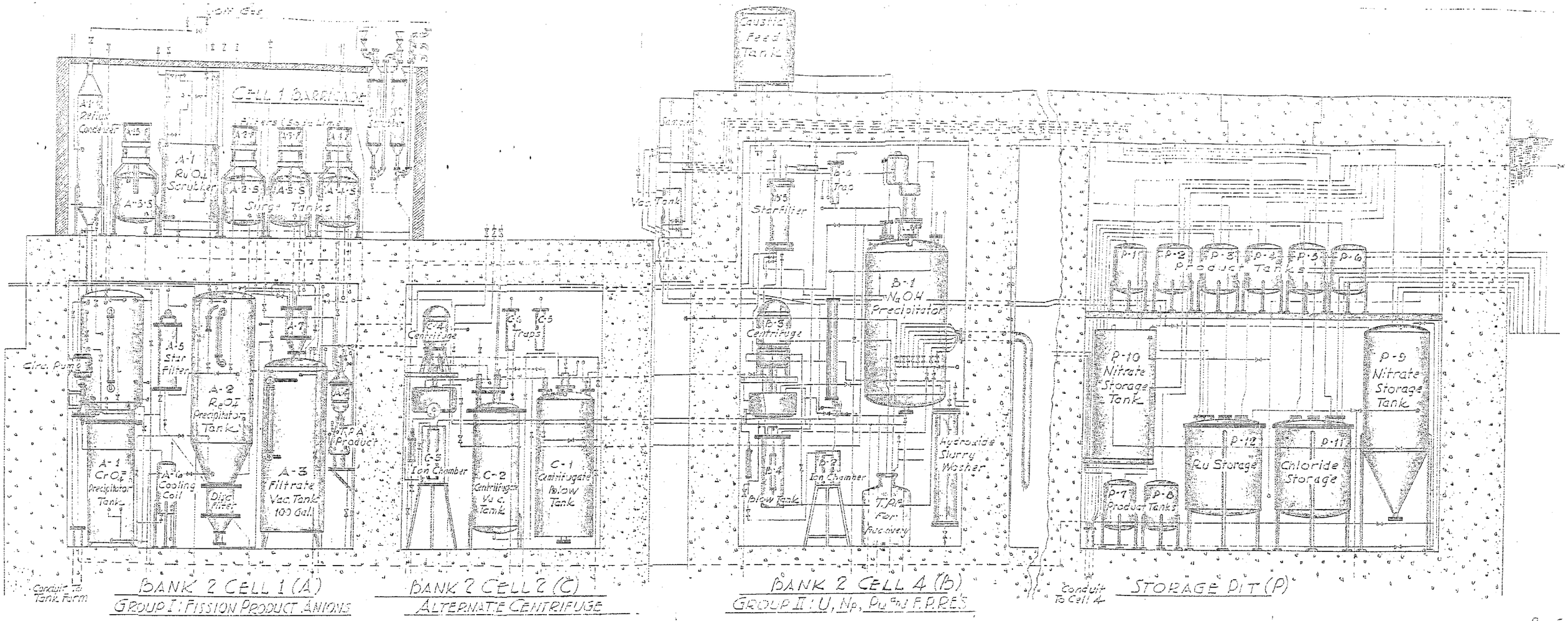


FIG. 14 SCHEMATIC CELL DIAGRAM - RC SEPARATIONS 706-C

Scale 1/8" = 1'9"

P. 5

C-77

quantities of lead chromate. The pre-filter consists of alternate layers of stainless screen filter cloth, glass cloth and Welsbach filter plate which form the cylindrical walls of an inside vessel concentric with the lower half of A-1.

In operation, 200 liters (~ 3000 curies) of raffinate are drawn into this tank; the carrier rhenium is added with about 15 lbs of $Na_2S_2O_8$ for the oxidation of Cr(III). The mixture is then heated to boiling and held at this temperature for 1-2 hours. During this operation a strong negative pressure (10-20 inches of H_2O) is provided by means of the off-gas vacuum through the reflux condenser and the A-1 scrubber. The scrubber is designed to trap large quantities of RuO_4 which vaporize from the strongly oxidizing solution.

Because of the hold-up volume outside of the pre-filter, a circulating pump, a specially adapted Alsop centrifugal, is used to bring all of this portion of the solution back into the heated section of the tank.

After cooling, sufficient lead acetate (40 lbs) is added to the tank for complete $CrO_4^{=}$ removal. Again the liquid is circulated by means of the pump through a sight glass until the pre-filter is sufficiently clogged to give a clear filtrate. This filtrate is then drawn by vacuum through a fine stainless star-type filter (A-6) enclosed in glass pipe into Tank A-2.

Tank A-2 is also equipped for heating as well as refrigerated water cooling. The lower section is conical leading into a glass pipe section (for visual operation) connected to a bottom supported stainless filter plate of Carpenter #20 alloy.

If the filtrate from A-1 is clear and free of chromium the solution is heated to about 90°C, after adding a reducing agent for the Np(V)$\longrightarrow$Np(IV) reaction and before adding about 200 grams of tetraphenyl arsonium chloride. The solution (~ 80 gallons) is next cooled to room temperature and then cooled with refrigerated water to 2-10°C. During overnight cooling, large needles of Ph_4AsReO_4 and Ph_4AsTcO_4 are formed and settle out. Extra cooling is required because of the small quantity of precipitate formed in the 80 gallons of solution. Even at room temperature the solubilities of the tetraphenyl compounds are high enough to materially lessen the yield. Filtration is accomplished by vacuum on A-3.

The vessel A-4 is nearly all glass and is designed for transfer of the organic product slurry from the fliter plate in A-2 onto a 6 in. pyrex filter for washing and dissolution in concentrated H_2SO_4.

Since relatively little hard radiation is present, this initial product in sulfuric acid is withdrawn from the cell for fractionation and purification elsewhere. An alternate filter (A-7) may be used if necessary.

Cell 4, Bank II: The *B* series includes the principal sodium hydroxide digester, (B-1), capacity about 200 gallons; and a 12 in. bowl-type Bird centrifuge (B-3), and monitoring ion-chamber (B-2).

In order to avoid accumulation of aluminum hydroxide upon addition of caustic which is agitated in B-1, the 80 gallons of nearly 1 *M* $Al(NO_3)_3$ solution is slowly added to about 60 gallons of caustic in this order to form sodium aluminate and precipitate the rare earth and associated hydroxides on $Ce(OH)_3$ carrier.

This mixture may be heated and cooled for digestion or may be centrifuged directly at about 0.2 - 0.4 gallons per minute. The bowl solids are then plowed out into the "Hydroxide Slurry Washer," mixed with more caustic to dilute out the aluminum and recentrifuged or sucked dry on the star filter (B-5). After several water washes, the $Ce(OH)_3$ and $Ce(OH)_4$ (oxidation in air) is dissolved in strong HNO_3 which is received in B-4. From this point, through the pipe manifold, it may be sampled, or placed in storage in the pit tanks (P 1-8).

Cell 2, Bank II: During the centrifugation of the mix in B-1, the centrifugate is collected in one of the *C* tanks C-1 or C-2 which are alternately used under vacuum for collection or under pressure to blow the waste solution into the Tank Farm (W-14) holding tank.

An alternate centrifuge C-4 and an associated ion-chamber have been provided in case of necessity.

Hot Storage Pit. A new hot storage facility connected to the tank farm and to the hot cells provides a variety of storage space for hot solutions in nitric acid, hydrochloric acid or alkaline media. Each of the tanks may be sampled through small plastic lines connected to a common "sampler" on top of Cell 2.

The large tanks (100 gallons) P-9, P-10 and P-13 (not shown) are to be used first to store the 240 gallons of raffinate from run 7 which was made from rather green Hanford metal. This will be held until all of the older material from the fuel rods has been concentrated before processing.

Rate of Reduction of Cr(VI) to Cr(III) by Radiation. Since the complete absence of Cr(III) in even very small concentrations is so important in the hydroxide carrying of rare earths and neptunium, it has been necessary to follow carefully the growth of Cr(III) in the Redox raffinates in order to be able to perform an efficient oxidation and removal as $PbCrO_4$.

It was at first thought possible to obtain the raffinates for processing early enough that the reduction might be negligible. This appeared to be nearly true with the low-level runs CR-1 and CR-2; however, after some delay in the Pilot Plant, Run 3 showed a much greater amount of reduction (~ 30%) when it was first available for sampling. Subsequent runs CR-3, 4, 5 and 6 also were proportionately reduced as the activity level increased.

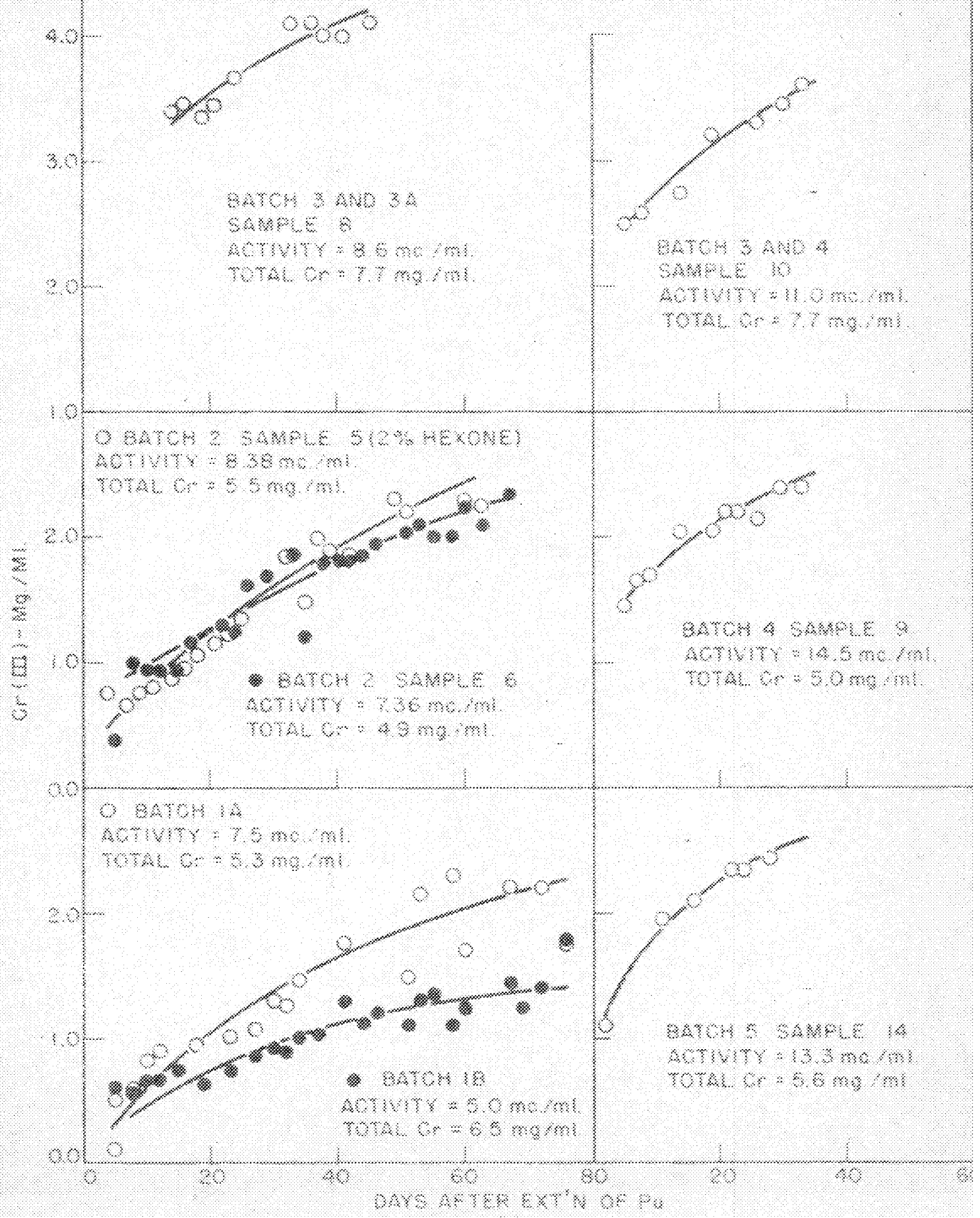
With the cooperation of the Analytical Division, a great many analyses of each batch were made from a 5-10 ml sample taken in glass. Due to the size of sample possible to handle safely, the points are scattered; however, the general curves show a gradual tapering off of the reduction rate and a rough correlation with the activity level and total chromium content. Figure 15 illustrates the progress of the reduction in the 40 to 60 days elapsed. It may be of interest to continue to follow the reduction and to re-examine the data after a longer period of time. It is also of interest to speculate whether the starting reduction rate is sufficiently higher than that observed to make it difficult to obtain complete separation of the chromium.

Co-precipitation of Neptunium Hydroxide with $Ce(OH)_3$. The essential conclusions that have been drawn from the erratic recovery of neptunium tracer from various test-tube and pilot-plant scale cold runs are:

(1) Cerium hydroxide is a satisfactory carrier precipitant in concentrations around or above .001 molar (139 mg/liter). It differentiates very little between Np(IV) and Np(V) at this concentration, although the solubility of the hydroxides are high and differ by a factor of 100.

(2) As with the other carriers proposed (La and U), $Ce(OH)_3$ is sensitive to concentrations of Cr(III) above about 0.0002 molar. At about 0.001 molar, the carrying is reduced by a factor of two.

FIG 15
REDUCTION OF Cr(VI) BY RADIATION
(R.C. REDOX RAFFINATES)



(3) Uranium, which has been found to be abnormally high in the best part of the CR wastes (1.0 g/l) is a satisfactory carrier for Np(IV) only and only in the absence of CR(III) and $CO_3^{=}$ in the excess caustic used to dissolve $Al(OH)_3$.

A summary of the collected data obtained from various types of runs is given in Table III. Since it has been shown that with a moderate increase in Ce carrier, the same yield can be expected, it is not likely that a reduction will be used. Instead, more attention will be directed toward complete removal of Cr(III).

TABLE III

Gross Beta Activity in CR-1AW Raffinates

STORAGE LOCATION	CR-1AW BATCH NO.	VOLUME (gallons)	SP. ACTIVITY* (mc/ml)	GROSS ACTIVITY (curies)	PU** IN FEED (grams)
Tank W-15	1	160	4.15	2,510	33
	2	148	6.9	3,860	47
Tank W-13	3	197	10.1	7,540	80
	4	150	16.1	9,130	98
	5	167	19.6	12,370	115
	6	180	28.1	19,120	188
Tank W-14	7 (Hanford)	240	25.3	15,760	86

* At mica-end window absorber; corrected for decay to 6/30/50.

** By analysis; heels not included.

TABLE IV

Composition of Alpha Activity in CR-1AW Raffinates

RAFFINATE BATCH NO.	U CONTENT (mg/ml)	GROSS ALPHA BY LaF_3 CARRYING (c/m/ml)	Am & Cm BY LaF_3 (Pu oxidized) (c/m/ml)	Pu BY TTA (c/m/ml)	Np BY TTA (specific for Np) (c/m/ml)*
CR-3,4,5,6 Composite	1.00	$3.4-3.5 \times 10^5$	$3.1-3.3 \times 10^5$	$3.4-4.5 \times 10^4$	680-840**
CR-7 (Hanford)	0.058	$3.2-3.8 \times 10^5$	1.9×10^5	$1.3-1.7 \times 10^5$	240-280**

* Theoretical for about two grams in 3100 liters = 924 c/m/ml

** Results tentative due to very low counting rate

TABLE V

Co-precipitation of Neptunium Hydroxide Tracer

CARRIER CONC. Ce(III): UO_2^{++} AS U (mg/l)		Cr(III) INTERFERENCE	REDUCING AGENT	NEPTUNIUM IV	NEPTUNIUM V	Np TRACER CARRIED
				(Percent carried on LaF_3)		
200		0	---	100 (prep. tracer)	0	~ 94
100		0	---	>.98	~ 2	85-89
	1000	0	---	100 (prep. tracer)	0	~ 97($CO_3^=$ free caustic)
	600	~ .0002 M	None	>.98	~ 2	~ 25(0.5% $CO_3^=$ in caustic)
100	500	~ .001 M	0.1 N_2H_4*	60	40	~ 50(0.5% $CO_3^=$ in caustic)
100	500	0	0.1 N_2H_4*	60	40	~ 91(0.5% $CO_3^=$ in caustic)
200		~ .0002	None	>.98	~ 2	89-92(0.5% $CO_3^=$ in caustic)

* Solution heated to 90°C for five minutes, cooled for 36 hours.

OTHER ELEMENTS

THE SZILARD-CHALMERS PROCESS IN $KBrO_3$ IN THE ORNL PILE

J. W. Cobble and G. E. Boyd

The Szilard-Chalmers method for obtaining high specific activities of 35.9 h Br^{82} in the pile has been studied under a variety of conditions. Preliminary specific activity values computed from data of Sol Wexler have already been reported in a previous report.[17] During this quarter, among other things, an attempt was made to assign the total decomposition of the salt to the various radiative causes. It is largely the radiation decomposition which lowers the specific activities with bombardment time. If one assumes that the decomposition can be related by a simple first order equation to the power of the pile, then

$$\text{Decomposition in ppm} = \text{Power} \times \text{Time} \times k_T, \qquad (1)$$

where k_T is the gross decomposition rate constant. A plot of the decomposition in ppm of Br_2 and Br^- formed in $KBrO_3$ vs. time should give a straight line at constant power of slope k_T. This is found to be the case, and the value of k_T for a thermal neutron flux of 6.7×10^{11} neutrons/cm^2 sec was 0.96×10^2 ppm hr^{-1}.

The radiation primarily responsible for the decomposition of the salt is believed to be made up mainly of neutrons and gamma rays. There may be a slight effect of beta rays, but this must be comparatively small, arising perhaps only as secondary radiation from the other two sources. One can then, in principle, define the total decomposition rate constant as the sum of the neutron and gamma ray constants,

$$k_T = k_n + k_\gamma = 0.97 \times 10^2. \qquad (2)$$

The problem resolves itself, therefore, to a determination of k_n and k_γ.

(17) Cobble, J. W. and Boyd, G. E., "Szilard-Chalmers Processes in the Chain Reacting Pile," *op. cit.*, ORNL 685, 75.

Determination of k_γ. A high gamma flux cobalt source of about 500 curies has been calibrated recently by C. Hochanadel in terms of the amount of oxidation of ferrous iron to ferric in sulphuric acid solution. If one uses the value of 19.7 micromoles of ferrous iron oxidized per liter per kilo-roentgen,[18] then a figure of 3930 roentgen per minute at the maximum exposure position in this "gamma-pile" may be derived.

The gamma heat of the ORNL pile has been determined for hole 12 by Richardson[19] for various substances. The gamma heat for most light elements is 0.000370 cal/gm-sec. This figure gives a value of 11,150 roentgen/minute at 3500 kw at the maximum position in hole 12. This can be adjusted and correlated to any other position in the pile if the relative flux values are known. Using the value of 6.7×10^{11} neutrons/cm^2-sec at 3500 kw for the pneumatic tube (hole 22) terminal, one can compute that the roentgen value of the high intensity cobalt source is 44% that of hole 22. One should then be able to determine k_γ for the ORNL pile by dividing the decomposition constant in the gamma-pile (cobalt source) by 0.44. This was done for potassium bromate, and the value of k_γ of 0.46×10^2 ppm hr^{-1} was obtained.

Therefore,

$$k_n = k_t - k_\gamma = 0.51 \times 10^2 \text{ ppm hr}^{-1}.$$

Evidently the neutrons are responsible for about one-half of the total $KBrO_3$ radiation in the ORNL pile.

It is possible to devise an experiment to determine the value of k_n in independent manner. According to the data and method presented in the report by Richardson,[19] one can calculate the average ORNL pile gamma energy as 0.8 Mev. By surrounding a sample of potassium bromate with a known amount of lead, and then bombarding this sample in the pile at a position of known flux, one should be able to calculate the effect on the observed decomposition rate constant, and calculate k_n as above:

$$k_n = k_t \text{ (in Pb)} - ak_\gamma = 0.48 \times 10^2 \text{ ppm hr}^{-1}.$$

(18) Lewis, W. B., *Progress Report for December 1949 and January 1950; Chemistry and Engineering Sub-Division* (Atomic Energy Project (Canada)), PR-CE-5 (n.d.).

(19) Richardson, D. M., *Calorimetric Measurement of Radiation Energy Dissipated by Various Materials Placed in the Oak Ridge Pile*, ORNL 129 (Oct. 1, 1948).

In this equation, a represents the fractional decrease in the gamma intensity due to the lead; in the experiments performed, this constant had a value of 0.31. The value of k_n calculated from this experiment agrees very well with the one given above, 0.48×10^2 ppm hr^{-1}.

While such good agreement is probably fortuitous, because of the errors in estimating the fluxes at various positions in the pile, it does suggest that the total decomposition observed can be explained as the sum of the component radiative decomposition processes occurring.

One would like to be able to resolve the neutron effects into the slow and fast components. Presumably this can be done by surrounding a sample with a "black" slow neutron absorber (such as Cd) and determining the effect on the decomposition. Experiments performed with cadmium, however, *increased* the decomposition over that of a normal bombardment rate by about four-fold. Qualitatively this can be explained by the increase in the gamma flux due to the capture gammas in cadmium (E max of 8.7 Mev), but attempts to resolve the effects on more quantitative terms have so far proved unsuccessful. This is due to the fact that the spectrum of the capture gammas from the cadmium is not known with sufficient accuracy to allow anything but order of magnitude calculations. Future experiments are planned using boron filters; the capture gamma spectrum from boron is simple and well known.

The absolute specific activities of Br^{82} from irradiated potassium bromate samples have been determined under a variety of conditions. Simple theory[20] predicts that the specific activity of the separable Br^{82} can be expressed as

$$S = \frac{i\phi\sigma}{k} \frac{(1-e^{-\lambda t})}{\lambda t}$$

where i is the isotopic abundance of Br^{81}, σ the absorption cross section for Br^{81}, ϕ the separation factor (0.70), k the decomposition rate constant, and t the total bombardment time. As t approaches zero, the specific activity, S, approaches the limiting value of $i\phi\sigma/k$ which has the value of 1190 Rd/mg. At times other than $t = 0$, S can be expressed as

$$S_t = \frac{S^0}{\lambda t} (1-e^{-\lambda t}) ,$$

where S^0 is the limiting specific activity at zero time.

(20) Williams, R. R., *Phys. Coll. Chem. J.* 52, 603 (1948).

The ratio of the specific activity at a time other than zero to that at zero time is given by

$$S_t/S^0 = (1-e^{-\lambda t})/\lambda t \ .$$

The observed specific activities are given in Table VI for a flux of 6.7×10^{11} n/cm^2-sec.

TABLE VI

Variation of Relative Specific Activity with Irradiation Time

S^0 = 900 Rd/mg (Experimental)

BOMBARDMENT TIME (Hours)	S/S^0 (Exptl.)
0.0	(1.00)
0.5	0.95
2.0	0.85
6.0	0.67
8.0	0.60
10.0	0.55
12.0	0.52
22.0	0.40
46.2	0.35

Specific activities in Table V of ORNL 685 p. 75 computed from the data of Sol Wexler are too low by a factor of 20.54 due to an uncertainty in the resistance scale ratio of the ion-chamber at the time of his measurements and subsequent calibration.

The specific activities drop much faster than the simple theory presented would predict. Preliminary results seem to indicate this rapid decrease may be due to a recombination (back reaction) of the "hot" recoil Br^{82} atoms which is not undergone by the bromine atoms formed by radiation decomposition. The

observed "leveling off" of the specific activity merely indicates that a "psuedo" equilibrium has been reached between the processes competing for the Br^{82} atoms.

The effect of the lead shielding on the specific activities of the Br^{82} is to increase them by a factor of about two. This factor, when added to the high specific activities obtainable by the unshielded Szilard-Chalmers process, will give specific activities many thousands of times higher than those obtainable by the bombardment of potassium bromide, a non-enriching procedure.

RADIO-ORGANIC CHEMISTRY

SUMMARY

The preparation of potassium acetate-2-C^{14} and acetic acid-2-C^{14} has been accomplished on a production basis. Thirty-six millicuries of the former and 4.66 mc of the latter have been prepared.

Two hundred sixty-seven milligrams of sublimed malonic acid-2-C^{14} (2.54 mc) have been prepared in 55% radiochemical yield from acetic acid-2-C^{14}.

Fifty-six millicuries of potassium cyanide-C^{14} (4 mc/mmole) were prepared by the modified Loftfield procedure.

Attempted preparation of methylene labeled maleic anhydride from dibromoacetic acid anhydride by reaction with zinc failed because of extensive polymerization.

The rearrangement of 11-benz(b)fluorene-11-methanol-12-C^{14} by the action of phosphorus pentoxide in boiling xylene has been found to give benz-anthracene-5,6-$C_1{}^{14}$ in 93% yield. Degradation of the benzanthracene has shown that the relative proportions of C^{14} in the 5 and 6 positions are 45/55.

Chrysene-5,6-$C_1{}^{14}$ has been synthesized through the Wagner rearrangement of 1,2-benzofluorene-9-methanol-10-C^{14}. The distribution of the isotope has been shown to be 60% and 40% in the 5- and 6- positions, respectively.

The radioactive polystyrene, 8 mc, has been diluted and purified, and a portion has been laid down as film and divided into standard one and one-quarter inch squares.

Three lithium boralkoxides were prepared for testing as possible scintillation counters. They were obtained as microcrystalline powders. Search for suitable solvents from which to grow large crystals is being conducted.

A gas sampling apparatus has been devised which allows facile determination of radioactivities of vapors of high specific activities.

A simple inexpensive instrument for the determination of the ion current produced by Carbon-14 beta disintegration has been developed by combining a Borkowski ionization chamber with a Lauritson electroscope.

Absolute calibration of counting methods employed at this laboratory against standardized sodium carbonate-C^{14} from the National Bureau of Standards has led to the accumulation of considerable data relating the factors for converting readings obtained with the vibrating reed electrometer to microcuries of carbon-14 activity. Work has been and is in progress on the intercalibration of the three resistances and two condensers of the electrometer through all four voltage ranges. Some conclusions have been drawn regarding the stability of the reed, the variabilities of the chambers and the precision which can be expected during ordinary use of the analytical procedure.

Because of the importance and widespread use of decolorizing carbon, chromatographic adsorption and fractional distillation for the purification of organic compounds obtained by the technique of isotopic dilution, it was found necessary to determine whether isotope effects occurred during the use of these procedures in order to validate the technique. During the use of decolorizing carbon, no isotope effect was observed within the limits of error of the procedure (0.2%).

A study of the radiation chemistry of organic compounds has been initiated.

THE SYNTHESIS OF LOW MOLECULAR WEIGHT INTERMEDIATES CONTAINING C^{14}

Acetic Acid-2-C^{14}

D. N. Hess

Discussion. Thirty-six millicuries of potassium acetate-2-C^{14} has been prepared in 91% yield from methanol-C^{14} by the procedure previously described.[1]

A portion of the potassium acetate containing 6.23 millicuries was converted in 76% yield to anhydrous acetic acid-2-C^{14} by a method which removed possible potassium cyanide and potassium formate impurities. The purification procedure and preparation of the anhydrous acetic acid are described below. The 4.66 millicuries acetic acid obtained (4.12 millimoles) was used in the preparation of malonic acid-2-C^{14}.

Experimental. The aqueous solution of 6.23 millicuries of potassium acetate-2-C^{14} was acidified with approximately 0.6 ml 70% phosphoric acid. A saturated solution of potassium permanganate was added dropwise until the permanganate color persisted and the acetic acid was steam distilled by the addition of successive small portions of water. The distillate was neutralized with 1.0 *N* potassium hydroxide solution and evaporated. The residue was dried by heating at 150°C *in vacuo* for 16 hours at 10^{-4} mm. Sufficient phosphoric acid saturated with phosphorus pentoxide was added to wet the dried salt, and the acetic acid was distilled at 10^{-4} mm and 120°C into a receiver immersed in liquid nitrogen. Yield, 4.66 millicuries acetic acid-2-C^{14} (4.12 millimoles).

POTASSIUM CYANIDE-C^{14}

W. J. Skraba

Discussion. Fifty-six millicuries of potassium cyanide-C^{14} (4 mc/mmole) was prepared by the modified Loftfield procedure previously described.[2]

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(1) Hess, D. N., "Acetic Acid-2-C^{14}," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950*, ORNL-685, 78 (June 16, 1950).

(2) Skraba, W. J., "Potassium Cyanide-C^{14}," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950*, ORNL-685, 79 (June 16, 1950).

THE SYNTHESIS OF HIGH MOLECULAR WEIGHT COMPOUNDS CONTAINING CARBON-14

THE MECHANISM OF THE WAGNER REARRANGEMENT. I. THE SYNTHESIS OF BENZANTHRACENE-5,6-C_1^{14}

C. J. Collins and J. G. Burr, Jr.

Discussion. The rearrangement of 11-benz(b)fluorene-11-methanol-12-C^{14} by the action of phosphorus pentoxide in boiling xylene has been found to give benzanthracene-5,6-C_1^{14} in 93% yield. This is an extension of the method which has been used to prepare phenanthrene,[3] and phenanthrene-9-C^{14}.[4]

An unsymmetrical distribution of C^{14} between the 5 and 6 positions of the benzanthracene was anticipated, since unlike the case of fluorenemethanol[5] the carbinol here concerned would give a carbonium ion with an unsymmetrical environment. In fact, degradation of the benzanthracene has shown that the relative proportions of C^{14} in the 5 and 6 positions are 45/55. The synthesis of benz(a)anthracene-5,6-C_1^{14}(VI) was reported earlier.[6]

Degradation of this hydrocarbon at the 5,6-bond was accomplished through a preliminary hydroxylation at the 5,6 position with osmium tetraoxide[7] to give the dihydro-diol (I) in 74% yield. The attempted cleavage of this diol with lead tetraacetate and oxidation of the resulting dialdehyde led to a series of intractable gums. The diol was therefore oxidized to the quinone (II) (66% yield from the hydrocarbon) with chromium trioxide in acetic acid. The quinone was cleaved with 30% hydrogen peroxide to the dibasic acid (III).[8] Distillation of this acid at atmospheric pressure gave a mixture of chrysoketone (IV) and a chrysoketone carboxylic acid (V). The keto-carbon atom in the

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(3) Brown, W. G. and Bluestein, B., "Dehydration of 9-Fluorenylcarbinol: A New Synthesis of Phenanthrene," *Am. Chem. Soc. J.* 62, 3256 (1940).

(4) Collins, C. J., "The Synthesis of Phenanthrene-9-C^{14}," *Am. Chem. Soc. J.* 70, 2418 (1948).

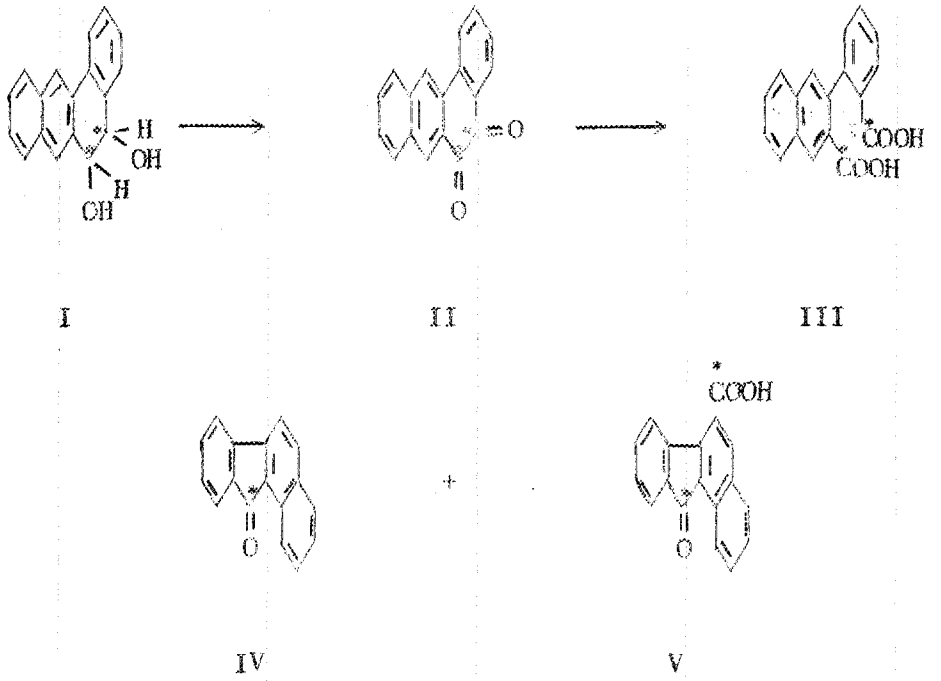
(5) *Ibid.*

(6) Collins, C. J. and Burr, J. G., "Benz(a)Anthracene-5,6(?)-C^{14}," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950, ORNL-685*, 82, (June 16, 1950).

(7) Cook, J. W. and Schoental, R., "Oxidation of Carcinogenic Hydrocarbons by Osmium Tetraoxide," *Am. Chem. Soc. J.* 172 (1948).

(8) Fieser, L. F. and Dietz, E. M., "1,2-Benz-3,4-Anthraquinone," *Am. Chem. Soc. J.* 51-3143 (1929).

chrysoketone is the one which occupied the 5-position of the original benzanthracene, and thus assay of the chrysoketone gave directly the C-14 content of that position.



The formation of a ketone through interaction of the two carboxyl groups would give a keto group derived at random from either of the two carboxyl carbon atoms. This is unlikely in the absence of a strong inorganic base, and would result in any case in the formation of the linear benzfluorenone. This was not observed.

Experimental. 1. *5,6-Dihydroxy-5,6-dihydrobenz(a)anthracene-5,6-C_1^{14} (I).* The sample of benzanthracene (930 mg containing 1.73 μcuries/mmole of C^{14}) was dissolved in 40 ml of benzene in a 250 ml glass-stoppered bottle. A 1 g vial of osmium tetraoxide was broken in the bottle, and 1 ml of pyridine added. The bottle was stoppered, the contents were magnetically stirred for one hour, and then allowed to stand for two days. At the end of this time, 50 ml of methylene

chloride and 100 ml of 3% potassium hydroxide solution containing 10 g of mannitol were added and the bottle was mechanically shaken for five hours. The heavy organic layer was then separated, and evaporated to dryness in an air blast at room temperature. The residue was taken up in benzene-chloroform, filtered, and the filtrate evaporated to dryness. The residue was crystallized from chloroform to give 773 mg (74%) of the diol as a cotton-like white solid, melting at 205-206°, and 310 mg of residual material (a deep orange solid).

2. *5,6-Benz(a)anthraquinone-5,6-C_1^{14} (II).* The diol (I, 773 mg) was dissolved in 25 ml of acetic acid, and this solution mixed with a solution of 0.78 g of chromium trioxide in a mixture of 1.5 ml of water and 13.5 ml of acetic acid. A heavy red precipitate formed immediately; after standing for fifteen minutes, the mixture was chilled in a refrigerator, and filtered. The product was 432 mg of orange-red quinone (II), melting at 263-265°. The filtrate was added to the residual material from the diol preparation. Another 0.5 g of chromium trioxide was added, and the solution after reaction was evaporated in a stream of air. The residue was diluted with water; the precipitate was filtered and washed with alcohol to give an additional 255 mg of the quinone. The overall yield of quinone was 66% from the hydrocarbon.

3. *2-(o-Carboxyphenyl)-3-naphthoic Acid (III).* A solution of the quinone (II, 688 mg) in 70 ml of acetic acid was heated on the steam bath, and 0.45 ml of 30% hydrogen peroxide was added. After an hour, a second and similar addition of peroxide was made, and heating was continued for another hour. After standing overnight, a third addition of peroxide was made and the solution evaporated on the steam bath in an air stream. The residue was washed with water by decantation and warmed with aqueous sodium bicarbonate solution. The material insoluble in bicarbonate amounted to 221 mg of an orange powder. The cold bicarbonate solution was slowly acidified with concentrated hydrochloric acid. The precipitated acid, after filtering and air drying, weighed 445 mg and melted at about 130°. A sample was dissolved in hot dilute methanol. The solution was cooled, decanted from precipitated tar, and chilled. The light purple micro needles which deposited melted at 243-246° (Lit.[9] 246°).

4. *Chrysoketone-11-C^{14} and Chrysoketone-6-carboxylic Acid-11,12-C_1^{14}.* The crude dicarboxylic acid (III), weighing about 400 mg, was distilled with

(9) Fieser, L. F. and Dietz, E. M., *op cit.*

a free flame at atmospheric pressure, finishing at 22 mm pressure. The orange-yellow sublimate weighed 310 mg. It was crystallized from benzene. The pale yellow micro needles which deposited weighed 46.7 mg, and melted at 261-262° (Lit.[10] for chrysoketone-6-carboxylic acid is 262°).

The filtrate from this solid was passed through an alumina column and eluted with benzene. The substance recovered from the eluate was an orange solid, weighing 33.7 mg. After crystallization from hexane, the yellow needles melted at 125-130°. The melting point was not depressed by admixture with a sample of authentic chrysoketone. Assay of this ketone revealed the presence of 0.770 μcuries of C^{14}/mmole ketone. This represents 45% of the activity present in the initial hydrocarbon sample.

THE MECHANISM OF THE WAGNER REARRANGEMENT. II. THE SYNTHESIS OF CHRYSENE-5,6-C_1^{14}

C. J. Collins A. R. Jones
G. M. Toffel[11]

Discussion. The synthesis of phenanthrene-9-C^{14} in this laboratory was reported previously.[12] In an attempt to demonstrate the generality of this synthetic method, and to gain information on the mechanism of the Wagner rearrangement, this reaction has been extended to the preparation of carbon-14 labeled chrysene (V). 1,2-Benzofluorene (I) was prepared by the method of Orchin and Reggel.[13] Following the same procedure[14] utilized in the synthesis of phenanthrene-9-C^{14}, this hydrocarbon (I) was converted to chrysene-

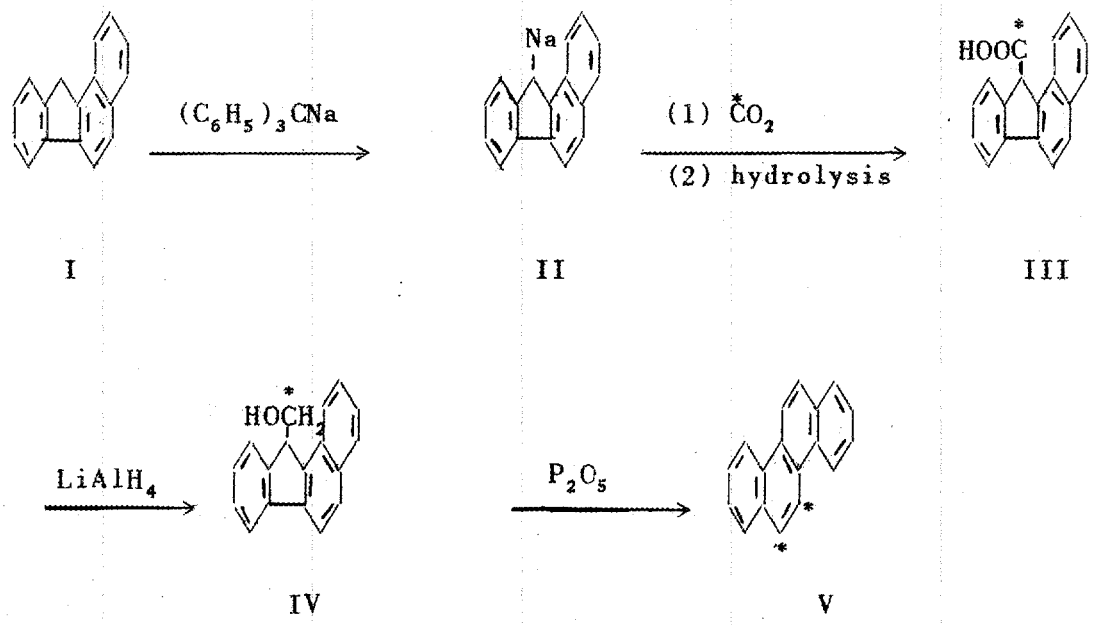
(10) Fieser, L. F. and Dietz, E. M., *op. cit.*

(11) Present address: School of Chemistry, University of Alabama, Tuscaloosa, Alabama.

(12) Collins, C. J., "The Synthesis of Phenanthrene-9-C^{14}," *Am. Chem. Soc. J.* 70, 2418 (1948).

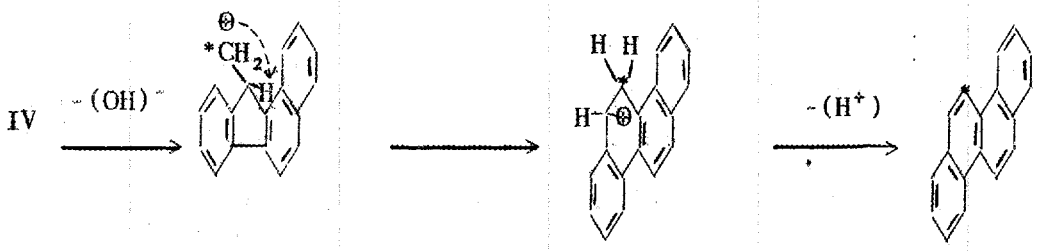
(13) Dr. Milton Orchin kindly supplied us with his experimental procedure for the preparation of this hydrocarbon prior to publication.

(14) Collins, C. J., "The Synthesis of Phenanthrene-9-C^{14}," *Am. Chem. Soc. J.* 70, 2418 (1948).

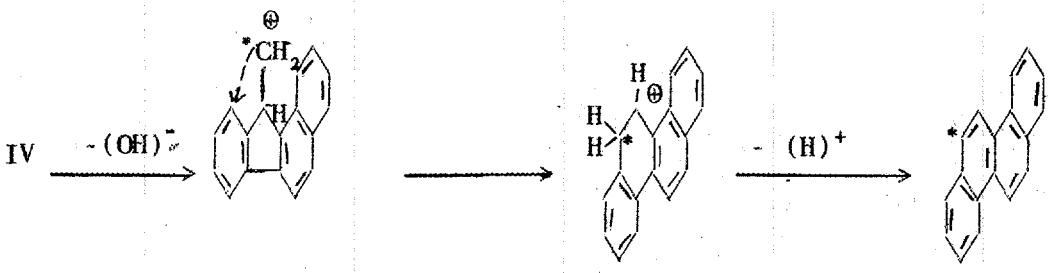


5,6-$C_1{}^{14}$ (V). During the rearrangement of 1,2-benzofluorene-9-methanol-10-C^{14} (IV), two possible courses are open. These may be illustrated by the following two mechanisms:

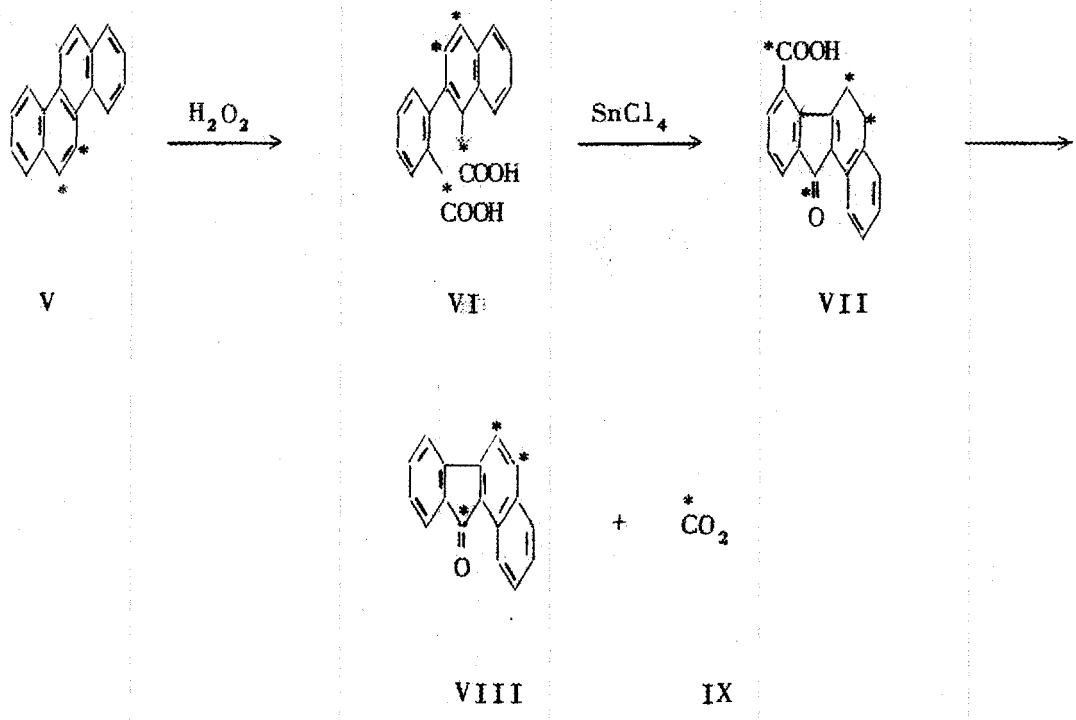
Mechanism 1



Mechanism 2



Mechanism 1 leads to chrysene-5-C^{14}, while mechanism 2 leads to chrysene-6-C^{14}. In order to demonstrate the extent of the contribution of each of these two possible courses to the rearrangement, the carbon-14 labeled chrysene was degraded according to the following scheme:



If chrysene-5-C^{14} (Mechanism 1) were the product, then the molar activity of VIII with respect to carbon-14 should be identical to the molar activity of the chrysene (V). If, however, chrysene-6-C^{14} (Mechanism 2) had been formed, then the molar activity of VIII should be equal to that of the carbon dioxide evolved (IX), and equal to one-half of the molar activity of the chrysene (V). Since in fact the 1,2-benzofluorene (VIII) was found to have lost one-fifth of the original radioactivity of the chrysene (V), we have concluded that carbon-14 is present in both the 5- and 6- positions in the chrysene obtained by the dehydration of I, and that the distribution of the isotope between these two positions is approximately 60% and 40%, respectively.

Our calculations have assumed no isotope effect in the oxidation of V $\longrightarrow$ VI. This question is now being investigated and will be the subject of a later report.

Experimental. **1.** *1,2-Benzofluorenone.* This material was prepared using the method of Orchin and Reggel.[15]

2. *1,2-Benzofluorene (1).* A normal pressure hydrogenation using 3.023 g 1,2-benzofluorenone, 3.127 g palladium-on-carbon catalyst and 15 cc alcohol was allowed to proceed with magnetic stirring overnight. The catalyst was filtered, yielding 0.713 g of the hydrocarbon (I), melting 181-183.5°. By suspending the catalyst repeatedly in boiling alcohol and filtering and concentrating, an additional 1.043 g hydrocarbon was obtained. The purified material twice crystallized from 95% ethanol melted 185.4-186.0°.

3. *1,2-Benzofluorene-9-carboxylic acid-10-C^{14} (III).* Utilizing the procedure described previously,[16] the acid was prepared from 651 mg hydrocarbon (I), 14 ml of triphenylmethylsodium solution, and 633 mg $BaC^{14}O_3$. (Specific activity 25.5 microcuries carbon-14 per millimole). Yield of acid, 660 mgms, 83.2% on basis of unrecovered carbon dioxide-C^{14}.

Anal. 26.5 microcuries carbon-14 per millimole compound.

4. *Chrysene-5,6-C_1^{14} (V).* Several attempts to esterify III failed, so 558 mg of the acid was treated directly with 25 ml ether containing approximately 1 g $LiAlH_4$. The solution immediately became a yellow-green color. After boiling for 20 minutes, dilute HCl was added. Allowing sufficient time for both layers to become clear, the product then was removed from the solution by means of a continuous ether extraction. On concentration, the product weighed 523 mg. Removal of any unchanged acid was effected by treatment with bicarbonate, followed by acidification and extraction with ether. In this way, 222 mg unreacted acid was recovered. Yield of carbinol, 318 mg, 100% of theory on basis of oily, crude product. Attempts at crystallization of this carbinol were unsuccessful, so 90.0 mg of the oil was dissolved in 20 ml dry xylene, and 300 mg P_2O_5 was added. After heating under reflux for 30 minutes, the xylene was removed in an air-stream. To the dark oil was added a saturated aqueous solution of bicarbonate, and the mixture was vigorously stirred for 15

(15) Orchin, Milton, *op. cit.*

(16) Collins, C. J., "The Synthesis of Phenanthrene-9-C^{14}," *Am. Chem. Soc. J.* 70, 2418 (1948).

minutes. After extraction with ether and desiccation, 79 mg brown crystals were obtained. Passage of a benzene solution of this material through a small alumina column produced 44 mg pure chrysene-5,6-C_1^{14}. After benzene then acetic acid crystallizations, a white, crystalline solid was obtained melting at 252-255°. Amixed melting point with an authentic chrysene sample showed no depression.

Anal. 26.5 microcuries carbon-14 per millimole compound.

5. *Oxidation of chrysene-5,6-C_1^{14} (V) to 2-phenylnaphthalene-1,2'-dicarboxylic acid-3,4,9,7'-C_1^{14} (VI).* 0.5 g Chrysene-5,6-C_1^{14} (anal. 1.14 microcuries carbon-14 per millimole) in 100 ml glacial acetic acid was treated under reflux with 15 ml 30% peroxide for eight hours. In one hour the color turned deep red, then gradually became a light yellow. The solution was taken to dryness and the residue was treated with a saturated bicarbonate solution; the solution was washed with ether, acidified, and subjected to a continuous ether extraction. On concentration and desiccation, 0.3 g of a dark semi-solid material was obtained. This solid was dissolved in the least amount of acetic acid and treated with an excess of water in a centrifuge tube. After centrifuging, pale yellow crystals appeared over a dark oil. These crystals on solution in bicarbonate and precipitation with acid melted at 200-201°. A mixed melting point with an authentic sample gave no depression.[17]

6. *Conversion of 2-phenylnaphthalene-1,2'-dicarboxylic acid-3,4,9,7'-C_1^{14} to 1,2-benzofluorene-3,4,9-C_1^{14} (VIII).* 0.1 g VI in a test tube in a nitrogen atmosphere was heated directly with a free flame above its melting point for a few minutes. The cooled melt was then dissolved in benzene and passed through a small alumina column; yielding approximately 35 mg pure ketone (VIII). One crystallization from benzene yielded yellow crystals melting 122.5°.[18]

Anal. 0.915 microcuries per millimole compound.

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(17) An authentic sample was prepared by the method of Graebe, C. and Gnehm, R., "Uber Chrysodiphensaure (2-phenylnaphalin-1 dicarbonsaure)." *Ber.* 35, 2744 (1902).

(18) Orchin, Milton, *op. cit.*

COUNTING METHODS AND STANDARDS

POLYSTYRENE COUNTING STANDARDS

H. E. Heller

Discussion. The entire quantity of radioactive polystyrene, 8 mc, has been laid down once as thin sheets in order to allow release of solvent remaining from the precipitation step.[19] A value for the activity 40% as great as that of the "hot" polystyrene was chosen. The polymer was mixed with one-and-one-half times its weight of Dow "Styron," and dissolved in methylene chloride. The solution so prepared contained a considerable amount of dust accumulated during previous operations. Since this would result in uneven surfaces on the sheets to be prepared, the polystyrene, dissolved in sufficient methylene chloride to make a fairly non-viscous solution, was filtered through glass wool. The removal of dust appeared substantially complete.

Preparation of Compounds for Possible Use in Scintillation Counters. Various organic compounds of boron and lithium might be expected to perform well as luminescent elements of scintillation counters. The reaction between lithium borohydride and active hydrogen-containing compounds or carbonyl compounds supplies a path to a large number of lithium-boron organics:

$$LiBH_4 + 4\ R\text{-}OH \longrightarrow LiB(O\text{-}R)_4 + 4\ H_2$$

$$LiBH_4 + 4\ R\text{-}CHO \longrightarrow LiB(O\text{-}CH_2\text{-}R)_4$$

The products of reaction between lithium borohydride and salicylic acid, salicylaldehyde, and alpha-napthol have been prepared in order to study their properties.

There appears to be two major difficulties barring the way to use of these compounds. First, the compounds are not very stable in air, undergoing oxidation and hydrolysis. They must be handled in an inert atmosphere, and as a result, their usefulness is considerably reduced. Second, the compounds are not soluble in, or react with, most of the common solvents from which they

(19) Heller, H. E. and Weinberger, A. J., "Polystyrene Counting Standards," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950*, ORNL-685, 88 (June 16, 1950).

might be crystallized. As originally prepared, they are micro-crystalline white powders, unsuitable as scintillators. They do not melt at any reasonable temperature, but darken and undergo extensive decomposition. The attempt to grow large crystals from these substances seems to hinge on finding suitable solvents, and a search for such solvents is being conducted.

Experimental. Lithium borohydride was dissolved in diethyl ether to give a solution containing 0.27 moles of reagent per liter of solution. To 100 ml of this solution was added 100 ml of ether containing the corresponding amount of the active hydrogen- or carbonyl-containing reagent. The mixtures were stirred for several hours, and allowed to stand until used. The procedures were the usual ones for handling of hydride reagents.[20]

The lithium-boron derivatives of salicylic acid, salicylaldehyde, and alpha-naphthol have been prepared in this manner. Although large crystals of these compounds have not yet been prepared, samples of the fine powders have been submitted to P. R. Bell of the Physics Division for preliminary testing.

CONSTRUCTION OF AN APPARATUS FOR ALIQUOTING MINUTE QUANTITIES OF RADIOACTIVE GASES

W. J. Skraba and A. J. Weinberger

To facilitate the activity determinations of highly radioactive vapors and gases, an apparatus was constructed and used with carbon dioxide-C^{14} and methanol-C^{14}.

For the production of radioactive organic compounds of high specific activity, carbon dioxide-C^{14} is usually the starting material. Heretofore the analytical procedure consisted of the acid decomposition of a weighed minute aliquot of barium carbonate-C^{14} in a special apparatus and gas counting the evolved carbon dioxide-C^{14} with a vibrating reed electrometer. The main portion of the barium carbonate was then decomposed and the carbon dioxide was stored in a bulb on the production manifold to be aliquoted as needed on the basis of the activity determined for the very tiny barium carbonate sample initially taken.

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(20) Nystrom, R. F. and Brown, W. G., "Reduction of Organic Compounds by Lithium Aluminum Hydride. I. Aldehydes, Ketones, Esters, Acid Chlorides and Acid Anhydrides, *Am. Chem. Soc. J.* 69, 1197 (1947).

With the device described below the specific activity not only of the starting material, carbon dioxide, in the production manifold can be determined, but, often, that of the intermediate or final products as well.

Description of the Apparatus. The apparatus consists of a short section of calibrated 1 mm capillary tubing located between a two-way and a three-way stopcock (Fig. 16). One side arm of the three-way stopcock serves as an inlet for inert carbon dioxide used as the fill gas of the ionization chamber. At the end of each stopcock is a 12/30 female joint.

Operation of the Apparatus. The device is attached vertically to the vacuum manifold *via* the 12/30 female joint adjacent to the three-way stopcock and to the other joint is attached an ionization chamber. A high vacuum is produced in the apparatus and the ionization chamber is isolated from the system by closing the two-way stopcock. Radioactive gas is then introduced into the manifold including the capillary tube and the bore of three-way stopcock (this space constituting the calibrated portion of the apparatus). The pressure and temperature is recorded and the quantity of gas calculated. The vapor in the calibrated portion is then introduced into the ionization chamber and swept in with inert carbon dioxide to atmospheric pressure. The activity is determined in the usual manner. Direct weighing of the apparatus, both evacuated and filled with mercury, was the method employed for calibration.

THE USE OF THE LAURITSEN ELECTROSCOPE

G. M. Toffel O. K. Neville
J. B. Davidson*

A simple, inexpensive instrument for the determination of the ion current produced by carbon-14 beta disintegration has been developed using a Borkowski[21] ionization chamber connected parallel with a Lauritsen electroscope. The advantages of the present design over the Henriques[22] modification of the electroscope lie in the lower cost and ease of conversion of the commercial model. Similar use of the Lindemann[23,24] electrometer has involved electronic balancing systems, which have been avoided in the present work in order to maintain maximum simplicity.

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*Instrument Department, Y-12 area, Bldg. 9207.

(21) Borkowski, C. J., "Ionization Chamber for Carbon-14 Measurements," MDDC-1099.

(22) Henriques, F. C. and Margnetti, C., "Radioactive Studies. I. Measurement of Radioactive Sulfur with a Lauritsen Electroscope," *Ind. Eng. Chem., Anal. Ed.* 18, 417 (1946).

(23) Janney, C. D., and Meyer, B. J., "A Method of Assay for C^{14}," AEC, MDDC 1303 (July 31, 1947).

(24) Jesse, W. P., Hannum, C. A., Forstat, H., and Hart, "Ionization Chamber Techniques in the Measurement of Carbon-14," *Phys. Rev.*, 71, 478 (1947).

NOT CLASSIFIED
DWG. 9163

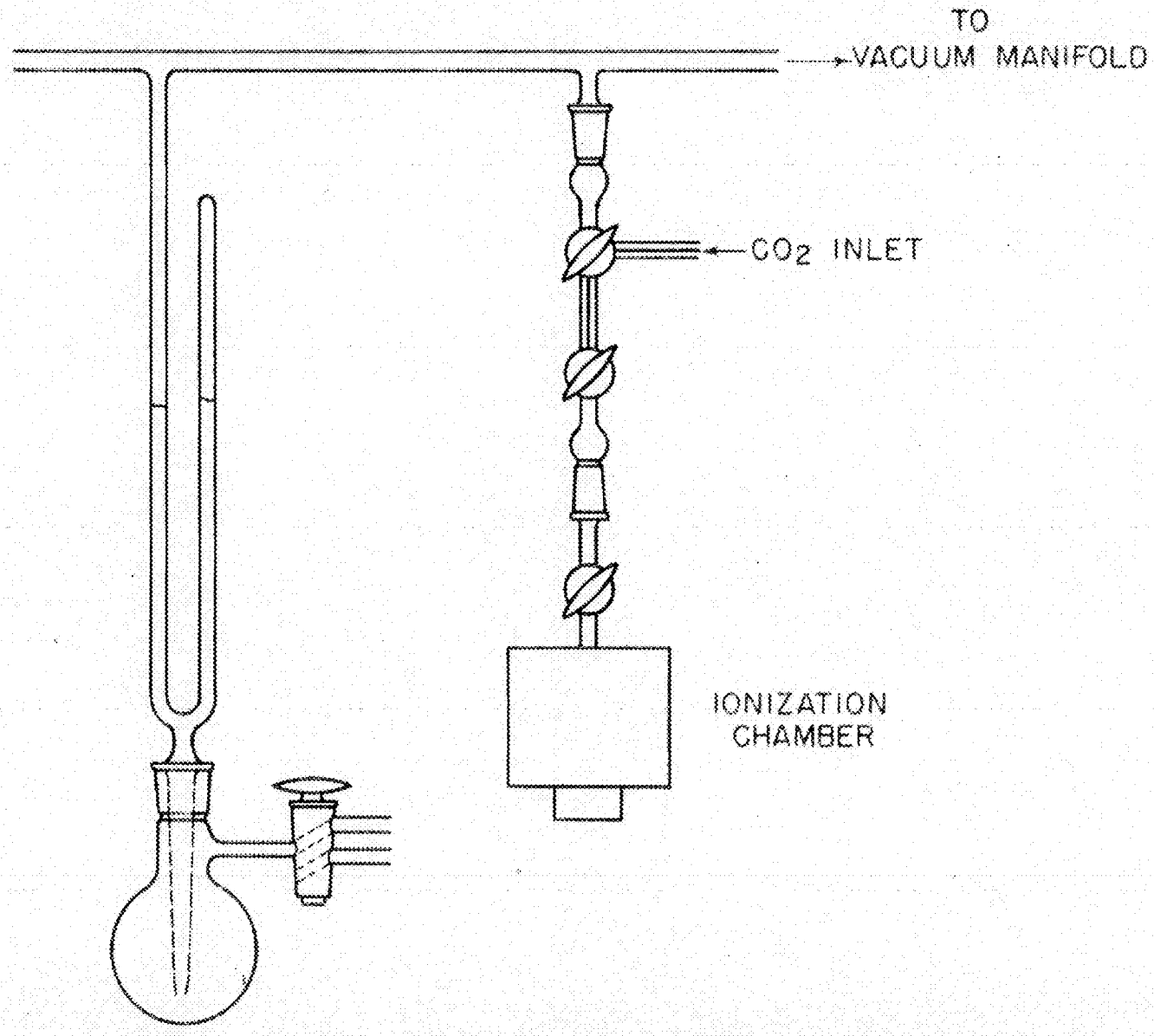

FIG. 16
VACUUM MANIFOLD AND APPARATUS
FOR ALIQUOTING GASES

This instrument should find use wherever the cost of the equipment or the lack of instrument service precludes the use of electronic equipment.

Figure 17 shows the circuit diagram of the electroscope as it is used with the ionization chamber. The hard-rubber insulator at *A* was replaced by a Teflon insulator, in which was inserted a threaded rod. Wire *B*, which originally touched the repelling post, *D*, only when the charging lever *E* was depressed, was bent so as to make permanent contact with *D*. Wire *C* was connected to a metal strip, *F* (mounted on a teflon block), which touched the center electrode of the ion chamber. The shell of the ion chamber, *G*, was connected to the electroscope chamber, *H*. The guard ring, *J*, of the ion chamber was connected to ground. The *B*-battery voltage supply and the charging lever of the electroscope were left unchanged.

Although insufficient data have been collected to define properly the limitations of the instrument, the following characteristics have been observed:

1. The reading scale is linear with respect to time over more than three-fourths of the range. For fairly low activities only small parts of the scale need be used.
2. The background time for full scale drift is about 24 hours.
3. The instrument has been used successfully for measuring activities in the range, 1-.001 microcuries. The most convenient range is .01-.1 microcuries. Drift rates in this range have been found reproducible to 0.1%.

A precaution which must be observed in the use of the instrument is the necessity of waiting for five to twenty minutes after the instrument has been charged before a reading is taken. In the case of low activity samples this time may be allowed after the chamber is inserted since the drift-rate is slow. For higher activity samples, the time should be allowed prior to insertion of the ion chamber.

STANDARDIZATION AND EVALUATION OF THE VIBRATING-REED ELECTROMETER

A. J. Weinberger and O. K. Neville

The standardization of ion current measurements as determined with the vibrating reed electrometer, by the use of National Bureau of Standards sodium

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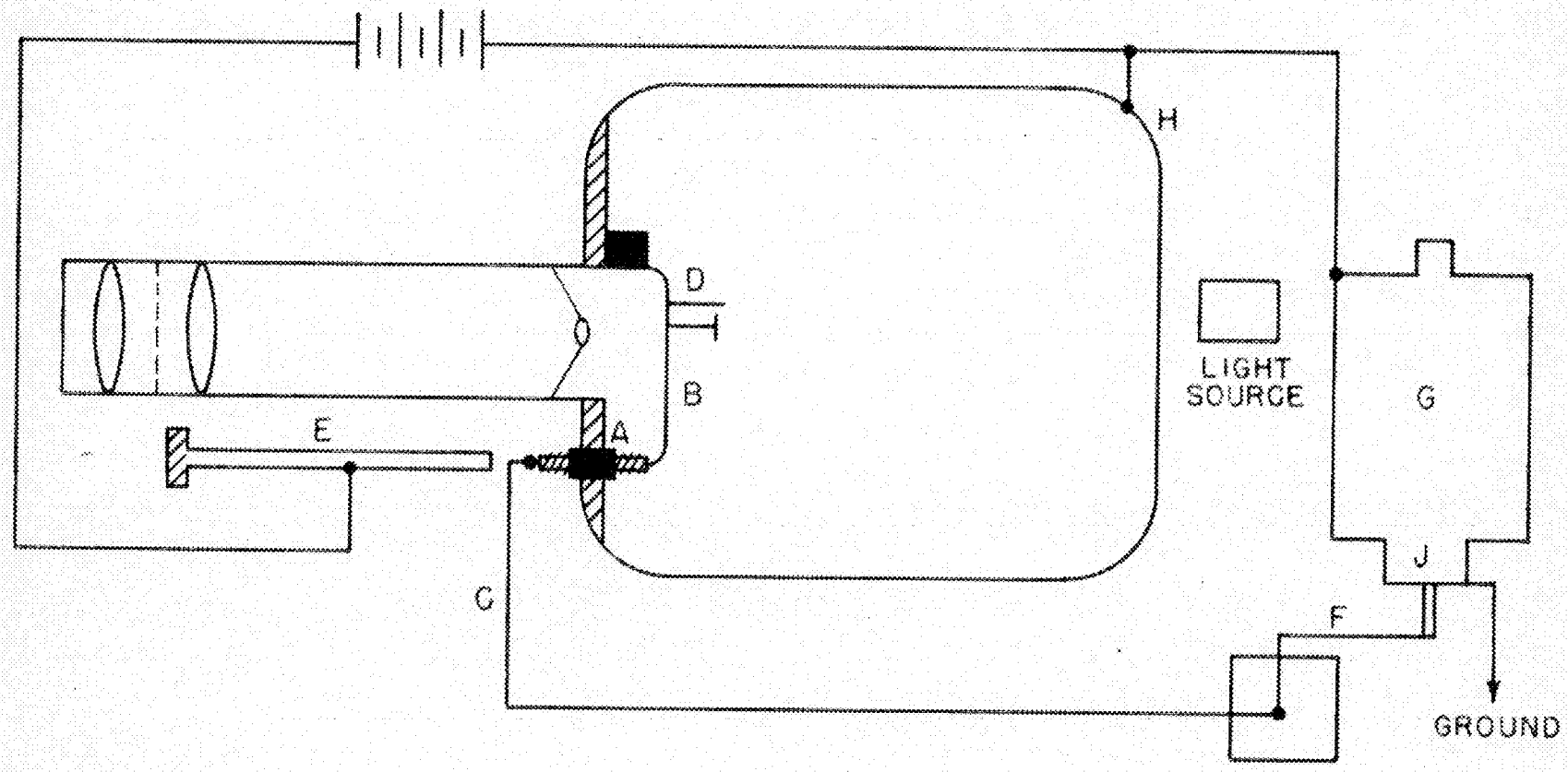

A. TEFLON INSULATOR
B. REPELLING POST WIRE
C. ION CHAMBER LEAD
D. REPELLING POST
E. CHARGING LEVER
F. METAL CONTACT
G. ION CHAMBER
H. ELECTROSCOPE SHELL
J. GUARD RING

FIG. 17
LAURITSEN ELECTROSCOPE – ION CHAMBER DIAGRAM

carbonate-C^{14} solution is now complete. As a part of this program, an evaluation has been made of the Model 30 Applied Physics Corporation electrometer together with the Borkowski[25] ionization chamber for the determination of carbon-14 beta-disintegration. Identification of some of the determinate errors and an estimation of the probable magnitude of the total error inherent in this counting method with various operating procedures has been accomplished.

In order to insure permanent standardization, ion chambers containing known carbon-14 dioxide samples have been prepared and an apparatus has been constructed with which working chambers can be filled with known volumes of standardized carbon dioxide for cross-calibration.

This latter operation has been found to be necessary due to slight, but significant, differences in the performance of various chambers of nearly identical volume. These differences which are of the order of two percent between chambers of one type, *e.g.*, stainless steel with a teflon insulator, have been shown to be as large as six percent between chambers of different materials, *e.g.*, gold plated brass versus stainless steel or between chambers having different insulator materials, *e.g.*, teflon versus fluorothene.

The factor, microcuries per ampere, determined with standard carbon-14 dioxide can be given with high precision only for a given chamber. A mean value of 2.1×10^{11} has been determined for stainless steel chambers of 250 ml volume having a fluorothene insulator.

Two gold-plated brass chambers of identical volume, having fluorothene insulators were found to give a 4 to 6% higher amperage for a given amount of activity than did the stainless steel chambers, although the internal consistency was good.

The intercalibration factors between various pairs of the three resistor settings and the two capacitances were also found to be dependent on the chamber being used.

The daily fluctuation of the apparent amperage of a standard chamber as measured by the electrometer was less than one percent. A sudden three percent decrease in apparent activity occurred once during the three-month period of careful observation. Daily fluctuations at the lower reading have remained approximately the same since that time.

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(25) Borkowski, C. J., *op. cit.*, MDDC-1099.

The maximum deviation from the arithmetic mean of a series of identical determinations over a long period of time has been shown to be less than 0.5% when a linear correction from a standard chamber measurement was applied.

INVESTIGATION OF ISOTOPE EFFECTS IN PHYSICAL PROCESSES

FRACTIONAL DISTILLATION

H. E. Heller and A. R. Jones

With the considerable amount of organic chemistry now being reported involving the use of various isotopes, it seemed desirable to investigate the extent to which these isotopes affect the ordinary laboratory operations, *i.e.*, is a fractionation of the isotopic molecule likely to occur which would modify or invalidate the results of tracer studies? To answer this question with regard to fractional distillation, a sample of tracer-level methanol-C^{14} was subjected to fractionation through a Podbielniak column. The sample was allowed to stand at substantially total reflux for 24 hours, and samples were then taken from the overhead and from the pot. Analyses of these samples are in progress.

PRECISE C^{14} ANALYSIS: THE ISOTOPE EFFECT DURING ADSORPTION

C. J. Collins, A. R. Jones and W. J. Skraba

Considerable isotope effects have been reported during chemical reactions involving molecules in which some of the carbon atoms are C^{14} or C^{13} labeled. For example, during the saponification of ethyl benzoate[26] containing C^{14} in the carbonyl group, the benzoic acid first formed was of lower specific activity (counts/minute/milligram counted as sodium benzoate) than the benzoic acid produced by complete saponification.

It seemed of interest to determine whether such effects occurred during treatment of these molecules by common laboratory procedures. Treatment with decolorizing carbon appeared to be the simplest choice.

Because of the importance and widespread use of decolorizing carbon for the purification of organic compounds, and further, because of its relation to the procedure of chromatographic adsorption, it can be seen that the presence

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

or lack of an isotope effect in this case had to be precisely determined if the dilution technique, involving as it does the careful purification of a radioactive derivative, was to be validated.

Within the limits of error of this procedure (± 0.2%) no isotope effect was observed.

Procedure. A dilute water solution of pure acetic acid containing a tracer quantity of acetic acid-1-C^{14} was prepared and the molal concentration was determined. Radioactive assays, expressed as microcuries per millimole (μc/mmol) were performed by the dry combustion of weighed aliquots of the solution taken with a special weighing pipette.

The remainder of the solution was heated to gentle reflux with an amount of decolorizing carbon sufficient (as determined by preliminary experiments) to adsorb about 10% of the acetic acid. The suspension was allowed to cool to room temperature and was then filtered through a fine-fritted funnel. The molality and radioactivity of the filtrate were determined as before.

Apparatus and Precautions. The combustion apparatus (Fig. 18) consisted of a 12 in. × 1¼ in. copper oxide-packed quartz tube with a fore-section of 12 mm tubing to decrease the dead space. The sample holder and a 6 in. roll of well oxidized copper screen were inserted in this space and the tube was swept with oxygen.

Interesting features are the pressure regulator and the spiral absorption trap. The efficiency of this trap, which is a self-acting pump, is so great that total absorption of carbon dioxide from mixtures of that gas and oxygen occurs over wide limits of concentration and sweep rate. The absorbent is about 1.3 ml of 1 *N* sodium hydroxide solution at room temperature. Amounts of carbon dioxide ranging from 0.05 to 5 mmoles have been quantitatively absorbed by this 1.3 mmoles of dilute base.

It has been found possible to burn liquid aliquots of any desired size by the use of a weighing pipette constructed of quartz as shown in the inset of Fig. 18. A micropipette syringe, roughly calibrated by scratches on the cylinder and piston, is used to suck the desired amount of liquid into the pipette. The capillary is emptied by continued withdrawal of the piston. The wet end is then wiped and briefly flamed. Oscillation of the piston quickly clears the capillary. With larger samples the liquid assumes positions shown by the dotted lines of the figure and is difficult to dislodge.

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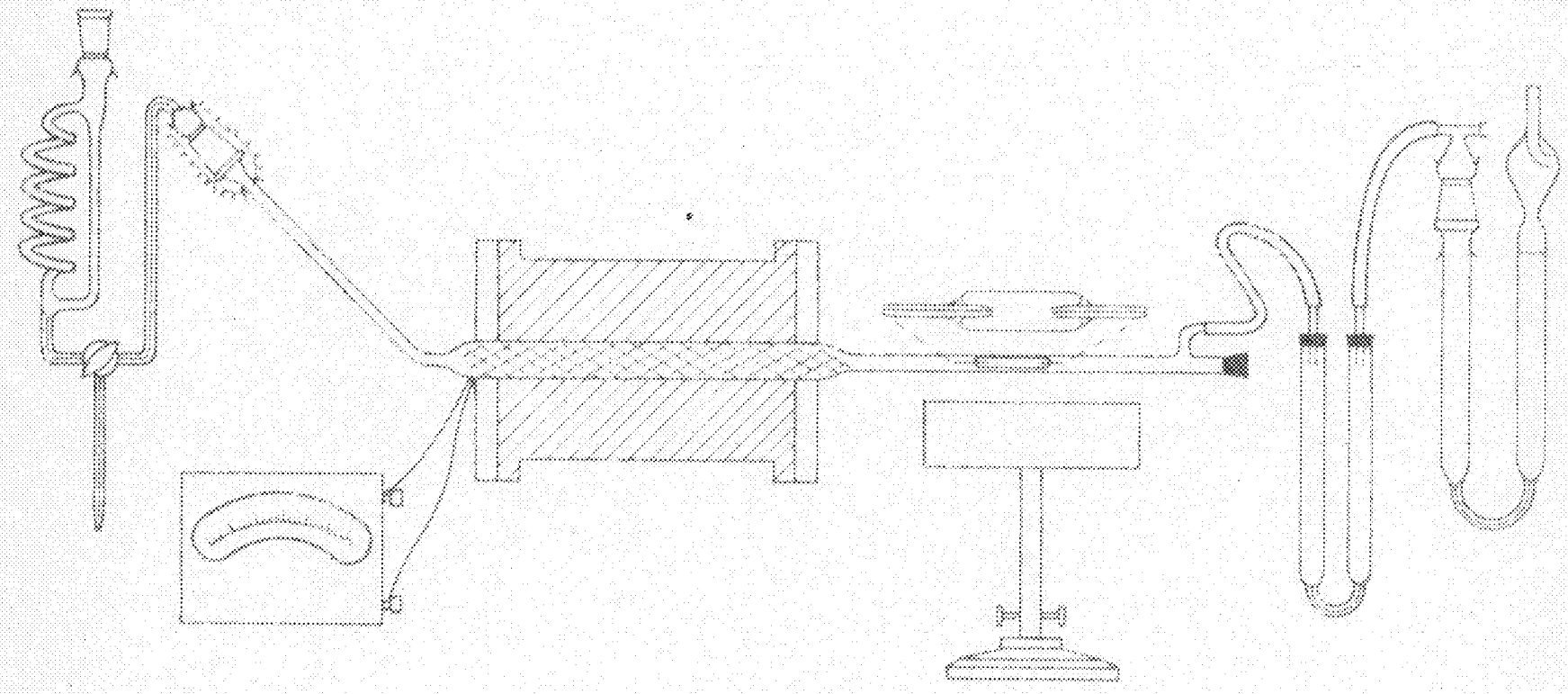

FIG. 18

DRY COMBUSTION APPARATUS FOR C^{14} SAMPLES

The pipette is weighed and placed in the furnace in a small platinum boat which serves both to hold it in place during weighings and to keep it from contact with copper oxide dust on the bottom of the combustion tube. If contact is not prevented the pipette gradually becomes opaque.

The sample is burned and the tube is swept with oxygen during twenty minutes. Then the three-way stopcock on the trap is closed; the entrance stopper is removed and a small (ca. 100 mg) piece of dry ice is quickly inserted. The stopper is replaced, the stopcock reopened, and sweeping is continued until the burst of carbon dioxide has been absorbed as shown by a decrease in bubble size soon followed by a return to normal bubble size.

The absorbing solution is transferred to a bottle containing a glass enclosed magnetic stirrer bar inserted in a piece of thin rubber tubing. The trap is washed by allowing it to remain filled with distilled water for a moment and then adding this to the bottle also.

Decomposition of the carbonate solution was performed in the apparatus shown in Fig. 19 with 85% phosphoric acid. After heating the acid solution to boiling, inactive carbon dioxide was bubbled through the solution until the previously evacuated ionization chamber was filled to room pressure. The pressure regulator which allows this transfer of gas from room pressure to an evacuated chamber is described by O. K. Neville.[27]

The radioactive assays, expressed in terms of microcuries per millimole (μc/mmole) were performed on a 450 cycle vibrating reed electrometer by measurements of the rate of drift (time required to charge a condenser to 70 millivolts).

Data. A solution of 2 g of hot acetic acid in 20 ml of distilled water was prepared. Two aliquots were titrated with 0.10100 *N* sodium hydroxide solution to a phenolphthalein endpoint. 2.0952 g required 33.12 ml base; thus 1.5966 meq/g. The average, 1.5950 meq/g of solution, was used for further calculations.

Two aliquots were burned and the average time required to change a 565×10^{-12} farad condenser to 70 millivolts was determined. Using the formula

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(27) Neville, O. K., "C^{14} Tracer Studies in the Rearrangement of Unsymmetrical α-Diketones: Phenylglyoxal to Mandelic Acid," *Am. Chem. Soc. J.* 70, 3499 (1948).

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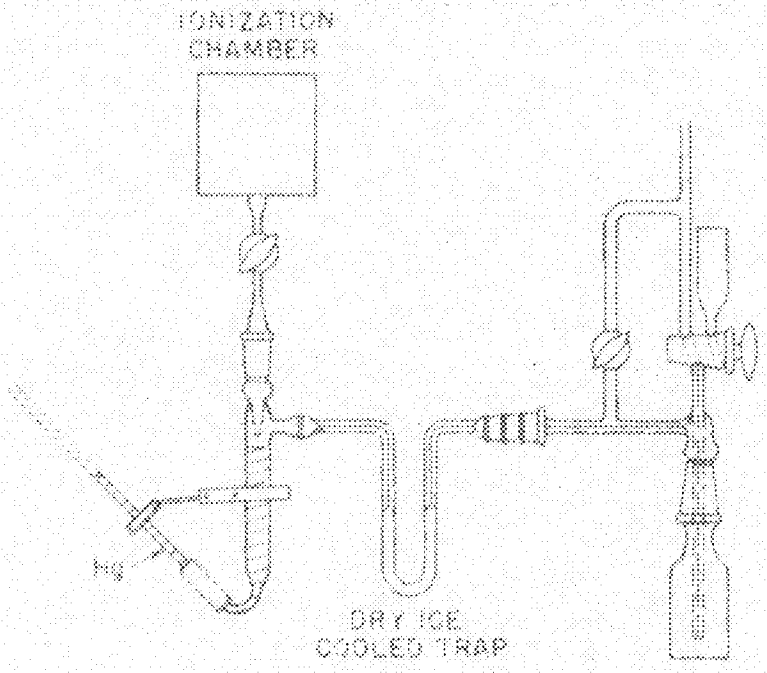

FIG. 19
DECOMPOSITION APPARATUS

$$\mu c/meq = \frac{565 \times 10^{-12} \text{ farads} \times 70 \times 10^{-3} \text{ volts}}{1.42 \times 10^{-16} \text{ amps/dis/sec} \times 3.7 \times 10^{4} \text{ dis/sec}/\mu c \times \text{meq burned} \times t_{sec}}$$

it was determined and calculated that for aliquots of

94.59 mg, t = 49.0 sec and $\mu c/meq$ = 1.0205

114.35 mg, t = 40.6 sec and $\mu c/meq$ = 1.0166

The remainder of the solution was heated just to reflux with 1.10 g of Darco G-60 decolorizing carbon and allowed to stand for five minutes. It was then cooled to room temperature and filtered through a fine glass fritted funnel.

Aliquots were again removed and titrated with standard base:

2.1248 g required 31.29 ml base; thus 1.4874 meq/g

2.0699 g required 30.45 ml base; thus 1.4858 meq/g.

The average, 1.4866 meq/g of solution, was used for further calculations.

Three aliquots were burned and the activities calculated. For

93.10 mg, t = 53.6 sec and $\mu c/meq$ = 1.015

98.68 mg, t = 49.9 sec and $\mu c/meq$ = 1.028

92.02 mg, t = 54.0 sec and $\mu c/meq$ = 1.019.

The average activity before treatment with decolorizing carbon was 1.019 $\mu c/meq$. The average activity of the acetic acid after partial adsorption was 1.021 $\mu c/meq$. The average of all five analyses was 1.020 with a standard deviation of 0.0022. Thus, we may conclude that within the error of the determinations made above there was no isotope effect.

CHEMISTRY OF SEPARATIONS PROCESSES

VOLATILITY STUDIES

P. A. Agron E. G. Bohlmann

The studies on the interaction of thorium fluoride and the phosphorus fluorides have been continued. While some evidence of interaction is indicated by experiments involving contact between the liquid or gaseous phosphorus fluorides and thorium fluoride, no data suggesting the formation of a complex compound stable above room temperature have been obtained. However, physical examinations of thorium fluoride which has been exposed to phosphorus trifluoride or phosphorus pentafluoride indicate a substantial reduction in ultimate particle size as a result of such contact. Since such disruption of thorium fluoride lattice might be of interest in overcoming the sintering problems encountered by F. T. Miles and co-workers in their studies of a thorium fluoride-fluorine blanket, this development is being examined carefully. The data available at the present time do not completely establish the extent of the particle break-up phenomena, so they will be reserved until a later report.

SOLVENT EXTRACTION PRINCIPLES AND APPLICATIONS

INORGANIC SPECIES EXTRACTED IN SOLVENT EXTRACTION

O. E. Myers R. W. Stoughton

A thorough study of the distribution of nitric acid between its aqueous solutions and TBP solutions has been undertaken in the hope that the resultant information might provide a better understanding of the mechanism of TBP extraction. A number of correlations have been made which seem to be worth reporting here, although a detailed mathematical analysis has not yet been obtained.

1. There exists a complex of the form $HNO_3 \cdot TBP$. This is based on the evidence that a graph of the logarithm of the equilibrium formal nitric acid concentration in the organic phase, denoted as log $\{HNO_3\}^{eq}_{org}$, plotted against log $\{HNO_3\}^{eq}_{aq}$ shows an inflection point at very nearly a 1:1 mole ratio of $HNO_3 : TBP$, irrespective of diluent. There appears to be no other simple explanation for an inflection point in this region of the curve than the existence of the 1:1 complex. (Diluents which have been tested are benzene, carbon tetrachloride, and chloroform.)

2. Equilibrium is attained rapidly. There is no evidence for incomplete distribution in experiments with a shaking time of only thirty minutes.

3. There is a decrease in the distribution coefficient,

$$D_a^{\,0} = \{HNO_3\}^{eq}_{org}/\{HNO_3\}^{eq}_{aq}$$

with increasing temperature (25 to 50°C) in the region $0.005\ f < \{HNO_3\}^{eq}_{aq} < 5f$, at least when no diluent is present. This is the region in which the effects of the $HNO_3 \cdot TBP$ complex are most pronounced.

4. The amount of HNO_3 extracted in the region where the 1:1 complex predominates (0.005 to 5 f) is markedly affected by the *nature* of the diluent. For otherwise identical conditions benzene permits the greatest extraction, carbon tetrachloride is second, and chloroform permits much less extraction.

5. Above the inflection point at a 1:1 mole ratio (which occurs at ca. 9 f $\{HNO_3\}^{eq}_{aq}$ for pure TBP and at a lower aqueous concentration for dilute

TBP) the situation appears to be quite complicated. The order of effectiveness of the three diluents seems to be reversed, and a concentration of more than *three* nitric acid molecules per TBP molecule has been obtained by equilibrating ten volume percent TBP in chloroform with strong nitric acid. From 25° to 50° there is no temperature effect in this region. The system is further complicated by nitration of the benzene diluent, and a large part of these data must be disregarded. Also, discoloration has been observed in chloroform solutions.

6. Below the range of the $HNO_3 \cdot TBP$ complex the data may be accounted for on the basis of a complex with different characteristics. The TBP dependence is no longer simple first order, and the effectiveness of diluent is altered.

The accompanying table records the magnitudes of the effects cited above.

TABLE I

Organic Phase Formal Concentrations of HNO_3 in Equilibrium with Various Concentrations of Aqueous HNO_3

$\{HNO_3\}^{eq.}_{aq.}$	0.001	0.01	0.10	1.00	10.0
100% TBP, 25°	0.0071	.0129	.0475	0.90	3.9
100% TBP, 50°	0.0071	.0122	.0326	0.77	3.9
50% TBP, C_6H_6	0.0027	.0078	.0162	0.40	2.1
50% TBP, CCl_4	-	.0075	.0140	0.30	2.0
50% TBP, $CHCl_3$	0.0025	.0072	.0080	0.072	(2.0)
25% TBP, C_6H_6	-	.00305	.0053	0.135	0.98
25% TBP, CCl_4	-	.00245	.00450	0.092	0.98
25% TBP, $CHCl_3$	-	.00280	.00355	0.021	1.10
10% TBP, C_6H_6	-	.00075	.0023	0.040	(0.50)
10% TBP, CCl_4	-	.00055	.0009	0.027	0.42
10% TBP, $CHCl_3$	-	.00102	.0014	0.008	0.55

It is felt that data on water solubilities in these solutions will help to resolve this problem and this work is in progress. Attempts to obtain a

complete mathematical equation have so far failed because of inability to separate the effects of the $HNO_3 \cdot TBP$ complex and the more complicated species at higher concentrations. Up to 0.2 $f\ \{HNO_3\}_{aq}^{eq}$ in the pure TBP system at 25°C it is possible to express the data by the following equation:

$$\{HNO_3\}_{org}^{eq} = \frac{15.9\sqrt{x}}{1180\sqrt{x+1}} + \frac{5.1\,x}{1+1.5\,x}$$

where x represents the activity product $(f \pm \{HNO_3\}_{aq}^{eq})^2$ with no correction for dissolved organic material. Activity coefficient data were derived from the Landolt-Bornstein Tables (III, p. 1245) for $\gamma_{\pm}$ and density data from Lange's Handbook (p. 1127).

EXTRACTION OF ZIRCONIUM AND HAFNIUM INTO TTA-BENZENE

J. P. McBride R. W. Stoughton

Summary. Investigation of the partition of Zr^{95} tracer between TTA(thenoyl trifluoroacetone)-benzene has continued. Extraction data obtained for HCl-NaCl solutions at constant μ equal to three and of various HCl concentrations show an inverse dependence of at least 3.6 power on acid above 0.7 *M* indicating that more than half the zirconium is in the form of Zr^{+4} and/or various complexes of Zr^{+4} with Cl^- ion.(1) Below 0.7 *M* hydrolytic species of lower charge become increasingly prominent. Distribution data for 1 *M* HCl ($\mu = 1$) and 3 *M* HCl ($\mu = 3$) as a function of TTA concentration show a direct dependence of nearly fourth power on TTA concentration. Equilibrium was approached from both sides in all the above experiments and consistent results were obtained. Further studies on the extraction of both Zr and Hf from chloride systems are planned.

Attention was also directed during the quarter to experiments set up to determine the efficiency of Nb stripping from TTA-benzene solutions in which it had been allowed to grow by the decay of Zr^{95}.(2) A discrepancy has been noted between the radiochemical assay of the organic solutions involved and

(1) McBride, J. P., "The Extraction of Hafnium from Nitric Acid Solutions with Thenoyl Trifluoroacetone," ORNL-303, p. 8 (Aug. 9, 1949).

(2) McBride, J. P. and Stoughton, R. W., "Extraction of Zirconium and Hafnium into TTA-Benzene," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950*, ORNL 685, 102 (June 16, 1950).

results predicted by the beta counting technique used to determine the fractional stripping (see below). The incomplete stripping reported last quarter[3] may or may not be correct. The use of a scintillation type gamma counter in this study is projected.

The Stripping of Nb from TTA-Benzene. The four equivolume mixtures of 0.06 *M* TTA-benzene and 1 *M* HCl, containing pure Zr^{95} tracer initially, which were set up last quarter to test the efficiency of Nb stripping upon continuous mixing were allowed to equilibrate for a total of 70 days. Aliquots of each phase were taken at intervals, evaporated on watch glasses, and counted on the second shelf of a standard beta chamber. Since the conditions were such that all Zr activity would remain in the organic phase, it was anticipated that the fraction of Nb stripping could be determined by comparing the beta activity appearing in the aqueous phase with the estimated total Nb activity in the system, organic plus aqueous. The total Nb activity was calculated by determining the difference between the count (Zr + Nb) at time, *t*, of an aliquot of the pure stock mounted at $t = 0$ and the estimated activity due to Zr at time, *t* (*i.e.*, equal to the count of the aliquot at $t = 0$ multiplied by the decay factor of Zr). Samples taken at 19, 40 and 70 days indicated the Nb stripping to be only 50% complete. However, radiochemical analysis by the analytical section of samples of the organic phases taken at the end of the equilibration showed them to contain only an amount of Nb which should have grown in between the time of sampling and the time of analysis. The reason for the discrepancy is unknown but may lie in the low beta counting efficiency of Nb which is one-twentieth that of the Zr. In addition, the low energy Nb beta may have led to greater counting errors because of self absorption and spread of the samples on the counting plates than was at first anticipated. It is planned to continue the investigation when a scintillation type gamma counter becomes available. On such an instrument the relative counting efficiency of Nb to Zr will be essentially 1 to 1 and the preparation of counting samples less critical.

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(3) McBride, J. P. and Stoughton, R. W., *op. cit.*, ORNL 685.

ELECTROCHEMISTRY

ELECTRODEPOSITION OF RUTHENIUM

J. C. Griess, Jr.

Introduction. Previous studies concerning the electrodeposition of traces of ruthenium have shown that complete electrodeposition could not be obtained at potentials which had given complete deposition at higher concentrations. Experiments on the so called "platable" portion of the ruthenium have been reported.[4] The present report covers the work that has been completed to date concerning the properties of the "unplatable" fraction of the ruthenium. Mercury and platinum black cathodes have been used to deposit the "unplatable" ruthenium.

1. Deposition of Ruthenium on a Mercury Cathode. In an acid solution it is impossible to increase the potential of a platinum cathode to high values because hydrogen evolution becomes excessive. Since mercury has a high hydrogen overvoltage, it is possible to increase the potential of a mercury cathode to quite high values before hydrogen evolution becomes appreciable. Thus an electrodeposition with mercury cathode was carried out in order to study the deposition of the "unplatable" ruthenium as a function of cathode potential.

The "platable" portion of the ruthenium is reduced by metallic mercury in an acid solution; therefore, before electrolyzing with a mercury cathode the ruthenium that was easily reduced was removed by electrolyzing the solution with a bright platinum cathode. The ruthenium that remained after electrolysis was not reduced by mercury.

The solution that was used for this study was 5×10^{-8} *M* in ruthenium nitroso chloride and 0.1 *M* in hydrochloric acid. After an electrolysis with a bright platinum cathode 76% of the ruthenium remained in solution. A 10 ml aliquot of this solution was placed in a cell containing a mercury cathode and a micro platinum anode. The cathode potential with reference to a saturated calomel electrode (SCE) was maintained for one hour at a given potential and then changed to a more negative potential for a similar period of time.

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(4) Lietzke, M. H. and Griess, J. C., Jr., "Electrodeposition of Ruthenium," *Chemistry Division Quarterly Report for Period Ending March 31, 1950*, ORNL-685, 104 (June 16, 1950).

The results of this experiment are given in Table II.

TABLE II

The Amount of Ruthenium Deposited on a Mercury Cathode at Various Potentials

POTENTIAL vs. SCE	PERCENT DEPOSITED
-0.60	0
-1.00	0
-1.30	0
-1.50	61
-2.00	99

The data are such that it is impossible to determine either the potential at which deposition began or the minimum potential at which it was essentially complete. All that can be said at present is that somewhere between -1.30 and -2.00 v vs. SCE complete deposition can be obtained.

At the completion of the electrolysis the mercury was separated from the solution and a count of the mercury indicated that essentially all of the ruthenium was present on the mercury surface. Samples of mercury from below the surface showed little or no activity. Hence it was concluded that even very small amounts of "ruthenium" are insoluble in mercury.

2. Deposition of Ruthenium on Platinum Black Electrodes. Experiments reported in the last quarterly report[5] indicated that there was relation between the percent ruthenium deposited and the hydrogen overvoltage of the metal on which it was deposited, the lower the overvoltage the greater the percent deposited. The results of this experiment suggested the deposition of ruthenium on a platinum black electrode.

Two different 10 ml aliquots were electrolyzed with platinum black cathodes. One was 5×10^{-8} *M* ruthenium nitroso chloride solution in 0.1 *M*

(5) Lietzke, M. H. and Griess, J. C., Jr., *op. cit.*, ORNL 685.

hydrochloric acid and the second was a 5×10^{-8} *M* ruthenium nitroso perchlorate solution in 0.1 *M* perchloric acid. Each solution was electrolyzed for three hours at cathode potentials of -0.40 v vs. SCE.

From the hydrochloric acid solution 95% of the ruthenium was deposited and from the perchloric acid solution 90% was deposited. In each case only 30-40% of the ruthenium could be deposited under the same conditions on bright platinum electrodes.

In order to determine the behavior of the non-platable fraction in the absence of the platable portion, aliquots of each of the above solutions were electrolyzed on smooth platinum electrodes and the ruthenium which did not deposit was subjected to a second electrolysis using platinum black electrodes. In each case the cathode potential was -0.40 v vs. SCE and during the course of the electrolysis samples were taken to obtain the rate of plating.

The results are given in Table III.

TABLE III

The Rate of Plating of Ruthenium from Ruthenium Nitroso Chloride and Ruthenium Nitroso Perchlorate on Platinum Black Electrodes

TIME OF ELECTROLYSIS (Minutes)	Ru DEPOSITED PERCHLORATE (Percent)	Ru DEPOSITED CHLORIDE (Percent)
30	74	55
60	90	75
90	92	88
120	94	93
150	94	95
180	94	96

The rate of plating appeared to be faster from the perchlorate solution than from the chloride solution, but the total amount of ruthenium plated from each solution was nearly the same. Since hydrochloric acid in the presence of oxygen is capable of dissolving platinum black, the slowness of the rate of deposition from the hydrochloric acid solution may have been due to a slow dissolution of the platinum black. For this reason all other experiments were carried out in perchloric acid media.

Since the possibility existed that the ruthenium was not actually electrodeposited but rather adsorbed on the very large surface of the platinum black cathode, two electrolyses were performed to determine the amount of ruthenium that was apparently adsorbed and the amount that was actually electrodeposited. The procedure was as follows: 20 ml of a 5×10^{-8} *M* ruthenium nitroso perchlorate solution in 0.1 *M* perchloric acid were electrolyzed at -0.60 v vs SCE using a bright platinum electrode. After equilibrium was reached 68% of the ruthenium remained in solution. This solution was then divided into two equal portions and 10 ml were placed in each of two cells containing platinum black cathodes. One cell was merely stirred for three hours and the other was electrolyzed at -0.4 v vs. SCE for the same length of time. At the completion of this time the cells were reversed, *i.e.*, the cell that had been electrolyzed was disconnected and stirred, and the cell that had been stirred was connected and electrolyzed. During the stirring and the electrolysis samples were taken.

The results are shown in Table IV.

TABLE IV

The Percent Ruthenium Remaining in Solution After Electrolyzing and Stirring a 5×10^{-8} *M* Ruthenium Nitroso Perchlorate Solution in 0.1 *M* Perchloric Acid Using Platinum Black Cathodes

TIME (Minutes)	PERCENT IN SOLUTION STIRRING ONLY	PERCENT IN SOLUTION ELECTROLYSIS
15	88	49
30	84	26
45	85	16
60	70	10
90	69	7.8
120	69	5.7
150	68	5.7
180	68	5.7
	ELECTROLYZED AT THIS POINT	STIRRED AT THIS POINT
15	33	3.5
30	19	3.2
45	13	3.8
60	8.8	4.0
90	5.7	-
120	4.1	-
135	4.7	-
150	4.7	-

At this point it should be mentioned that the potential of the platinum black with respect to the SCE was approximately -0.24 v before stirring the solution but rapidly changed approximately + 0.70 v as soon as stirring began. During the electrolysis the cathode potential was held constant at 0.40 v.

It should be noted that there was a certain amount of ruthenium removed from solution apparently by adsorption on platinum black even after the solution had been electrolyzed to completion. Furthermore, if the log of the percent remaining in solution is plotted against time, the heights of the adsorption curves are nearly equal and the heights of the electrolysis curves are nearly equal.

It thus appears that in the so called "unplatable" fraction of the ruthenium there are at least two species present, one that appears to plate on a platinum black electrode which is negatively charged with respect to the SCE and one that is either plated or adsorbed on a platinum black electrode which is positive with reference to the SCE.

Discussion and Future Work. The results of the plating experiments on a mercury cathode are straightforward, and, while incomplete, indicate that complete deposition is possible at sufficiently negative potentials. Future work in this system will involve obtaining a deposition curve (*i.e.*, percent plated vs. cathode potential).

The electrodeposition of ruthenium on platinum black cathodes has yielded results which are interesting, but at present insufficient data have been collected to be certain of any interpretation. It has definitely been shown, however, that essentially complete deposition from very dilute ruthenium solutions can be obtained on a platinum black electrode at cathode potentials as low as -0.40 v vs. SCE, and perhaps even at lower potentials.

Since the hydrogen overvoltage of platinum black is very low at low current densities and since previous work has shown that the lower the hydrogen overvoltage of the metal on which ruthenium is deposited the greater is the amount deposited, it is suggested that the deposition of the "unplatable" fraction of ruthenium is perhaps a hydrogen reduction which is catalyzed by the metal surface. If this is true, the answer to the question of why the deposition of ruthenium on smooth platinum electrodes is complete above the monoatomic layer region and incomplete below it could be given. One would have to assume that if more than a monolayer of ruthenium atoms were laid

down on an electrode the catalytic properties of the ruthenium during the deposition process would be similar to those of platinum black. Hence the hydrogen present on the ruthenium cathode would be capable of reducing the "non-platable" fraction and essentially complete deposition would be achieved. On the other hand if the ruthenium concentration is such that less than a mono-layer of ruthenium atoms is deposited, the ruthenium atoms are plated on the smooth platinum surface and not on an active ruthenium surface. Thus the catalyst behavior of the ruthenium is not exhibited and deposition is in-complete.

The above statements are largely speculation and future work will be directed at either establishing or disproving them.

ION EXCHANGE

LITHIUM ISOTOPE SEPARATION

J. H. Gross R. E. Wacker
G. E. Boyd J. F. Neely, Jr.
E. G. Bohlmann

Introduction. The proposal to use metallic lithium as a power reactor coolant requires the development of a low cost process for enriching Li^7 from its natural abundance of 92.5 atom percent to an abundance of at least 99.93 atom percent, in order to reduce the thermal neutron capture cross section to a value acceptable for reactor design. The capture cross section of Li^7 is reported[6] as 0.033 b, while that of Li^6, the isotope to be removed, is[7] 870 b.

Investigation of the use of ion exchangers to effect the required enrichment has continued during the quarter. Initial phases of the work have been reported previously.[8]

Experimental. Two experiments using different ion exchangers have been completed. Operational conditions for both were substantially the same to permit some comparison of the exchangers. In each case a resin bed 20 cm^2 in cross section was operated at a temperature of 30°C and a flow rate of 0.18 $ml/cm^2/min$, using 0.1 *M* HCl to develop a band of 240 milliequivalents of Li^+ through the hydrogen-form resin bed. In the first experiment, the exchange resin was Nalcite HCR, a sulfonated polystyrene exchanger of nominal 10% cross-linkage manufactured as standard Dowex 50 and marketed by the National Aluminate Company under the Nalcite name. The bed depth in this column was 146 cm, and the resin particle size was approximately -200 + 70 microns, wet hydrogen form. In the second experiment the exchange resin was a specially prepared Dowex 50 of 16% cross-linkage. The bed depth was 128 cm, and the particle size range was the same as in the first column. The results of these experiments are summarized in Table V and discussed thereafter.

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(6) Way, K. and Haines, G., *Thermal Neutron Capture Cross Sections for Elements and Isotopes*, AECD 2138 (Oct. 11, 1948).

(7) *Ibid.*

(8) Gross, J. H., Neely, J. F., Jr. and Boyd, G. E., "Lithium Isotope Separation," *Chemistry Division Quarterly Progress Report for the Period Ending March 31, 1950*, ORNL 685, 113 (June 16, 1950).

TABLE V

Mass Analyses, Columns II and III

	TOTAL DEVELOPED Li (Percent)	Li^7 (atom percent)
Column II	0.0 - 0.05	94.397 ± 0.021
Nalcite HCR	0.49 - 0.55	93.779 ± 0.012
	3.75 - 3.85	93.323 ± 0.012
	11.3 - 12.7	92.893 ± 0.023
	26.7 - 26.9	92.796 ± 0.010
Column III	0.0 - 0.30	92.840 ± 0.016
16% cross-linked	0.30 - 0.44	92.455 ± 0.042
Dowex 50		
Feed LiCl	-	92.476 ± 0.042

A simple method for continuously registering Li^+ concentration in the column effluent was used in the experiments described above. The conductivity of the effluent was continuously recorded on a strip-chart recorder as the effluent passed through a small jacketed conductivity cell attached to the bottom of the column. With constant total ionic concentration in the effluent, the change in Li^+ concentration is inversely proportional to the change in conductivity in passing from pure HCl to pure LiCl in solution. The conductivity recording equipment used consequently gave a nearly linear trace of Li concentration in the eluted band. The trace was calibrated by gravimetric analysis of a number of the small samples into which the effluents were divided. Conductivity measurement is not sufficiently sensitive to detect the first appearance of Li at very low concentrations; for this purpose it was necessary in these experiments to use frequent flame tests.

Discussion. The rate-determining process in the type of column operation used in these experiments is diffusion of ions through the resin. It is known that increasing the cross-linkage in the resin from 10% to 16% decreases

the diffusion coefficient one to two orders of magnitude.[9] In column II, Nalcite HCR, the effluent volume-concentration plot had the general shape to be expected for operation close to equilibrium, since the diffusion coefficient for this resin was sufficiently large to permit nearly complete equilibration at the flow-rate used. However, with 16% cross-linked Dowex 50 the diffusion coefficient was much lower, with the result that Column III operated far from equilibrium and the eluted band was diffuse.

In view of the poor enrichment of isotopes obtained with column III, as compared with the results in column II, it appears that the ion-exchange separation of isotopes may not be dependent upon a diffusion rate process, but rather upon a difference in isotopic chemical equilibrium constants.

The five mass analyses for column II show enrichment of Li^7 in an appreciably wide portion of the eluted band. From these data, a necessarily rough estimate of the average composition of the first 30% of the eluted band is 93.0% Li^7. This figure is not considered highly significant at this time, since two few mass analyses have been obtained for good accuracy in the estimate.

Nearly all mass spectrometer time available to us is now being used for further analyses in the Li^7-enriched region of the column II effluent. Analysis of the column III effluent has been abandoned, and analyses in the Li^6 enriched region in column II have been minimized.

Future Work. A third experiment similar to the two described above has been started. The exchanger being used is from special bath, XE-97 and is a carboxylic exchange resin manufactured by Rohm and Hass Company of the IRC-50 type. This experiment will be continued, and at least one column experiment with Nalcite HCR at higher temperature will be conducted.

One member of the group will spend some time assisting in the development by the Analytical Chemistry Division of a mass analysis procedure based on the counting of tritium from neutron-irradiated samples of lithium salts.

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(9) B. A. Soldano, private communication.

ION-EXCHANGE EQUILIBRIA: DISTRIBUTION OF INDIFFERENT ELECTROLYTE BETWEEN AQUEOUS SOLUTIONS AND ORGANIC ION-EXCHANGE POLYMERS

G. E. Boyd Q. V. Larson

The presence of diffusible anions (Cl^- and Br^-) in cation exchangers and diffusible cations (Na^+) in anion exchangers has been demonstrated using activation analysis techniques. In general, the concentration of diffusible anions (or cations) is less in the water of gelatin of the exchanger than in the external solution, as required by the Gibbs-Donnan equations assuming a membrane equilibrium. The relative exclusion was found to be greater the greater the cross-linking of the exchanger. At constant cross-linking the Br^- ion concentration inside was always less than Cl^- ion when the external molalities of HCl and HBr were the same. Also, the exclusion of diffusible Cl^- ion was greater with the Li form than with the H-form of the cation exchanger when the external solutions were LiCl and HCl respectively. The simple Donnan equations did not describe the quantitative data even when changes in volume due to swelling were taken into account. In connection with these studies moisture contents of the variously cross-linked preparations of cation exchanger were measured as a function of external electrolyte concentration. A simple relationship between the moisture content of the H-form in equilibrium with pure water and the degree of cross-linking was found. This was:

$$\frac{g\ H_2O}{g\ dry\ HR} \simeq \frac{2.380}{\sqrt{X}},$$

where X is the nominal percent divinyl benzene (DVB) content. An interesting additivity relation connecting the specific volume and the moisture content was also observed. The data on which these conclusions are based are given in Fig. 20 through 24.

ION EXCHANGE KINETICS: THE SELF-DIFFUSION OF IONS IN AND THROUGH ORGANIC ION-EXCHANGE POLYMERS

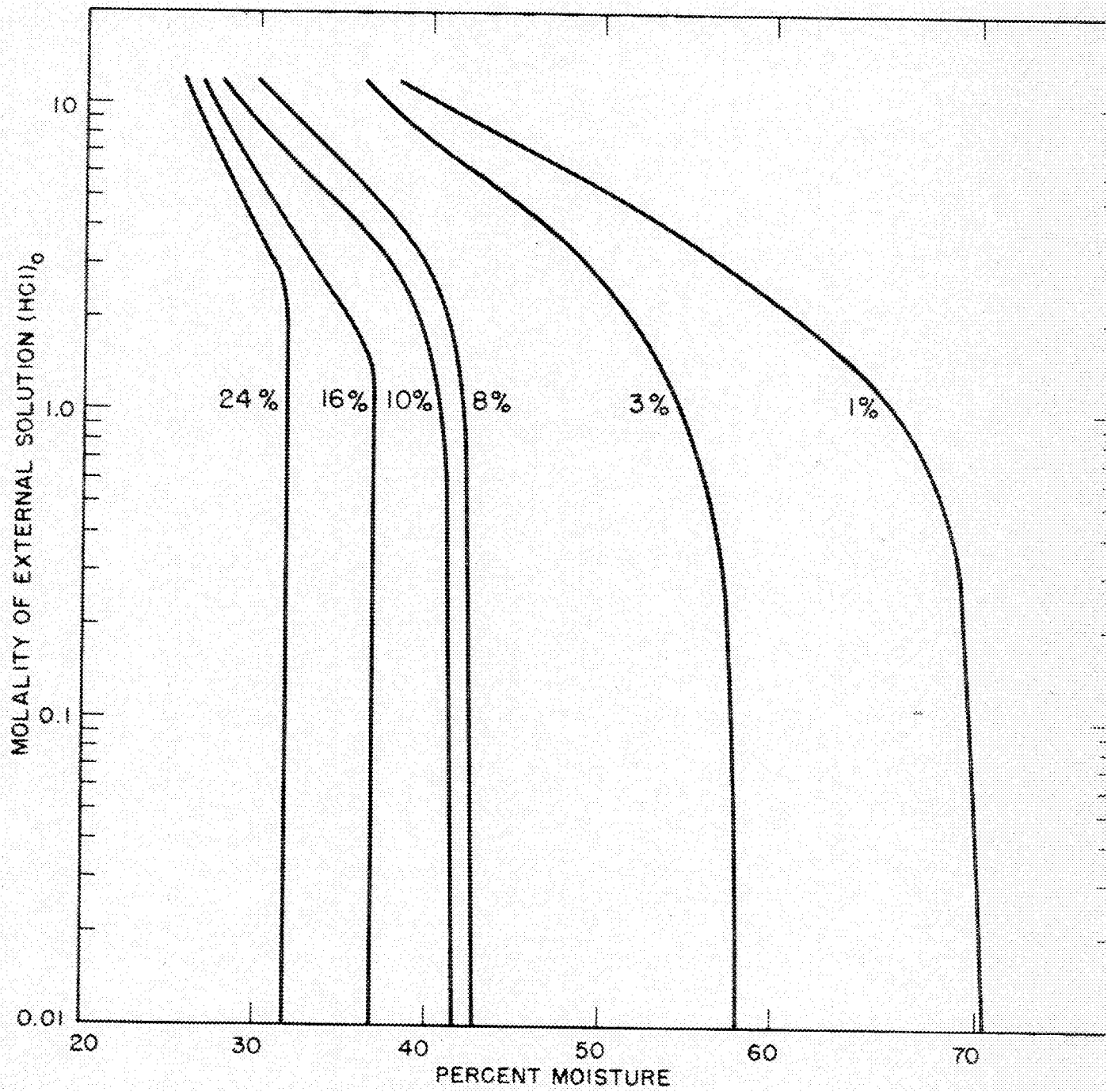
B. A. Soldano G. E. Boyd

Apparent self-diffusion coefficients for a variety of cations and anions in polystrene-divinyl benzene base cation and anion exchangers respectively

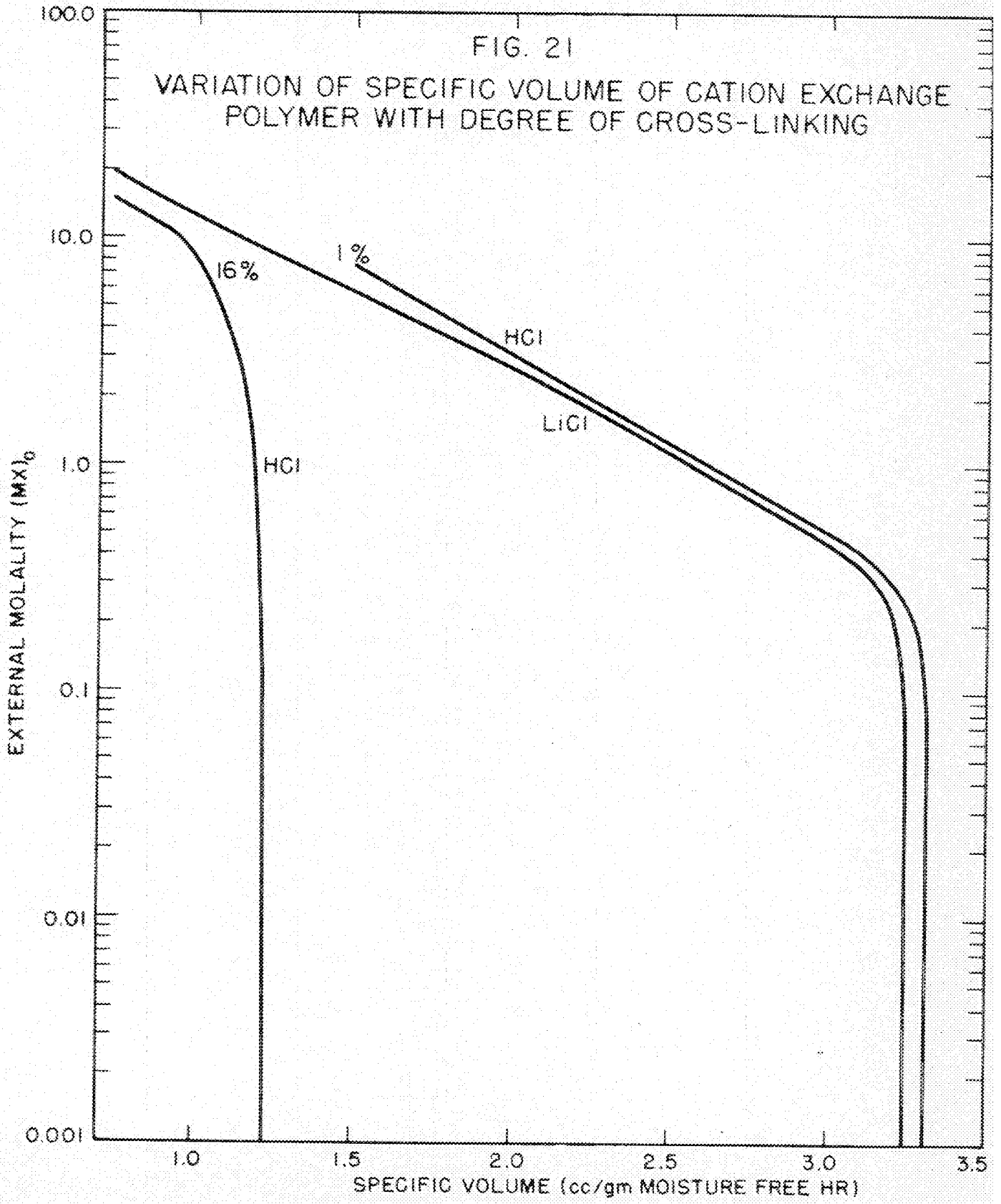
NOT CLASSIFIED
DWG. 9266

FIG. 20

DEPENDENCE OF MOISTURE CONTENT ON CROSS-LINKING AND EXTERNAL ELECTROLYTE CONCENTRATION



NOT CLASSIFIED
DWG. 9267



NOT CLASSIFIED
DWG. 9268

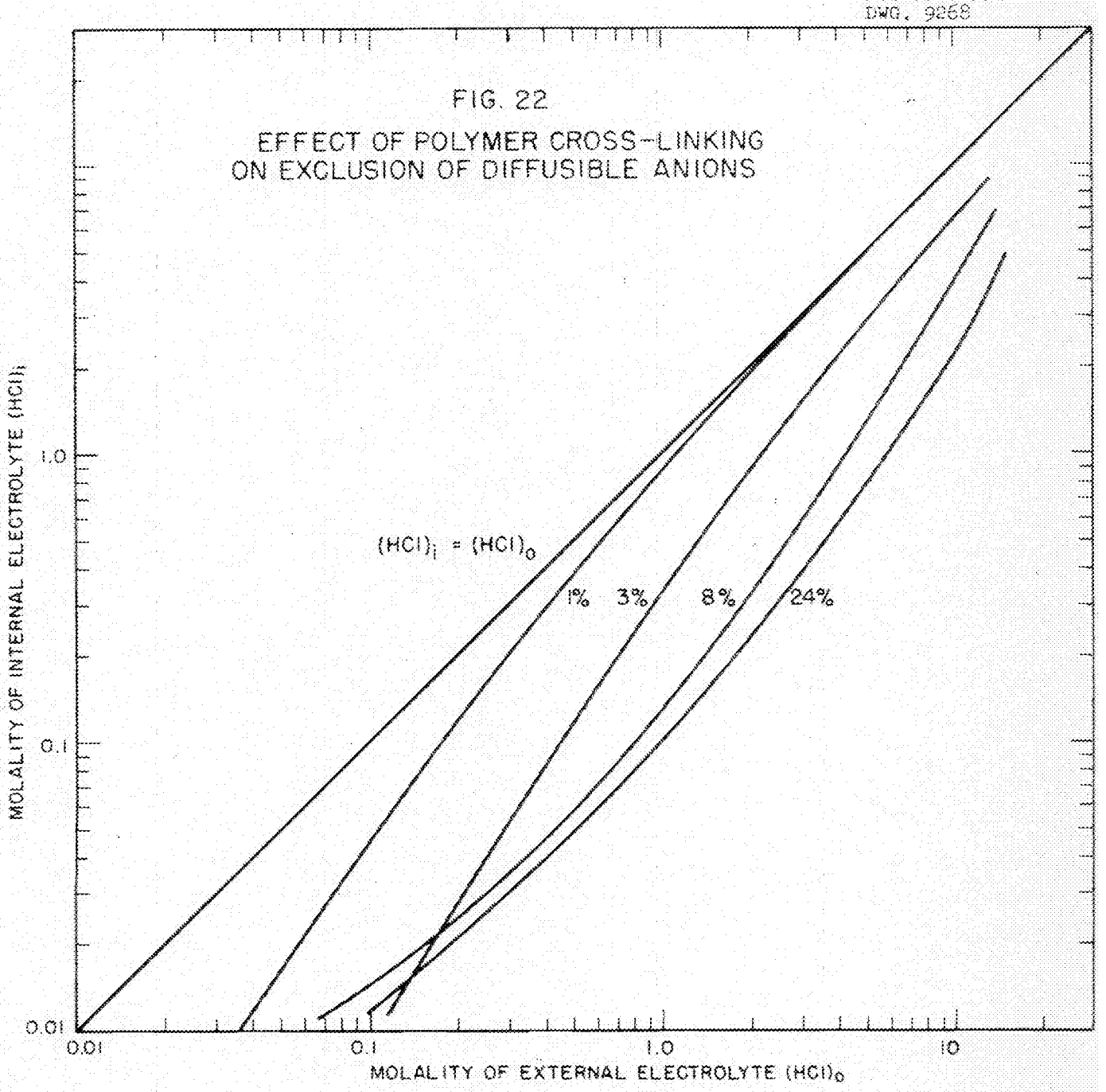


FIG. 22

EFFECT OF POLYMER CROSS-LINKING ON EXCLUSION OF DIFFUSIBLE ANIONS

NOT CLASSIFIED
DWG. 9269

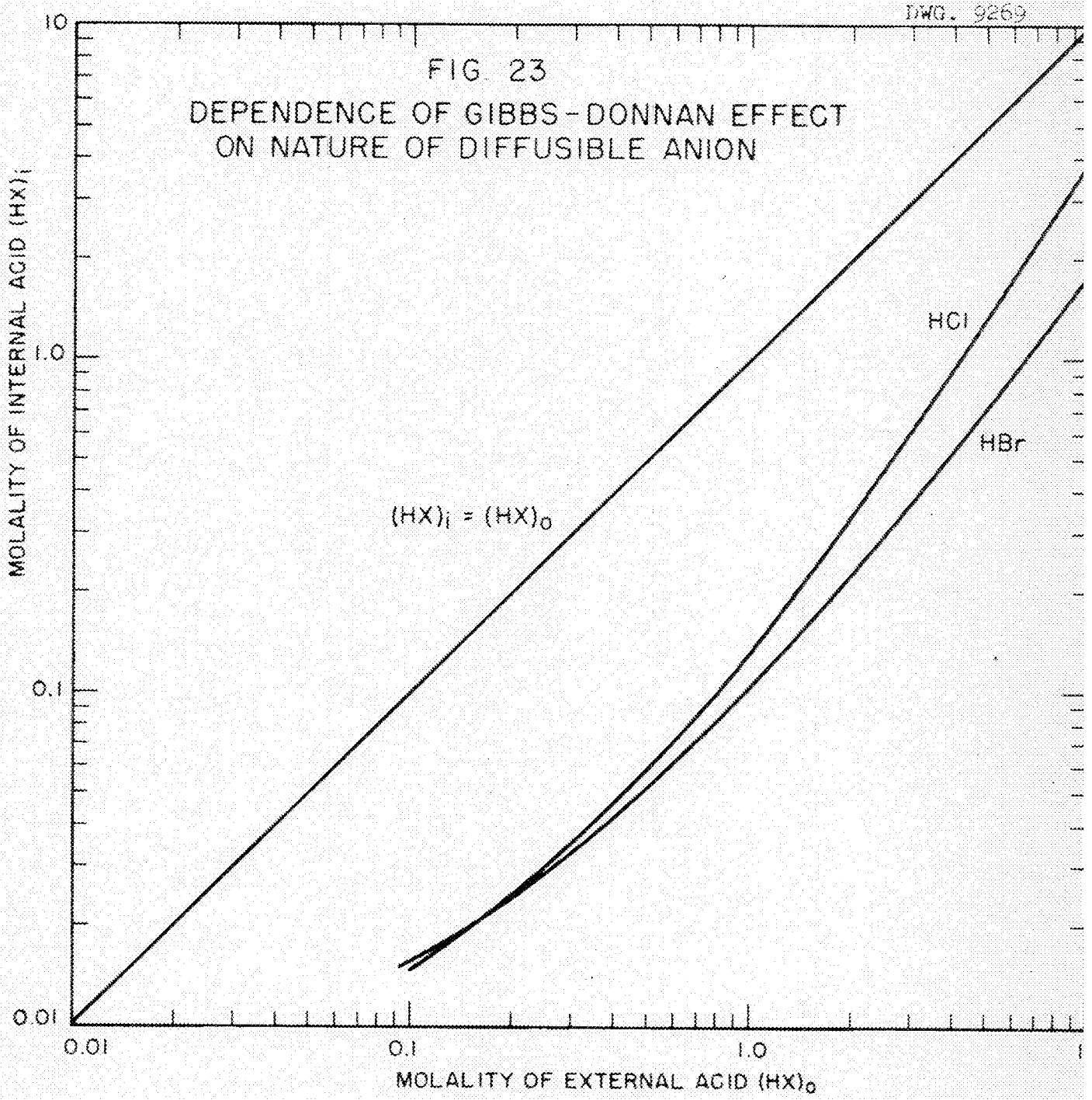
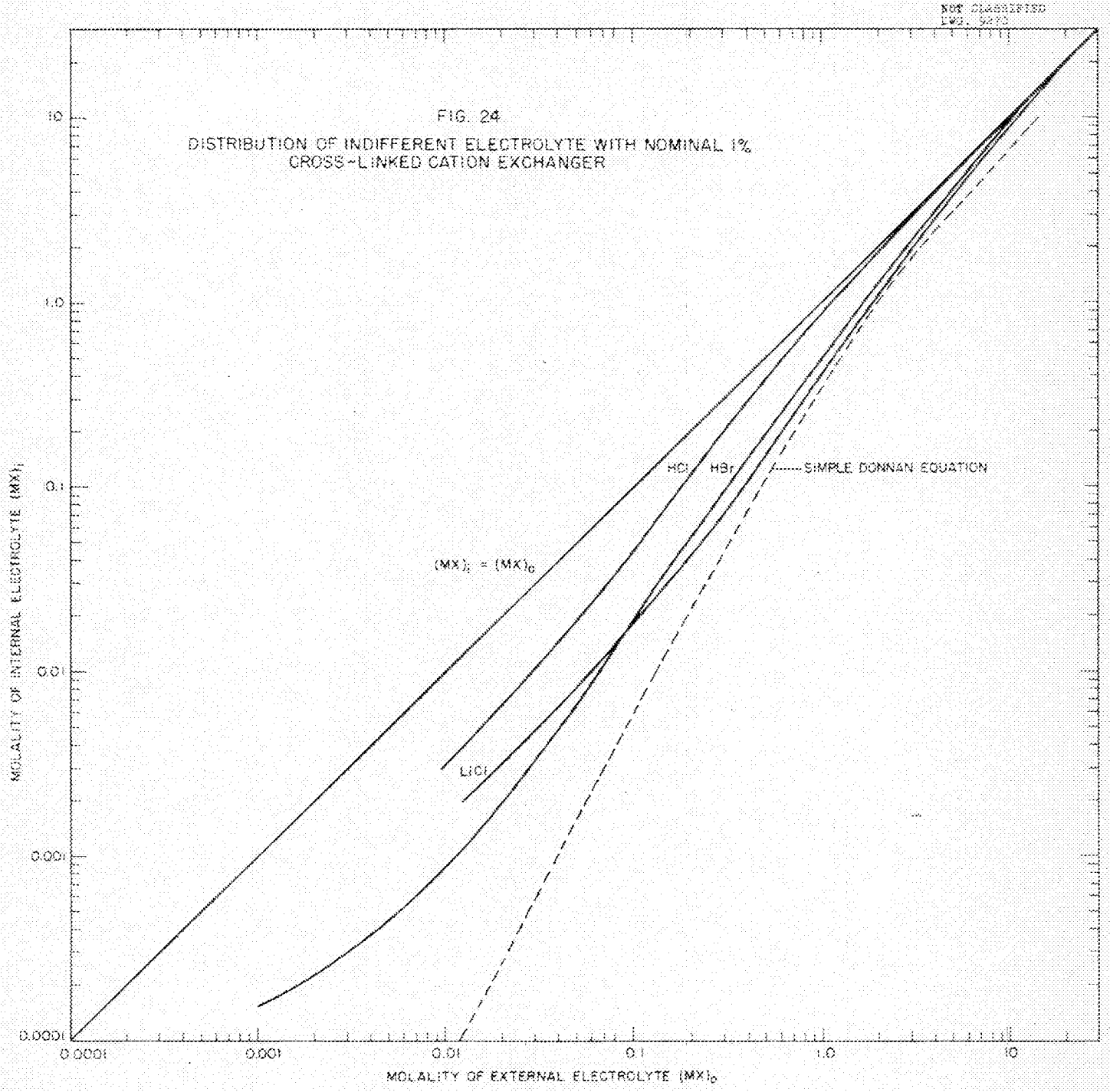


FIG. 23
DEPENDENCE OF GIBBS-DONNAN EFFECT ON NATURE OF DIFFUSIBLE ANION

NOT CLASSIFIED
FWS, 9/2/70

FIG. 24

DISTRIBUTION OF INDIFFERENT ELECTROLYTE WITH NOMINAL 1% CROSS-LINKED CATION EXCHANGER



have been measured using radioactive isotope tracer techniques. The results are given in Fig. 25 through 31. Increasing ionic charge was found to decrease the diffusion rate markedly, whereas the activation energy increased only from 5000 to approximately 10,000 cal/mole. Diffusion rates for a given ionic species decreased with increased cross-linkage from a nominal 1% divinyl benzene content up to 16%, while the activation energies rose only slightly. The influence of the chemical nature of the structurally bound exchange group on the diffusion rate was also determined.

Radioactivity measurements were performed with high accuracy using a 4π geometry scintillation counter.

ION EXCHANGE IN NON-AQUEOUS MEDIA

F. S. Change, Jr.* (with G. E. Boyd)

The feasibility of ion exchange from non-aqueous media has been investigated using Amberlite IRC-50 or Dowex 50 to remove sodium ions from 0.1 molar solutions in (1) methanol, (2) equal volumes methanol and benzene, (3) ethylene glycol, (4) mixtures of ethylene glycol and methanol, (5) one volume methanol mixed with three volumes acetone, and (6) ethylene glycol and acetone mixtures.

The sodium was put into solution as sodium hydroxide or sodium iodide and Na^{24} was used as a tracer. The resin bed was approximately 10 cm deep and 1 sq cm in cross section. Aqeuous acid was used for regeneration. The resin was equilibrated with the solvent to be used before starting the exhaustion, but no effort was made to make the resin moisture-free.

The following results have been obtained:

(1) Ion exchange takes place readily from non-aqueous media under the conditions investigated.

(2) The rate of exchange with Amberlite IRC-50 (weak acid exchanger) is greatly affected by the viscosity of the non-aqueous solution.

(3) Dowex 50 (strong acid exchanger) shows little change in rate of exchange as the solution properties vary.

(4) Amberlite IRC-50 increased in size when the organic solvent was passed through the water-wet bed, but Dowex 50 showed negligible change.

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* Member Dept. of Chemical Engineering, University of Tennessee and A.E.C. Predoctoral Fellow, ORINS, Oak Ridge, Tennessee.

NOT CLASSIFIED
DWG. 9259

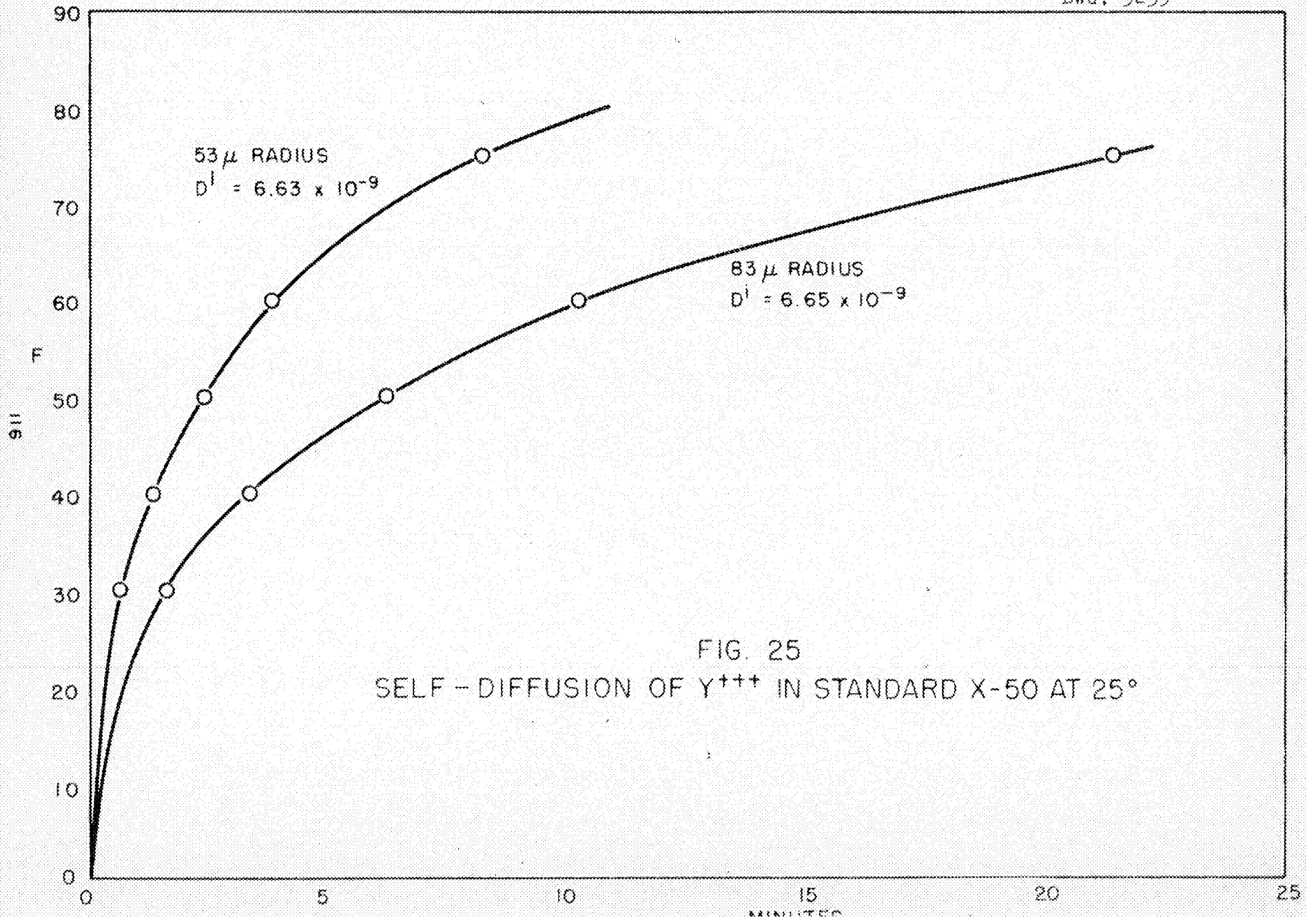


FIG. 25
SELF-DIFFUSION OF Y^{+++} IN STANDARD X-50 AT 25°

NOT CLASSIFIED
DWG. 9260

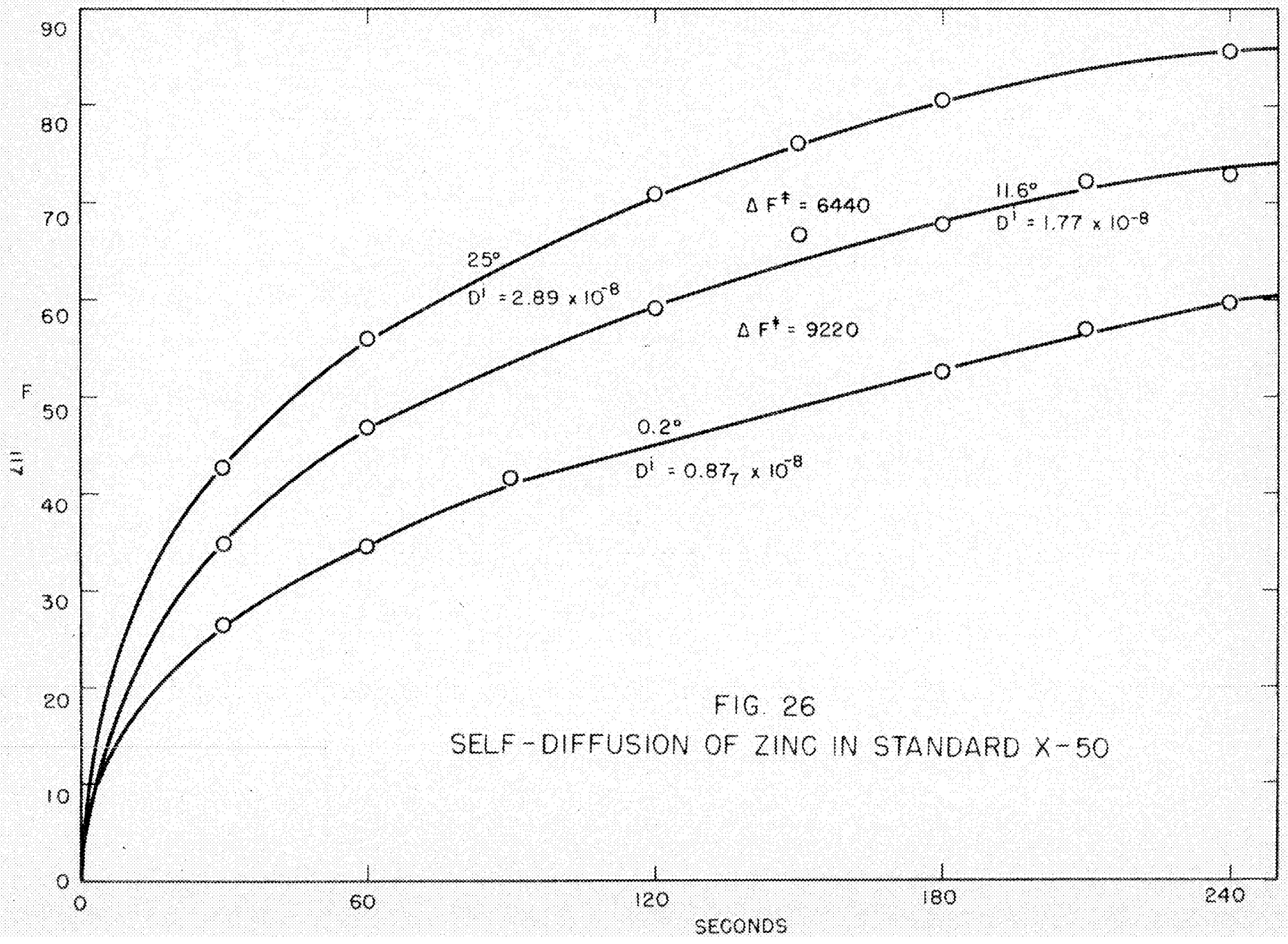


FIG. 26
SELF-DIFFUSION OF ZINC IN STANDARD X-50

NOT CLASSIFIED
DWG. 9261

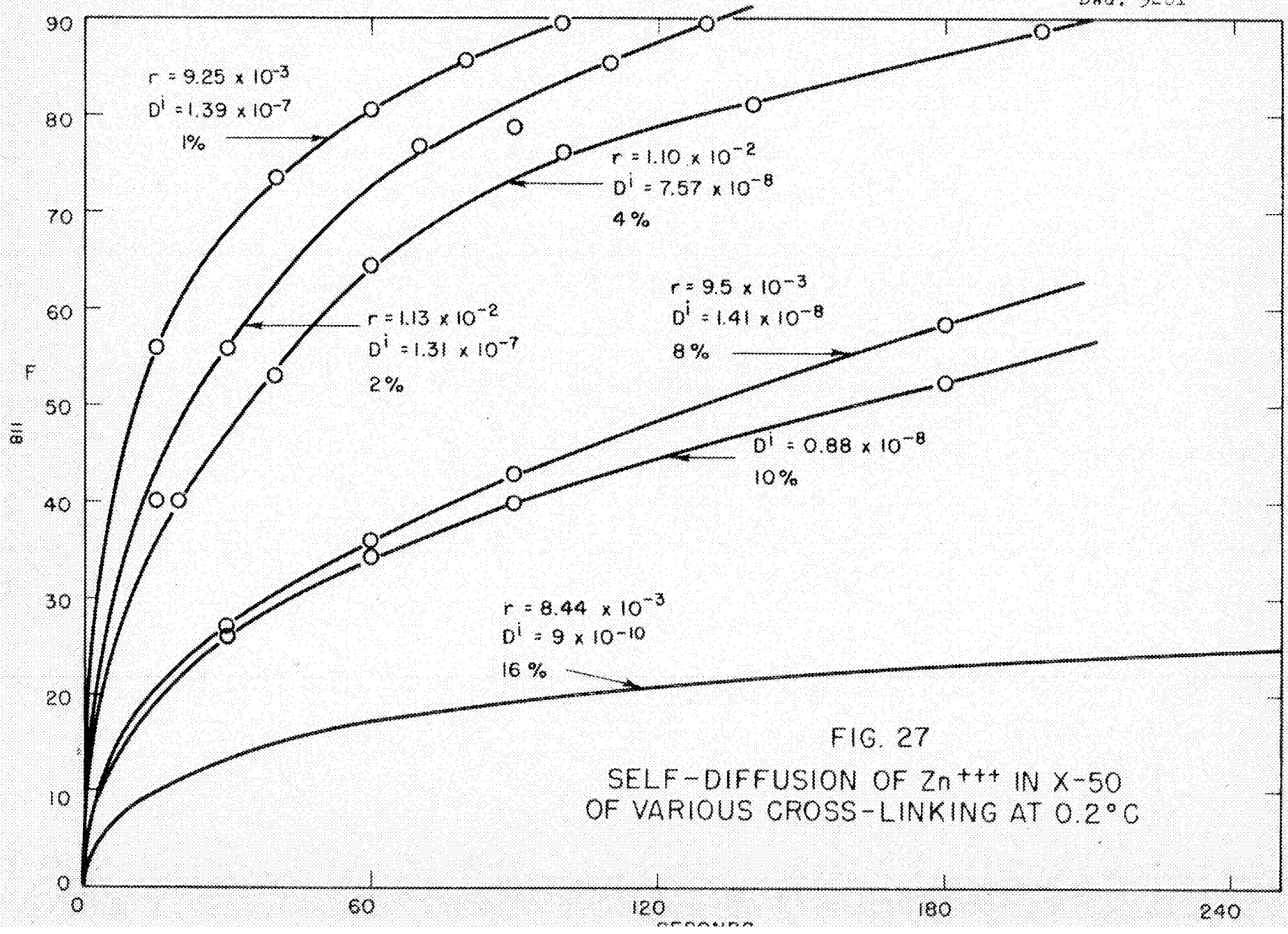


FIG. 27

SELF-DIFFUSION OF Zn^{+++} IN X-50
OF VARIOUS CROSS-LINKING AT 0.2°C

NOT CLASSIFIED
DWG. 9262

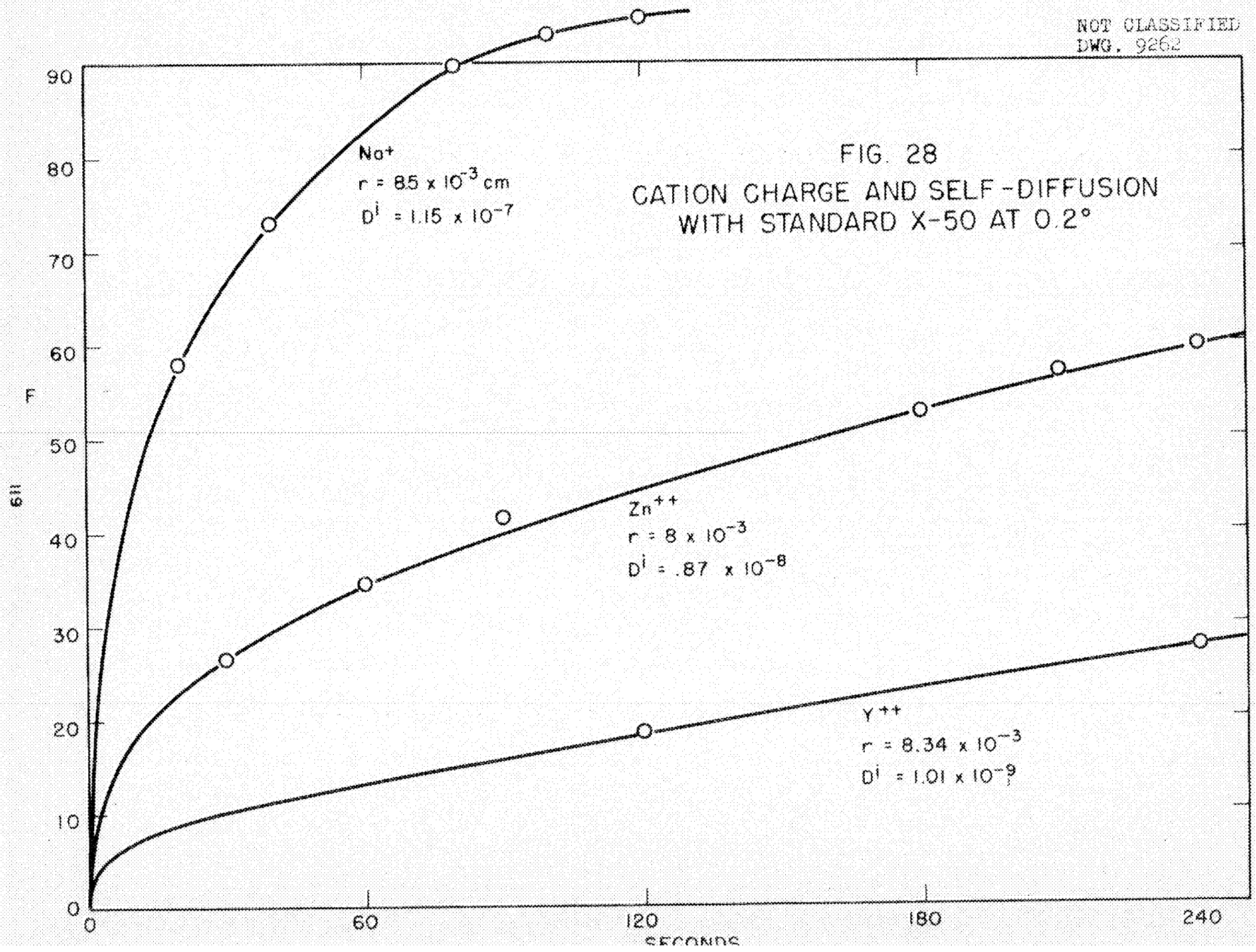


FIG. 28
CATION CHARGE AND SELF-DIFFUSION
WITH STANDARD X-50 AT 0.2°

DWG. 9263
NOT CLASSIFIED

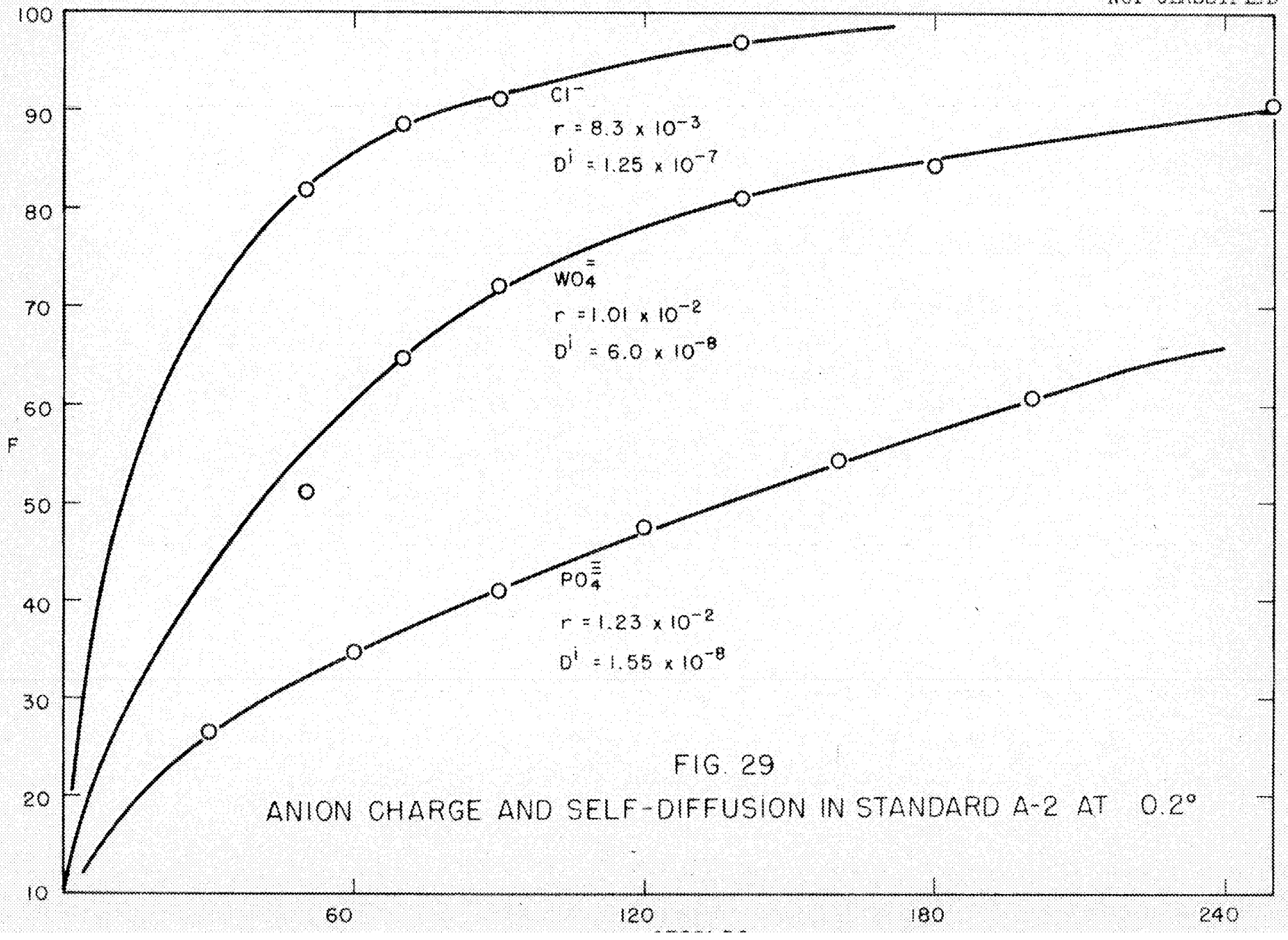


FIG. 29

ANION CHARGE AND SELF-DIFFUSION IN STANDARD A-2 AT 0.2°

NOT CLASSIFIED
DWG. 9264

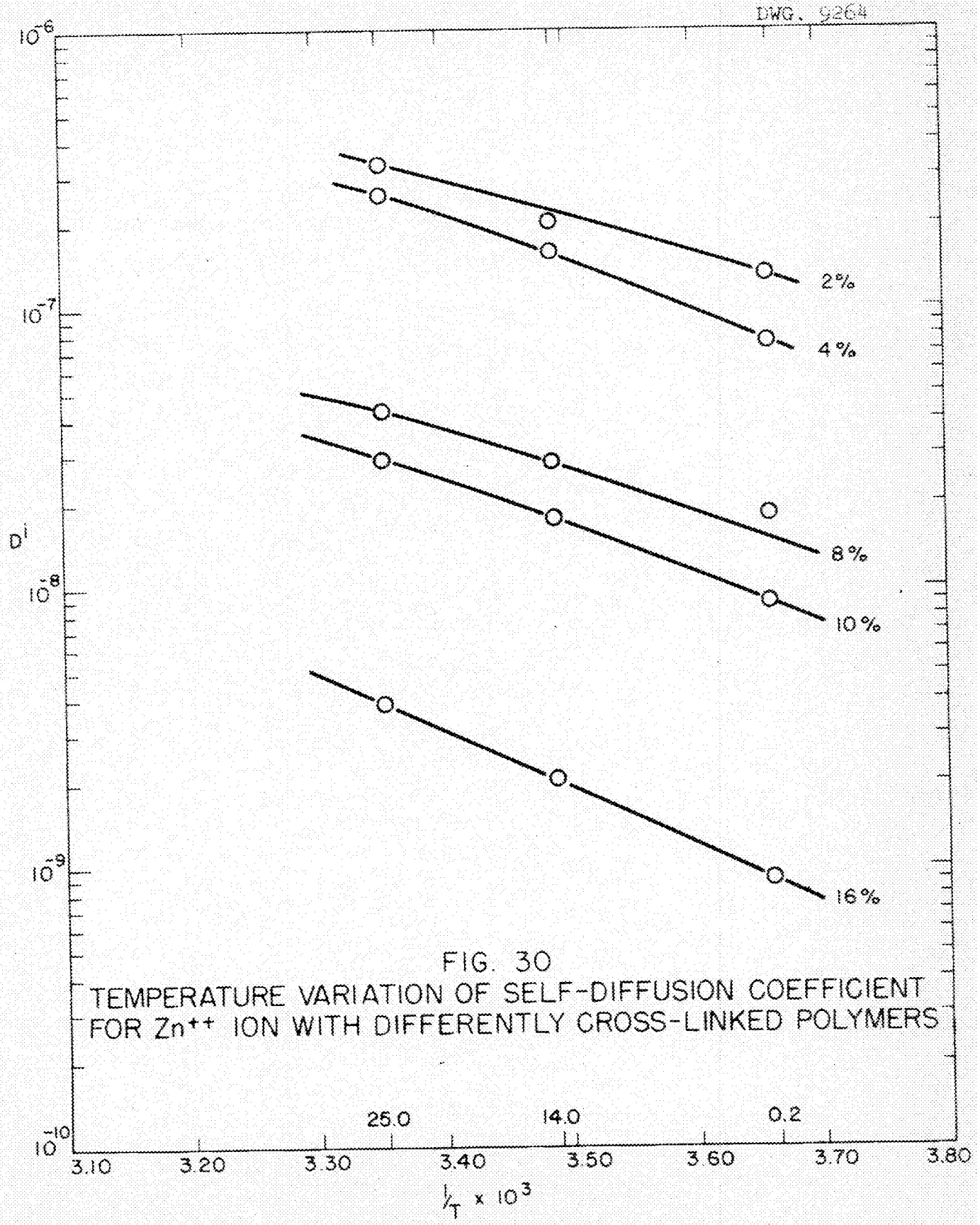
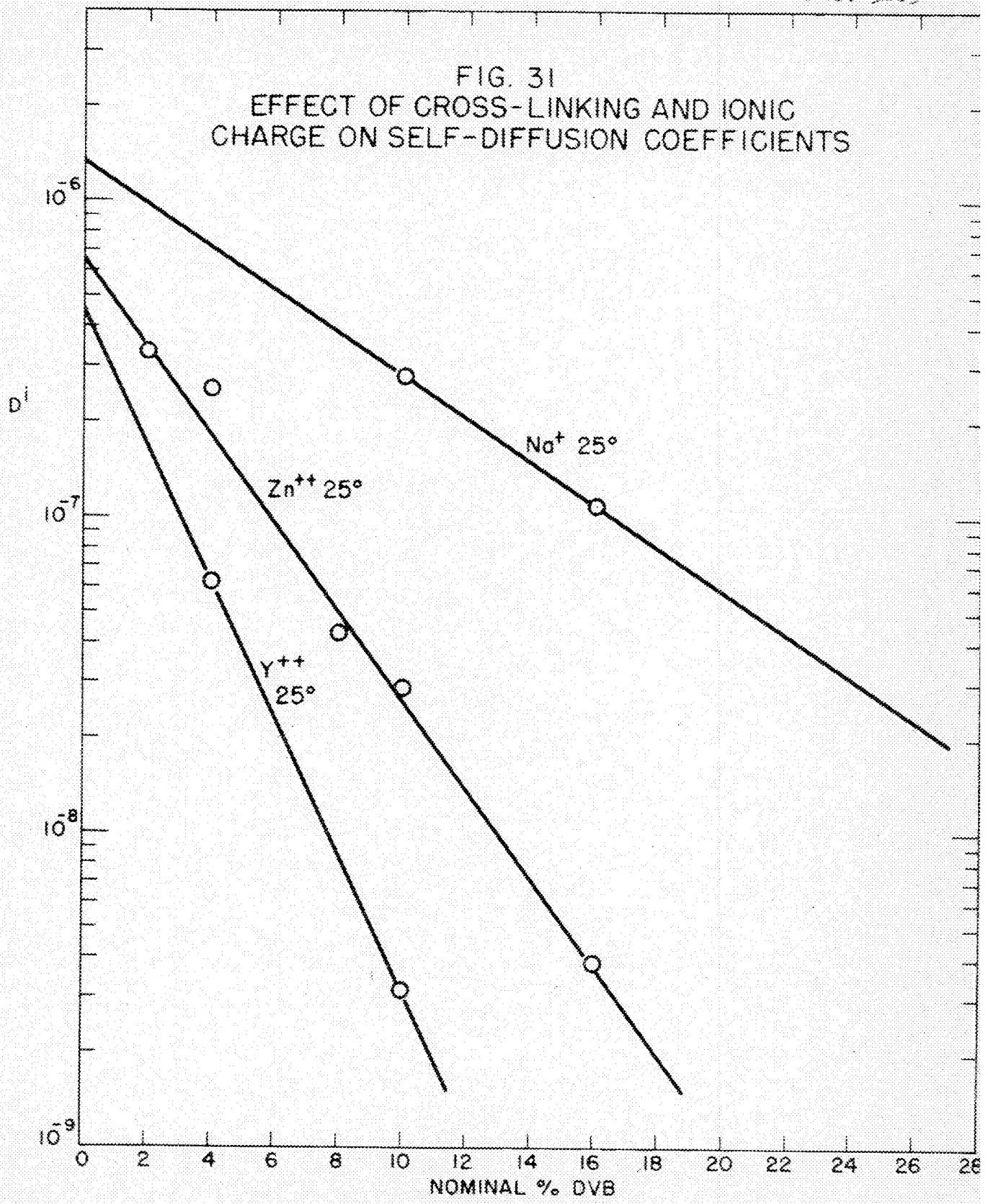


FIG. 30
TEMPERATURE VARIATION OF SELF-DIFFUSION COEFFICIENT FOR Zn^{++} ION WITH DIFFERENTLY CROSS-LINKED POLYMERS

NOT CLASSIFIED
DWG. 9265

FIG. 31
EFFECT OF CROSS-LINKING AND IONIC CHARGE ON SELF-DIFFUSION COEFFICIENTS



These findings indicate that the organic solvents employed do not remove the water of gelatin from the resin, and therefore that wet resins can be used for cation exchange in various non-aqueous solvents. When the resin undergoes further swelling by the solvent, some solvent is incorporated into the resin and may materially affect the rate of exchange.

Similar type investigations will be made for anion exchangers.

FISSION PRODUCT SEPARATIONS

SEPARATION OF FISSION PRODUCT ANIONS BY ION-EXCHANGE CHROMATOGRAPHY

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

A number of efficient separations of anionic fission product elements as well as the fractionation of the transition elements Mn, Fe, Co, Ni, Cu and Zn have been accomplished during the past quarter. Both solid and liquid chromatograms were measured in the monitoring of these separations. In the former case changes in the distribution of gamma emitting radioactivity in the bed were mapped out by scanning with a scintillation counter contrained to more parallel to the axis of the bed. The concentration history of radioactivity in effluent solutions from the column was determined using either beta proportional counting tubes or flow type ionization chambers connected through a dynamic condenser electrometer to a potentiometric recorder. The strong base anion exchangers Dowex-1 and Dowex-2 were used in the separations. Also, a complete separation of a mixture of the seventh group anions, Cl^-, Br^-, I^-, TcO_4^- and ReO_4^- was demonstrated using NO_3^- ion as an eluting agent.

CHEMICAL PHYSICS

NEUTRON DIFFRACTION

H. A. Levy and S. W. Peterson

The installation of the new neutron diffraction spectrometer has been completed during the present quarter. The NaCl monochromatizing crystal selects a wave length of 1.19 Å and provides a beam of about 10^6 neutrons per minute across the spectrometer table. Measurements of the energy spread and other calibrations are in progress.

Diffraction studies in progress include a variety of amorphous hydrated oxides (silica gel, chromic oxide) brought by Prof. W. O. Milligan, fused silica, α-quartz, and crystalline Cr_2O_3.

CALORIMETRY OF RADIOACTIVITY

G. H. Jenks and J. J. Hairston*

As discussed previously,[1] the calorimetry group has been cooperating with the MTR group in a determination of the efficiency of the ionization chambers used in monitoring the gamma flux in the MTR Mock-up. This determination has been completed and a report of the work is in preparation.

The method of carrying out the determination was outlined in some detail in the previous report.[2] Briefly, it consisted of measuring, calorimetrically, the heat generated in a small section of graphite placed in Hole 12 of the X-pile and comparing this quantity with that computed from readings obtained with an ion chamber in the same position. The rates of heat generation in graphite as determined by the two methods were found to agree closely. Detailed results will be included in the report of the work.

(1) Jenks, G. H. and Sweeton, F. H., "Calorimetry of Radioactivity," *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950*, ORNL 685, 129 (June 16, 1950).

(2) *Ibid.*

* Assigned from the MTR Development Group.

MICROWAVE SPECTROSCOPY

Ralph Livingston

The equipment for determining the nuclear spin of I^{131} is now essentially complete. Two test runs have been attempted. The first experiment was tried as a preliminary test of the remote control equipment. A sample of I^{129} with no added tracer activity was used. A few minor difficulties in the remote control system were found and corrected. Although the mechanical equipment worked well, the synthesis of methyl iodide was not successful. This may have been due to the use of an old ampoule of reagents left from the work of last year.

In the second test run, several micrograms of I^{129} plus 50 mc of I^{131} were used. The solution transfer and evaporation steps of the chemical synthesis were successful, but the run was terminated because of a leaky ball joint. Actually two ball joints developed high vacuum leaks, but only one of these was in a serious enough place to warrant termination of the test. This ball joint is being replaced with a standard taper joint, and a few mechanical changes are being made. The final equipment will be described in detail after test runs are completed.

Dr. O. R. Gilliam of Duke University is spending most of the summer at the Laboratory working on the iodine nuclear moment problem. He recently constructed, at Duke University, a stabilized microwave oscillator at 9000 megacycles and a harmonic multiplier. This equipment has been incorporated with the methyl iodide microwave spectrometer to give reference signals so that precise hyperfine line separations can be made.

Drs. J. Kilpatrick and J. Goldstein have joined the microwave group for the summer. Dr. Kilpatrick has started theoretical work concerning the zero point vibrational energy problem in the symmetric top molecule. Dr. Goldstein is concerned with some aspects of paramagnetic resonance phenomena. Simple paramagnetic resonance equipment is near completion. The equipment includes a new klystron power supply developed by E. Fairstein which is proving highly successful.

EXPERIMENTS IN CHEMICAL KINETICS WITH MOLECULAR BEAMS

P. J. P. Chastagner and E. H. Taylor

The first object of these experiments continues to be a study of the reactions of potassium with Br_2, HBr and organic bromides. Molecular beam techniques applied to such reactions offer the possibility of a more penetrating study of the fundamentals of chemical reactions than can be made by conventional means. Neutron activation is to be used to measure the minute amounts of bromine involved in the experiments.

The modified apparatus was assembled and tested at the beginning of this quarter. It was satisfactory except for the externally-operated movement of the surface ionization gage which showed considerable irreproducibility. This has been avoided by building a window in the vacuum tank through which the position of the gage can be measured with a microscope of long focal length.

Some irradiations of KBr on platinum foils were made to test further the separation and counting procedures. The separation of radio-bromine is carried out by exchange with an excess of ordinary gaseous Br_2 which is then reacted completely with a thin deposit of calcium. A blank irradiation of a cleaned platinum foil gave a satisfactorily low counting rate, less than one count per minute in the standard beta proportional counter. A small amount of KBr was similarly irradiated to give a sample for decay study. As previously observed with smaller quantities, the chlorine present as impurity is measurable after long decay, but appears to contribute only about 10^{-4} of the counting rate observed initially.

Difficulties have been observed in measurements at low counting rates because of non-statistical variations in the background over periods of time comparable to the times necessary for counting the samples. It is planned to eliminate such uncertainties by the use of twin proportional counters, using one for following the background.

RADIATION CHEMISTRY

J. W. Boyle
J. A. Ghormley
C. J. Hochanadel
J. F. Manneschmidt
A. W. Smith
F. H. Sweeton
E. H. Taylor
J. A. Wethington

GENERAL

Cobalt Gamma Ray Source. The cobalt gamma ray source mentioned previously has been in almost constant use during the quarter and has proved to be highly satisfactory. It will be described in detail in a separate report. The best present value for the dose rate at the center is 3880 r/min measured with the acid $FeSO_4$ actinometer, assuming a yield of 20.6 equiv. oxidized/100 ev.

Decomposition of Fused Sodium Hydroxide by 1.33 Mev Electrons. There is some interest in the use of NaOH in high temperature nuclear reactors, and its stability under irradiation is therefore important. A preliminary experiment was done to look for any decomposition.

Reagent grade NaOH (Baker's C. P., 98.9% NaOH) was melted under vacuum in a nickel crucible. After cooling, the crucible was transferred to a Pyrex irradiation cell which was evacuated and then irradiated for 40 minutes with 1.33 Mv electrons at 20 microamperes. The energy from the electron beam was sufficient to keep the NaOH at about 400°C (M. Pt. = 318°C). Upon analysis, about 0.05 ml H_2 (S.T.P.) was found in the gas phase, and no more was obtained on dissolving the solid. The resulting solution had no oxidizing power. A similar small amount of H_2 was found over NaOH which had been merely fused in a nickel crucible. There was little corrosion of the crucible in either case.

These results confirm expectations that NaOH would be rather stable under radiation.

Radiation Test of Karbate, a Proposed Reactor Reflector Material. Karbate, a phenol-formaldehyde impregnated graphite, has been proposed as a substitute for the beryllium reflector of the MTR in a contemplated experimental version of this reactor. It would be exposed to a high neutron and gamma ray flux while immersed in water, and radiation damage through decomposition of the impregnant might lead to disintegration of the reflector.

As an accelerated test for possible deterioration, a sample of Karbate is being exposed to electrons from the Van de Graff generator. The sample is in a water-filled cell in order to simulate actual surface conditions.

Miscellaneous Irradiations. The cobalt gamma ray source is exceptionally convenient for miscellaneous irradiations because of its constancy and freedom

from maintenance. A number of such irradiations made during this period are described briefly below:

Sucrose turned pink within one week. A sample of 1.5 g yielded about 0.1 ml of gas (evolved on solution in water) composed of 24% CO_2, 5% CO and 71% H_2. The solution was strongly reducing.

Solid phosphates are being irradiated to see whether oxidation or reduction by radiation are responsible for difficulties experienced in tracer studies using pile-irradiated phosphate rock in fertilizer experiments.

Aqueous solutions of various sulfur-containing salts were irradiated to help clarify the possibility of sulfate reduction in the proposed homogeneous reactor. No anion of oxidation state as high or higher than sulfite appeared by qualitative tests to be reduced. Thus $Na_2S_2O_3$ gave an odor of H_2S and a precipitate of S, but Na_2SO_3, K_2SO_4 and $Na_2S_2O_8$ gave no odor or precipitate. Sodium meta bisulfite, $Na_2S_2O_5$, gave a strong odor of SO_2.

Electrical conductance measurements on H_2O and on aqueous UO_2SO_4 were not measurably affected by the gamma ray field. This was to be expected, but a test was desired in view of the possibility of using conductance measurements as a concentration control in the proposed homogeneous reactor.

DECOMPOSITION OF AQUEOUS SOLUTIONS OF FISSIONABLE MATERIALS

J. W. Boyle J. F. Manneschmidt
A. W. Smith F. H. Sweeton

Most of the recent work in this problem has been summarized in the Homogeneous Reactor Experiment Feasibility Report (ORNL 730) which has just been issued. As indicated there, the principal problem seems now to be the effect of radiation on corrosion, and emphasis is therefore being placed on this aspect of the work.

One in-pile experiment has been completed since the issuance of the feasibility report. This experiment was done with an initial charge of O_2 in the bomb to determine the effect of this on the corrosion of the stainless steel. The results of the experiment were too complicated for interpretation without further work. There appeared to be either no gas production or a long delay (several days) in its inception, but this superficially promising result is offset by the fact that most or all of the uranium precipitated from the solution. A detailed examination of the corrosion behavior awaits radioactive cooling of the metal sample. Corrosion did not appear to be serious.

Further experiments are in progress to elucidate these results and to explore the possible usefulness of lower concentrations of oxygen (the initial partial pressure of O_2 in this experiment was 250 lb/in^2).

THE RADIATION DECOMPOSITION OF WATER AND AQUEOUS SOLUTIONS

C. J. Hochanadel

The availability of the cobalt gamma ray source makes precise yield measurements possible, and these have been started for various reactions of interest. Considerable effort has been spent in devising and building irradiation cells and holders to assure reproducible positioning of the samples in the source. The measurements already made will be reported briefly, deferring an extended discussion until more data have been accumulated.

The yield of the forward reaction, that is the fraction of water decomposed going directly to H_2 and H_2O_2 and not the net yield including the back reaction, was measured by the expedient of adding a solute which would react with the radicals and hence eliminate the back reaction. Ferrous ion was used to react with OH radicals in an O_2-saturated solution for which the yield of ferrous ion oxidation is well known and reproducible, and can therefore serve as an actinometer. The extent of the forward reaction was determined by measuring the amount of H_2 formed. The concentrations of the reactants and the yield calculated from the results are given below:

Initial H^+	0.4 *M* H_2SO_4
Initial Fe^{++}	5740 micromoles/liter
Initial O_2	approx. 1250 micromoles/liter
Fe^{++} oxidized	3820 micromoles/liter
H_2 produced	84 micromoles/liter

$G \cong$ molecules H_2/100 ev $\cong$ 0.45

This is in fair agreement with Fricke's value of 0.57[1] obtained with 110 Kv X-rays using other reducing agents. That value becomes 0.65 if calculated on the basis of $G \cong 20.6$ for Fe^{++} oxidation, the value used in the present work.

(1) Fricke, H. and Hart, E., "The Oxidation of the Nitrite to the Nitrate Ion by the Irradiation of Its Aqueous Solutions with X Rays, *J. Chem. Phys.* 3, 365 (1935).

The yield of the back reaction,

$$H_2 + H_2O_2 = 2H_2O ,$$

was likewise studied with the cobalt gamma source, giving the results in Table I. Values previously obtained with electrons are quoted for comparison.

TABLE I

Decomposition of Water by Gamma Rays and by Electrons

RADIATION	TEMPERATURE (°C)	INITIAL CONCENTRATION (micromol/liter)		INITIAL YIELD (micromol/liter, min)	G*
		H_2O	H_2		
Gamma	25.4	362	760	23.7	6.4
	45.8	362	760	27.0	7.3
	64.8	362	760	30.8	8.3
Electrons, 1.33 Mv					
0.68 microamp	ca. 25	392	770		~ 1.3
0.058 microamp.	ca. 25	392	770		~ 2.
0.0045 microamp.	ca. 25	392	770		~ 4.

* Gamma dose measured by acid $FeSO_4$ actinometer assuming $G = 20.6$ for oxidation of ferrous ion.

Electron dose measured by current and voltage measurements.

FLUORESCENCE AND PHOSPHORESCENSE SPECTRA OF SOME MATERIALS SUBJECTED TO Co^{60} GAMMA IRRADIATION

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

In connection with the study of storage and release of energy in irradiated alkali halides, the desirability of measurement of spectral distribution of emitted light is obvious. Several spectroradiometers have been described in the literature for measurement of emission spectra of phosphors such as are used in fluorescent lamps and cathode ray tubes, but these instruments do not have sufficient sensitivity for study of the light emitted from "pure" alkali halides. In order to obtain the necessary sensitivity, a spectroradiometer had been assembled employing a photomultiplier cooled with liquid nitrogen and used as a photon counter for detecting the light. A Beckman model Du Spectrophotometer serves as a monochromator. For the study of crystals during irradiation in the gamma-beam from our 300 curie Co^{60} source, light from the sample reaches the spectrophotometer slit through a quartz lens, a 90° quartz prism and another quartz lens. For phosphorescence studies the sample is merely placed in front of what is normally the exit slit of the spectrophotometer. Light emerging from the spectrophotometer passes through the quartz window of an evacuated vessel housing the 1P28 photomultiplier, pulses originating from single photoelectrons are amplified by a high gain preamplifier and an Al linear amplifier, and the counting rate is continuously recorded by means of a logarithmic count rate meter and Brown recorder. It is hoped that the present range of about 2200 to 6000 Å may soon be increased by a red-sensitive photomultiplier.

The observed dark count rate varies between 100 and 200 c/m. About 2000 c/m are required for a satisfactory measurement in reasonable time, and the estimated input to the photomultiplier cathode required to give this rate is 10^{-12} to 10^{-13} lumen. Since the efficiency of the optical system with a 1 mm slit is estimated to be 0.01%, the required light output from the source is $\sim 10^{-8}$ lumen/cm^2. The sensitivity is seen to be better by a factor of 10^5 than that of the instrument used by Zworykin[2] for study of emission spectra of more efficient phosphors.

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(2) Zworykin, V. K., "An Automatic Recording Spectroradiometer for Cathodoluminescent Materials," *J. Opt. Soc. Am.* 29, 84 (Feb. 1939).

Tracings of emission spectrum curves obtained from two different samples of NaCl during exposure to 20 r/min Co^{60} γ's are shown in Fig. 32. No corrections have been made for variation of photocathode response, dispersion of the prism and absorption in the optical system as a function of wave length, and for most purposes it will not be necessary to apply these corrections. The curves in Fig. 32 show clearly that the emission spectra for the two NaCl samples are quite different although the same three bands are observed for each. The differences in relative heights of the bands can probably be attributed to differences in concentration of impurities acting as activators or quenchers.

The emission spectra of several crystals and solutions of interest for scintillation counters have been measured during and after irradiation with γ's. Thallium activated KI during irradiation gave a single band with peak at 4300 Å and half-width about 800 Å. Five minutes after irradiation a peak at 4300 Å was still observed, but with greatly reduced intensity, and in addition another phosphorescence band at 5400 Å which was obscured during irradiation by the much more intense 4300 Å band. The phosphorescence spectrum of a CaF_2 sample after several minutes exposure at 5000 r/min showed relatively sharp bands at 2760, 3120, 3580, 3850, 4180, 4440, 4840, 5440, 5550, and 5770 Å. During exposure at 20 r/min the bands below 4840 Å were completely obscured by a much more intense fluorescence band with peak at 3200 Å and half width 1000 Å. A sample of anthracene during excitation with Co^{60} γ's, 2537 Å photons, or 3800 Å photons gave a spectrum consisting of a peak at 4500 Å with shoulders indicating unresolved peaks at about 4760 and 5100 Å respectively. A solution of anthracene in benzene during exposure to γ's gave two sharp peaks of about equal intensity at about 4100 and 4350 Å. Fluoranthene dissolved in benzene gave a broad band with peak at 4800 Å and half-width 1000 Å. No phosphorescence was observed in the organic materials.

The spectral distribution of thermostimulated phosphorescence of two different samples of LiF has been studied. The two samples when irradiated with X rays at liquid nitrogen temperature were found[3] to give glow curves which were nearly identical with respect to temperatures and relative heights of the peaks below 20°C, but different by a factor of about 10 in the indicated light output for corresponding peaks. For emission spectrum studies, samples were irradiated at -196°C for 40 min in a Co^{60} gamma-ray flux of 2000 r/min. In

(3) Ghormley, J. A. (With H. A. Levy), "Storage and Release of Energy in Ionic Crystals Subjected to Ionizing Radiation," *Chemistry Division Quarterly Progress Report for Period Ending December 31, 1949*, ORNL 687, 137 (Mar. 7, 1950).

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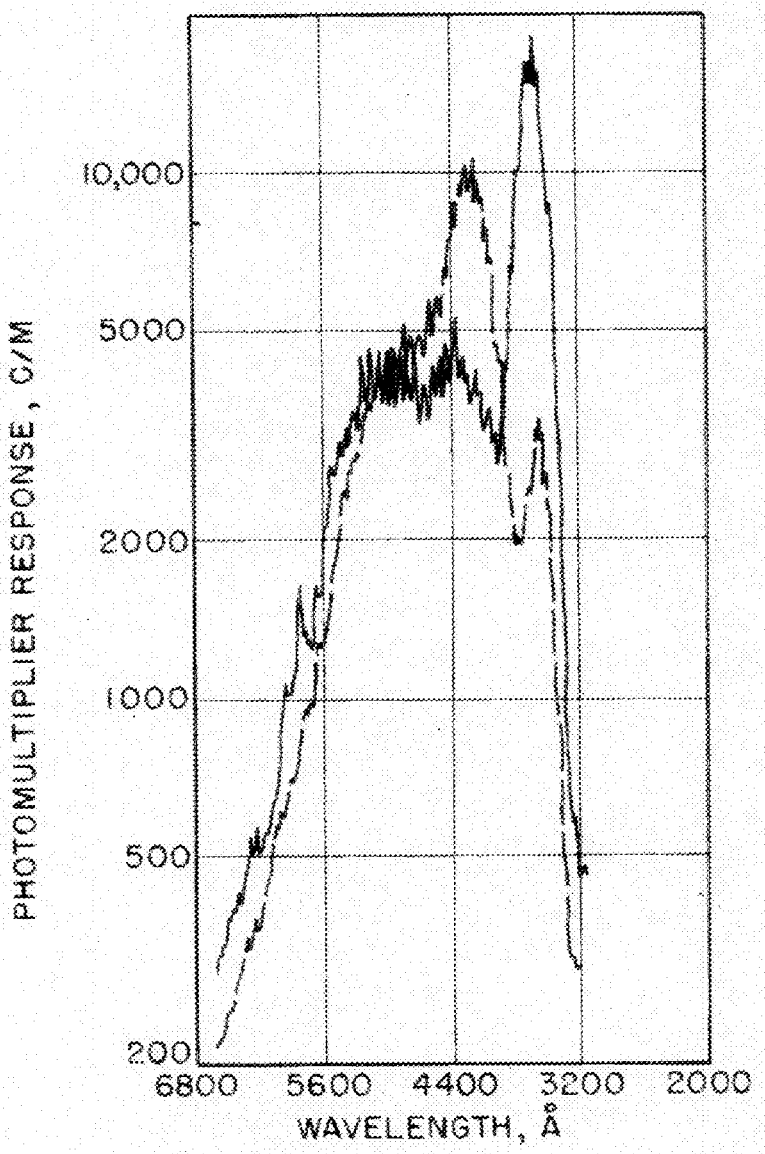

FIG. 32
EMISSION SPECTRA FOR TWO CRYSTALS
OF NaCl DURING EXPOSURE TO 20 R/MIN. Co^{60} γ-RAYS

both crystals the emission spectra for the two glow curve peaks below -70°C were characterized by two broad bands with peaks at 2700 Å and 4400 Å and half-widths of 800 Å and 1200 Å respectively. At temperatures above -70°C the 2700 Å peak consistently diminished in comparison with the peak at 4400 Å for the sample with the higher total emission (No. 501), and for the other sample (No. 41) no light was detected at 2700 Å above -70°C. For sample 501 the emission spectrum curves were the same (peak at about 4400 Å) at 95°C and 210°C, while sample 41 gave an emission spectrum peak at 5000 Å for 95°C and no glow curve peak at 210°C. Glow curves for emission at 4400 Å and 2700 Å for sample 501 are given in Fig. 33. The emission spectrum of sample 501 during exposure to a 20 r/min gamma beam at room temperature was very similar to the phosphorescence spectrum near room temperature with a peak at 4500 Å and half-width 1500 Å.

The data seem to indicate that for each peak in the glow curve between -196°C and +200°C there is a competition between the same two emission processes resulting in bands at 4400 Å and 2700 Å respectively. There are 10 distinct peaks or shoulders below 200°C on each glow curve indicating 10 different excitation (thermostimulation) processes. It seems likely that these processes must all be of the same type, either excitation of trapped electrons into the conduction band or excitation of electrons from the filled band into normally filled levels occupied by positive holes. It is not possible to determine from available data which type of stimulation process occurs here.

The intense peak in the glow curve for sample 501 at 210° was not observed at all for sample 41. This peak may be associated with the disappearance of an absorption band at 3100 Å[4] first reported by Ottmer.[5] This band was observed in sample 501 at 25°C after irradiation at liquid nitrogen temperature and also after irradiation at 25°C, but was not observed in another LiF sample similar to No. 41. The formation of absorption bands at 2500 and 3100 Å in a 3.2 mm thick sample of No. 501 exposed to Co^{60} γ's at 25°C at the center of the 300 Curie source (~ 4000 r/min) were as follows:

Exposure Time (min)		0	1	2	5	10	25	40	60
$\log \frac{I_0}{I}$	(2500 Å)	0.043	0.117	0.195	0.410	0.745	1.593	2.42	
	(3100 Å)	0.038	0.072	0.102	0.176	0.262	0.410	0.484	0.585

(4) See Fig. 32, Curves C, D and E of CENL 685, *Chemistry Division Quarterly Progress Report for Period Ending March 31, 1950. Part I. Chemical Research* (June 16, 1950). See also Fig. 17, Curve C, ANL 4380, *Summary Report for the Period April through September 1949; Chemistry Division, Section C-II*, (Mar. 20, 1950).

(5) Ottmer, R. L., *Physik* 48, 758 (1927).

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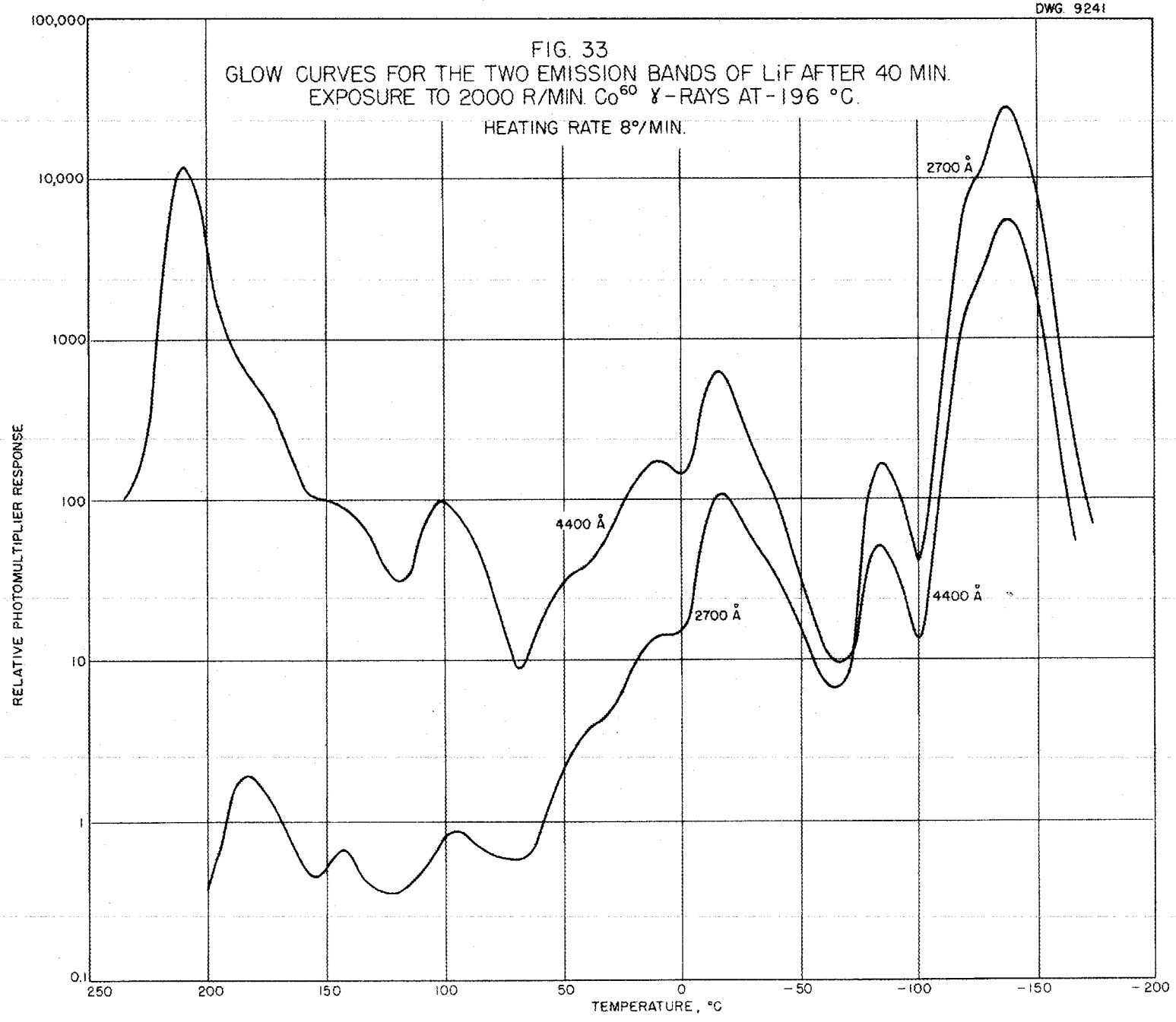

FIG. 33
GLOW CURVES FOR THE TWO EMISSION BANDS OF LiF AFTER 40 MIN. EXPOSURE TO 2000 R/MIN. Co^{60} γ-RAYS AT -196 °C.
HEATING RATE 8°/MIN.

The band with peak at 3100 Å is seen to approach a limiting density while the 2500 Å band continues to build up almost linearly with dose.

We hope that correlation of glow curves and corresponding emission spectra with formation and disappearance of color centers will be more enlightening for the alkali halides whose absorption bands have been identified with specific configurations.

EFFECT OF RADIATION ON HETEROGENEOUS CATALYSIS

J. A. Wethington

It was mentioned in the previous report that the exchange between H_2 and D_2 was to be used to assess possible effects of radiation upon catalytic activity. It was hoped to obtain measurement of the extent of exchange by mass spectroscopic determination of HD, but this proved to be impossible with the equipment available.

It is therefore intended to analyze for HD by thermal conductivity, a less sensitive but more reliable method than mass spectroscopy. A thermal conductivity gage has been designed for this purpose and should be in use shortly. It incorporates features which should make it simpler and more reliable than previous thermal conductivity gages.

INSTRUMENTATION

DISCRIMINATION AGAINST BACKGROUND FOR C^{14} COUNTING

C. J. Borkowski and E. Fairstein

Work has begun on the counting of C^{14} when the C^{14} rate is close to the normal background rate of the proportional counter. The feasibility of discriminating between the C^{14} counts and the background counts by means of energy measurements is being examined. To date, no significant data have been obtained. The major difficulty at present is the drift in counting yield in the chamber for a given pulse-height selector setting. Since it is necessary to take data over a period of 48 hours for each set of conditions, the drift becomes important.

The data which have been taken seems to indicate that in this particular chamber, the pulse-height distribution of the background is close to that of the C^{14}. However, most of the background is due to local gamma radiation and not to mesons. If the latter were the source, better discrimination against the background could be obtained.

The present chamber is a hemisphere, filled with 90% argon and 10% methane. The central wire configuration is such that a good peak is obtained for a 7 Kev X-ray emitter.

Ultimately, C^{14} will be measured by counting it in the gas phase, although the data so far obtained are for a solid source.

ALPHA ENERGY ANALYZER

E. Fairstein

The alpha energy analyzer showed the following faults after about a year's service:

1. The 6AG7 amplifier tubes and the 6BG6G high voltage regulator required replacement about twice as often as any of the other tubes.

2. The amplifier stability was not as good as desired with respect to voltage disturbances at the input circuit.

At present, there is no satisfactory substitute for the 6BG6G.

Both the main amplifier and the preamplifier were redesigned in an attempt to remove the other shortcomings mentioned. The circuit of the new amplifier appears in Fig. 34. The preamplifier has been simplified by using triodes where possible, and by using positive feedback between the second and third stages. The increase in gain which results from this application of feedback does away with the necessity for by-pass capacitors in these two stages. This represents an improvement in the reliability of operation since the limited space in the preamplifier box required the use of miniature (and in this case poor quality) capacitors.

The use of positive feedback is especially easy to apply in a three-tube feedback loop. The basic requirements which must be met for stability are:

1. The positive feedback loop must be smaller than and be within the negative feedback loop.

2. The stages within the positive feedback loop must have a wider pass band than the stages external to the loop. The low frequency response is especially important (to prevent motorboating). When these conditions are met, the negative feedback controls the amplifier gain and frequency response, which is the desirable situation.

Where bandwidth requirements permit these conditions to be met, it appears that the use of positive feedback can be used to advantage in many instrumentation problems.

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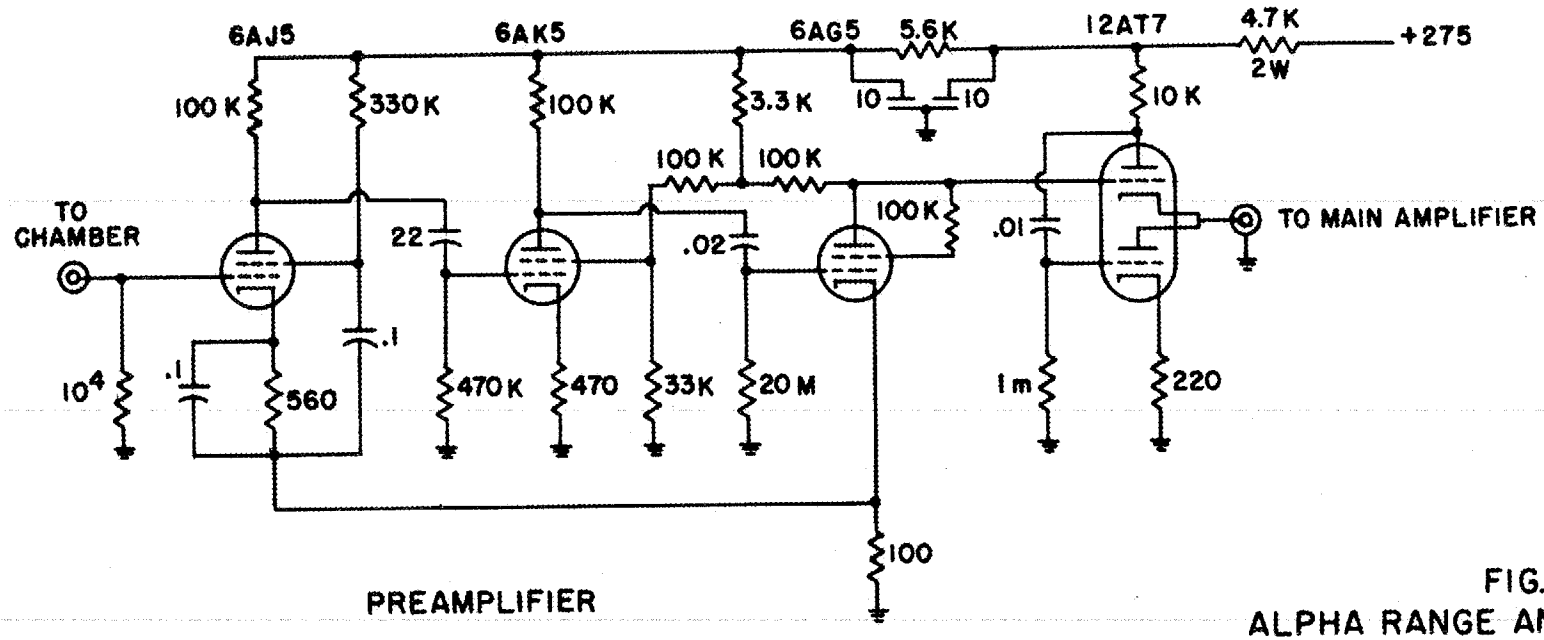
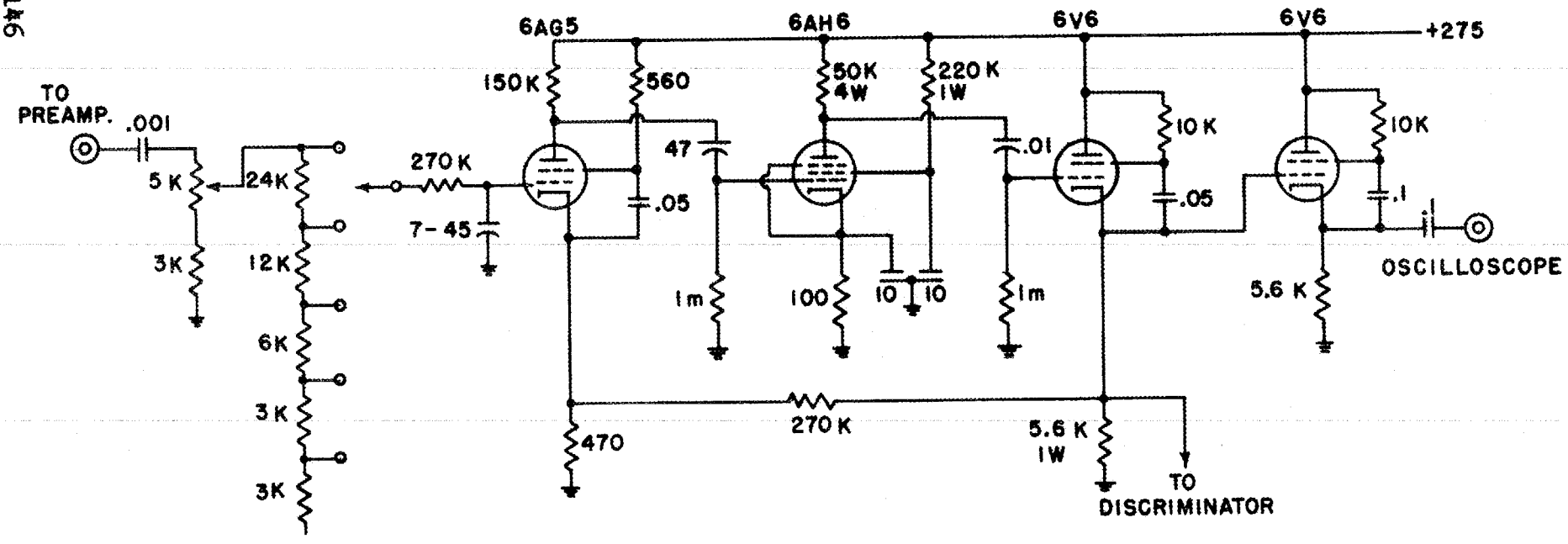


FIG. 34
ALPHA RANGE ANALYZER AMPLIFIER



The method of increasing the input signal size by feedback to a guard electrode was discontinued, since this can be shown to be an undesirable application of positive feedback. The positive feedback loop here is as large as the negative feedback loop, and the two feedback factors add algebraically. The effect is to decrease the net negative feedback and therefore the stability of the system. It is equivalent to breaking the positive feedback loop and decreasing the amount of negative feedback to restore the loss in signal height.

Instead of using feedback to the guard ring, the main amplifier was redesigned to give greater gain without a loss in stability. The 6AG7 tubes were also replaced by 6V6 tubes because of their longer life.

The bandwidth of the system is controlled external to the feedback loops, in the interest of stability. The rise-time of the system is about eight microseconds, while the fall time is about 25. These are not the optimum for best signal-to-noise ratio, but are necessary for good resolution. The signal-to-noise ratio for a five Mev alpha pulse is still 1000 to one, and represents only one-third of the total peak spread.

The preamplifier gain is 1000. The feedback factor is 300 (50 db). The main amplifier gain is 500. The feedback factor is 50 (34 db). The "cathode-follower" coupling stage between the units has a feedback factor of at least 30 db.

A comparison between a pentode and triode connected input stage was made to determine which gave the higher signal-to-noise ratio. It was found that the triode stage was poorer by at least 50 percent. This is contrary to what appears in the literature, but the evidence is indisputable. Extreme care was taken to make the tube operating conditions identical in the two cases.

Feedback had no effect on the ratio, as is to be expected.

Some minor changes were made in the discriminator circuit; the plate current of the pulse-height selectors was decreased to increase their life, and RC differentiation was used in another part of the discriminator to eliminate a costly delay line.

The power supply requires redesign to take advantage of higher quality components now stocked at the laboratory. This is of importance, since one transformer has already burned out and at least one more is ready to burn out. Both are being operated at well within the manufacturer's ratings, but neither is hermetically sealed.

MOVING FILM PULSE ANALYSIS

R. S. Stone and C. J. Borkowski

In taking energy distributions with conventional electronic pulse height analyzers one has the choice between a multichannel device which simultaneously counts the number of pulses in each of a finite number of energy ranges, and a single channel instrument which sweeps through the energy distribution, counting only one size pulse at a time. At present, the first type has the disadvantage of excessive circuitry, and its resolution is limited at the outset by the number of channels available. The second type is obviously much slower, since a separate count must be taken for each energy increment it is desired to resolve, and in the case of low counting rates this may be a serious drawback. For short lived samples this type of measurement may be out of the question. Moreover, reading only one pulse height at a time gives more chance for drifts to introduce errors in the final results.

One solution to this problem is to record on film every pulse which occurs, thus gaining the speed and accuracy of the multichannel analyzer, and then to extract the information from the film at leisure, giving as good resolution as is obtainable by sweeping the distribution with a single channel analyzer.

In our case, this film recording has been accomplished by feeding the pulses into an oscilloscope (Dumont 248) via an A-1 amplifier, and photographing the scope screen with a moving film camera (Fairchild Oscillo-Record Camera). The f 1.5 lens is used wide open, with Eastman Linagraph Ortho or Linagraph Pan recording film. The scope tube is a 5JP11, chosen for its highly photoactinic phosphor and relatively short persistence. The film is run at such a speed as to give about 10 counts per inch, so that a counting rate of 3000 c/m requires a film speed of about 5 in./sec. (The speed range of this camera is 1 in./min to 5 ft/sec; the General Radio Oscillograph Recorder runs from 5 ft/sec to 35 ft/sec.) The scope is used on driven sweep with the Z amplifier turned to full gain and its input paralleled with that of the Y amplifier. This permits blanking the spot on the tube face except when a pulse is being recorded. In the particular work done a pulse ion chamber supplied the pulses, but the method is equally adaptable to other counting techniques.

Two variations of this method were tried. In one the X gain of the scope is cut to zero, so as to give a series of vertical lines with heights proportional to pulse energy. In the other method the X gain is left on so as to get shaped pulse traces, again with heights proportional to energy. The former type of record would doubtless be much easier to design an automatic photoelectric scanner around, but the latter lends itself more easily to visual counting. Moreover, the "blip" at the base and top of the one-dimensional pulses tends to introduce some uncertainty as to the exact end points. Both types of records were made, however, and both gave good results when measured visually.

Reading was done on an Eastman Recordak microfilm reader, with a magnification of about 13-1/2 X. Since the image on the scope face is reduced on the film by a factor of 6, this sets the overall magnification between tube face and reader screen at around 2-1/4 X. The readings were made through a piece of waxed graph paper to the nearest 1/20 inch.

The method was first tested by feeding a constant Q Pulser (a mercury relay type signal generator) into the scope, varying the input voltage from 0 to 10 volts. The film, when developed, indicated that the lower bound of detectable voltage changes lay in the region of 1%-2%. Graphed, the deflection vs. input voltage curve gave excellent linearity up to 4 in. deflection on the microfilm reader, and good linearity to 5 in. Deflections up to 5 in. probably need not be corrected for scope nonlinearity, as at 5 in. deflection the departure is but 2%. This deflection corresponds to about a 2-1/4 in. trace on the 5 in. scope face.

Following this preliminary investigation, several actual energy measurements were made. The first was an attempt to separate the energy peaks of U^{233}, Pu^{239}, Pu^{238} and Pu^{236} from a composite sample in the alpha analyzer. These peaks lie at 4.82, 5.15, 5.50 and 5.75 Mev, respectively, or about 7% apart, and should furnish a measure of the resolving power of this method.

Figure 35 shows a plot of number of pulses vs. pulse height for a distribution of 349 points. It is seen that the four energy peaks are readily separated. Superimposed is the curve obtained from the electronic differential discriminator (a single channel sweep type analyzer). Energy calibration of the film curve was obtained by assuming the Pu^{239} peak to be at the correct position, 5.15 Mev. With this assumption the other peaks are found to be

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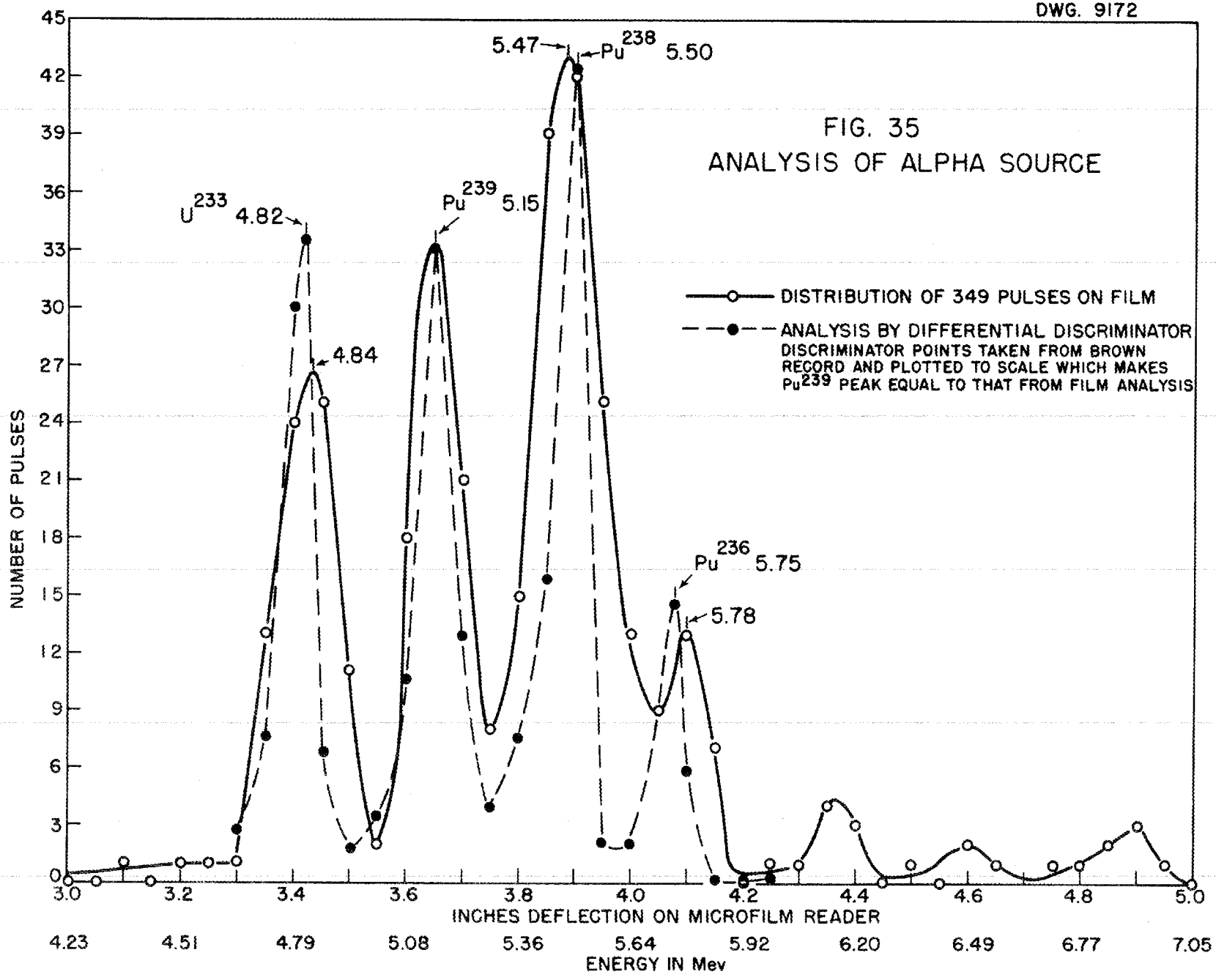

U^{233} = 4.84, Pu^{238} = 5.47, and Pu^{235} = 5.78 Mev. These are in excellent agreement with the correct values. The largest error (in Pu^{238}) is only 0.5%, giving considerably better accuracy than had been hoped for. Of course, this is all relative to Pu^{239}, a very close calibration point, and failures in linearity might be more serious over a greater range between calibration and measurement.

Points on the discriminator curve were taken from a Brown record, and plotted to a scale which makes the two Pu^{239} peaks equal in height. Comparisons of the resolution given by the two methods should probably not be made because of the vastly greater number of pulses evaluated by the discriminator. One evident difference between the two curves of Fig. 35 is that the differential discriminator gives U^{233} and U^{239} peaks of practically identical height, while the film curve shows the 233 peak lower than the 239. However, integral areas under these two peaks on the film are practically identical, and hence the total number of counts in each peak is about the same.

Another film was run on an Sn^{112} 24 Kv X-ray source, and the distribution of 244 pulses is plotted in Fig. 36. This source is seen to give a very pronounced peak, and would make a good calibration point for measurements in this region. There seems to be a secondary peak at about 25.8 Kv, which is about the right energy for the K β line, but there are really not enough pulses to be sure. (This secondary peak is only 10 pulses high.)

These data indicate that the film method gives good resolution and should be a useful tool in situations where either a quick count must be made or where an inordinately low counting rate precludes the use of a count rate meter. The principal objection to the method is the long and tedious process of reading the film. A projection system with a photoelectric scanner could be built to take care of this, the main obstacle being base line instability. Lateral shift in the film is probably negligible—sound recording practice holds this to 0.1 mm, or about 0.2% error for 4 in. on the microfilm reader—but d-c fluctuations in the scope cause the base line to change enough to vary results by several percent. Moreover, the intensity control must be set very carefully to yield a base line which is present but not heavily overexposed, particularly at the slower film speeds.

Film reading could be speeded up by using the time exposure type of pulse photography, wherein the film does not move, and successive pulses pile up to be read with a densitometer. Here one pass across the film with the densitometer would give the desired distribution. Moreover, one does away with

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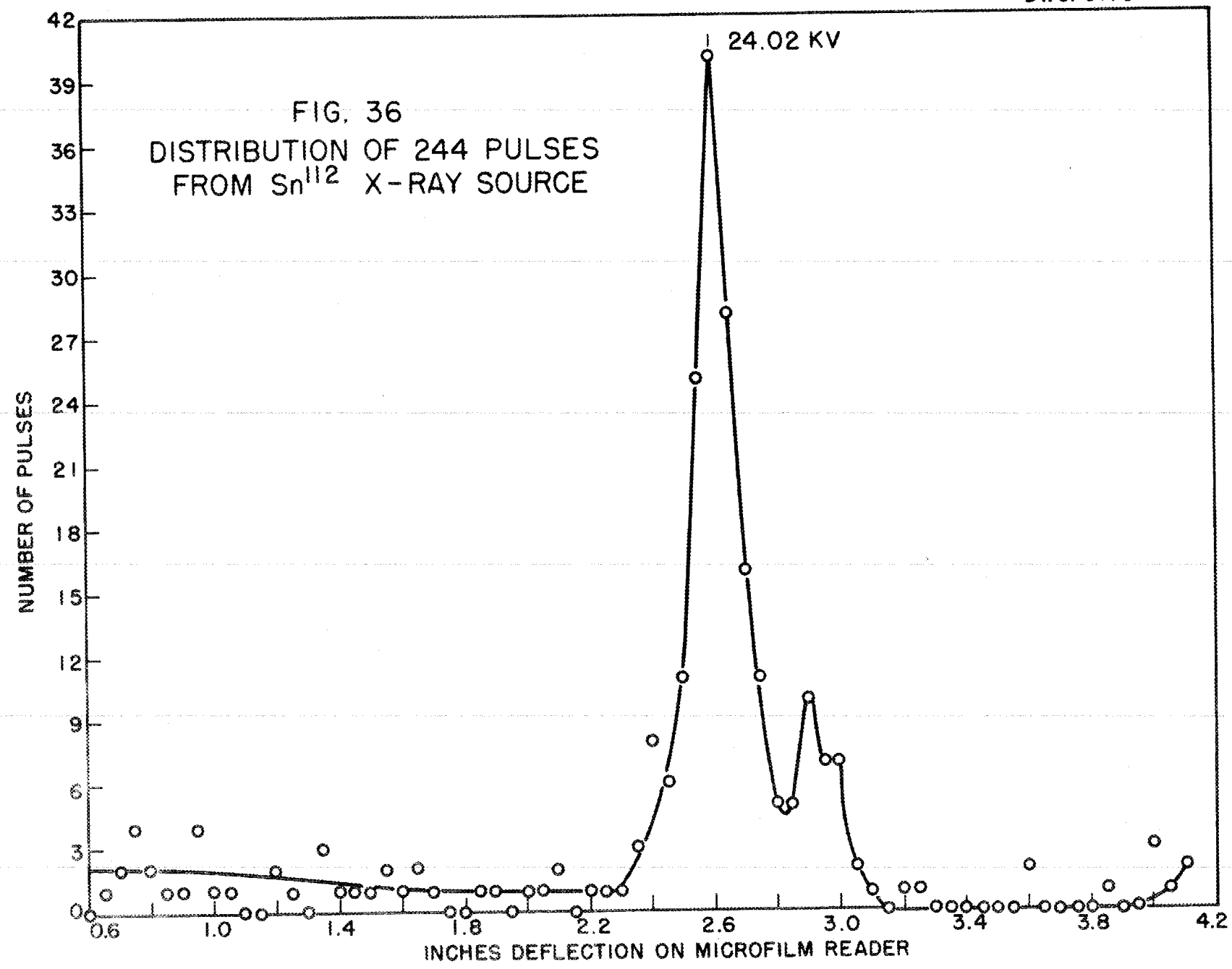


FIG. 36
DISTRIBUTION OF 244 PULSES
FROM Sn^{112} X-RAY SOURCE

processing long lengths of film. Disadvantages are messiness in absolute calibration of density—due to variables and non-linearities in film characteristics—and difficulty in resolving closely adjacent peaks because of film and tube phosphor halation. The first may be disregarded in a great number of cases, since in general we only wish to know the location of a given peak and to have a qualitative picture of its height relative to other portions of the energy spectrum. The second disadvantage may be eliminated by some sort of scale expansion, but in general would tend to limit the method to cases where energy peaks are not immediately adjacent. In other respects (speed of data gathering, large number of channels, etc.) it has the advantages of the moving film.

Both techniques no doubt have their place, the moving film method being the more absolute and potentially more reliable, and the time exposure method faster and more convenient.

NOT CLASSIFIED
DWG. 9561

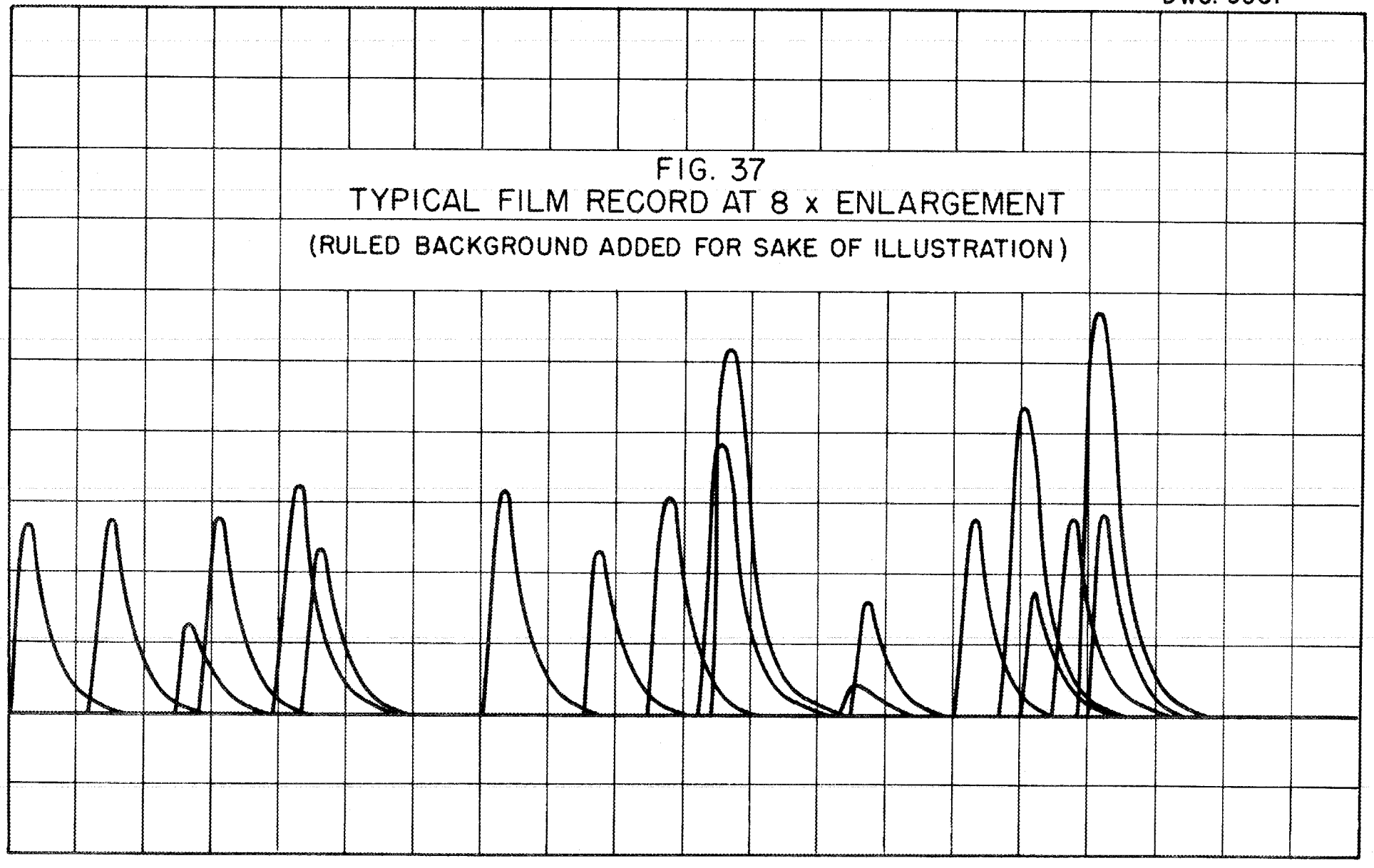
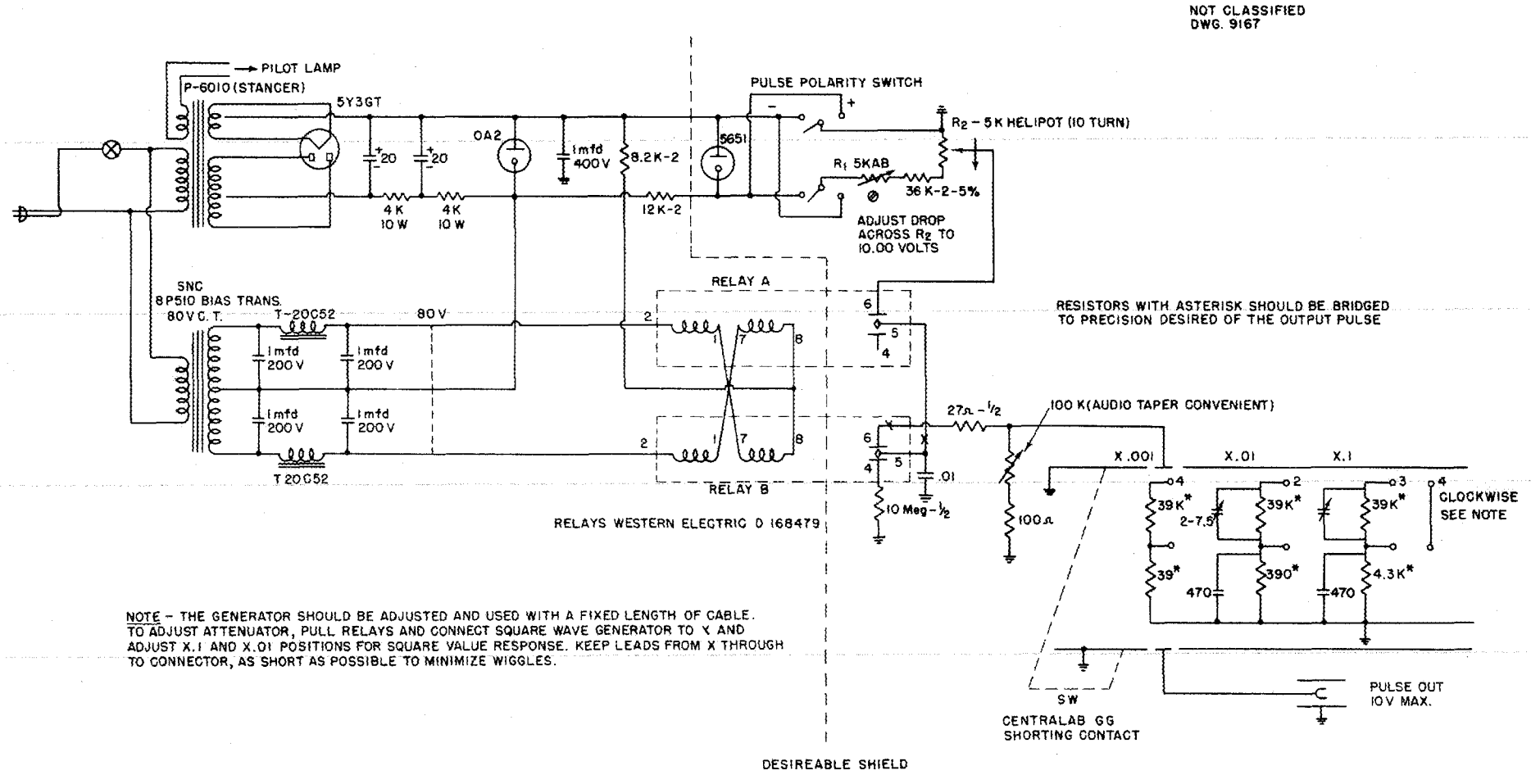


FIG. 37
TYPICAL FILM RECORD AT 8 x ENLARGEMENT
(RULED BACKGROUND ADDED FOR SAKE OF ILLUSTRATION)

CONSTANT Q PULSER

R. A. Dandl

The pulse generator shown in the accompanying diagram was built to test high-gain wide-band amplifiers and differential discriminators. The generator is especially useful for testing amplifiers because its pulse (+ or -) closely simulates a chamber pulse and it can be fed directly into a preamplifier. Its extremely high precision and stability make it a very useful instrument for the testing of amplifiers and differential discriminators either separately or in conjunction. The useful pulse output ranges from 50 μv to 10 volts at 60 cps. The rise time is approximately 10^{-8} seconds and fall time approximately 10^{-3} seconds. The stability is of the order of 0.1%.



NOTE - THE GENERATOR SHOULD BE ADJUSTED AND USED WITH A FIXED LENGTH OF CABLE. TO ADJUST ATTENUATOR, PULL RELAYS AND CONNECT SQUARE WAVE GENERATOR TO X AND ADJUST X.1 AND X.01 POSITIONS FOR SQUARE VALUE RESPONSE. KEEP LEADS FROM X THROUGH TO CONNECTOR, AS SHORT AS POSSIBLE TO MINIMIZE WIGGLES.

FIG. 38
CONSTANT Q PULSER