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REPORT OF THE CHEMISTRY DIVISION FOR THE MONTH

JUNE 15 - JULY 15, 1946

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J. R. Coe

Note: The names following the problem titles do not assign credit for the work, but rather indicate the person to be contacted when additional information is desired. Credit will be assigned when progress and final reports are issued.

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I. Work Relating to New Piles

CX5-7 - The Chemistry of Gas and Peroxide Formation Induced by Radiation in Water Solutions

Gas Evolution For Irradiated Uranium Solutions (E. Shapiro)

Enriched UO_2SO_4 solutions were irradiated at 100° C. in quartz capillaries. A curve was obtained for the pressure of H_2 as a function of irradiation time up to H_2 pressures of 700 atmospheres.

It is planned to irradiate this solution at 250° C. in order to obtain the pressure vs. time curve at this temperature.

Surface Studies (S. Ross)

In previous studies on the surface properties of palladium catalysts (MonN-27) for use in gas recombination, a radioactive exchange method was employed in an attempt to determine the extent of the catalyst surface. Since this exchange method is now of potentially very great utility owing to the availability of artificially radioactive substances, and since its validity has never been established, it was considered desirable to initiate a critical study using simple micro-crystalline solids.

It has been proposed to study the radioisotope exchange of Na^{24} ion in solution with Na^{23} ion in rock-salt crystals. An organic solvent is necessary for this study and preliminary experiments were done using absolute ethyl alcohol. It was soon found that NaCl is too soluble in this solvent for our purpose. A solubility product of about 10^{-10} is considered desirable, by analogy with experiments done on $PbSO_4$ in water.

It has been reported that NaCl dissolves in sec-butanol to the extent of 0.47 mg/100 g alcohol. A radiochemical determination of the solubility was made and gave a value of 0.062 mg NaCl dissolved in 100 g alcohol. This much lower value is obtained presumably because equilibrium is approached from the unsaturated side.

A preliminary exchange experiment, using $Na^{24}Cl$ tracer prepared by (n, γ) on NaCl in sec-butanol solution, showed that the rate of recrystallization of NaCl is relatively slow and can be distinguished readily from the surface exchange.

An investigation of the radiochemical composition of the tracer is now being conducted.

CX5-20 - Effects of Heavy Particles on Water and Aqueous Solutions (A. O. Allen)

Decomposition of Pure Water Previous results have shown that purified deaerated laboratory-distilled water decomposes in the pile to a steady state concentration of $O_2 + H_2O_2$ ranging for different samples from 10^{-5} to 9×10^{-4} N. P-9 directly

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from metal shipping drums (deaerated but not otherwise purified) showed less than 10^{-5} N oxidizing products after 2 to 4 hours in the pile, and only 2×10^{-5} N after 114 hours. Addition of CO_2 did not increase the amount of oxidizing products.

An apparatus has been prepared for determining the quantities of hydrogen and CO_2 as well as oxygen in the gases formed on exposure of water in the pile. This apparatus should help to clarify the role played by traces of organic matter in the water. An attempt is also being made to prepare water free of organic material by combining hydrogen and oxygen gases.

Fixation of Nitrogen in Water by Pile Irradiation Samples of water containing dissolved nitrogen or dissolved air have been exposed in the pile in the presence and absence of the gas phase in equilibrium with the water. The pH of the exposed water has been determined, and the sum of the nitrate and nitrite concentration in the water has been measured by a colorimetric method. Water saturated with nitrogen has been exposed as long as 136 hours in the absence of the gas phase without any noticeable formation of nitrate or nitrite ($< 1 \times 10^{-6}$ M). Some of these samples were analyzed for dissolved oxygen after exposure and showed a concentration of 3 to 8×10^{-5} N. Air-saturated water exposed in the absence of gas phase (dissolved O_2 1.1×10^{-3} N) showed noticeable nitrate and nitrite (4 to 10×10^{-6} M), but no significant drop in pH was found. Air-saturated water exposed in the presence of a gas phase showed 10^{-4} M nitrate and pH dropped to 4.5. Another sample with air in the gas phase at a pressure of only 5 cc showed 1.5×10^{-5} M nitrate and pH dropped to 6.0. Water exposed under nitrogen (with gas phase) gave similar results to that exposed under air. However, samples of this water analyzed for oxygen after exposure showed 9×10^{-4} N oxygen, arising from water decomposition. The gas phase, therefore, must have contained considerable oxygen in these experiments and there was no essential difference between them and the dissolved air experiments. The conclusion from these runs, subject to later verification, is that nitrogen is fixed to form nitrate or nitrite only when oxygen is present, and the rate of fixation is much greater in the gas phase over the water than it is in the water itself. A greater rate of fixation in the gas phase corresponds to the much higher concentration of nitrogen in the gas than in the liquid phase. Unlike more reactive solutes, nitrogen dissolved in water can react only when it is directly activated by the radiation; it is too inert to react with free radicals formed by activation of the water molecules. We do not yet know whether nitrogen in or over water essentially free of oxygen will remain inert under irradiation, or whether it may be fixed to compounds of a lower degree of oxidation than nitrite.

CX5-9 - The Recovery of Plutonium and Uranium from Chain Reacting Solutions
(F. T. Miles)

The distribution of nitric acid between hexone and aqueous aluminum nitrate solutions can be expressed by the empirical equation:

$$(HNO_3)_{Hex}\ (0.873 - 0.334\ M) = (HNO_3)_{Aq}\ (0.137 + 0.334\ M) - 0.029 - 0.036\ M$$

where M = moles $Al(NO_3)_3$ per liter in aqueous phase.

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A re-examination of the data on uranium distribution ratios in an attempt to distinguish between the salting out effectiveness of HNO_3 and $Al(NO_3)_3$ was not successful. The best equation is still:

$$\log (U)_{Hex} - \log (U)_{Aq} = -1.74 + 0.58 (NO_3^-)_{Aq}$$

where $(NO_3^-)_{Aq}$ includes ions from both HNO_3 and $Al(NO_3)_3$.

Decontamination factors for the first cycle, as measured by batch experiments, are 0.4 to 4 x 10^4 with $Na_2Cr_2O_7$ in the feed and 4 to 10 x 10^4 with reducing agents. It will probably be desirable to use oxidizing conditions in the first cycle to carry Np. Second cycle decontaminations (following oxidizing first cycles) show d.f's of only 13-20 unless reducing conditions are used. It was reported from Chicago that decontamination is improved by boiling with reducing agent. Using this treatment the d.f. was 250 to 340 for the second cycle or 2 to 5 x 10^6 over-all.

The column runs which have been made at Chicago under the direction of H. Hyman are summarized in Table 1. The bottom line gives the per cent loss calculated using the equations developed by Winsche (Technical Division, Section III, Report of July 15). These calculations involve the assumption that the distribution ratio is constant through each of the two column sections, scrub and extraction, which is not exact. The calculated values do not agree very closely with the observed results of column runs, but do show how sensitive the recovery is to small changes in relative flow rates.

TABLE 1

SUMMARY OF CHICAGO RUNS
Column IA

	First Hot Run 6/3	Waste Recovery	Cold Runs		Second Hot Run 7/22
Scrub, ml/min	5	5	10	7.5	7.5
Feed, ml/min	20	20	40	30	30
Hexone, ml/min	15	30	30	30	37.5
% U Loss Obsd.	ca. 40	< 0.1	<0.3	<0.1	--
% U Loss Calcd.	11.7	< 0.1	11.7	2.2	0.4

Scrub: 0.5 M $Al(NO_3)_3$, 0.2 M HNO_3
Feed: 1.13 M $Al(NO_3)_3$, 0.75 M HNO_3, 0.1 M $Na_2Cr_2O_7$, 0.003 M $UO_2(NO_3)_3$
Hexone: 0.5 M HNO_3

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The first hot run gave higher losses than calculated. This was apparently caused by: (1) a mistake in the feed plate connection which gave poor mixing and unsteady operation, (2) a very small flow of hexone (the dispersed phase) which resulted in channeling. After correction of the feed hook-up, a cold run at the same flow ratios but doubled rates gave only 0.3% loss.

Since a column can be operated to give either complete recovery or efficiency data but not both, it was decided to make the second hot run under conditions which would ensure complete recovery with some safety factor, and to take the resulting loss in volume reduction and decontamination factor. The proposed conditions are shown in the last column of Table 1. A slug containing 15 g of 25 as U_3O_8 was irradiated for 4 weeks and shipped to Chicago for this run. It will be 4 weeks old at the time of the run.

The stability of hexone to radiation under column conditions is being tested with the Chicago Van de Graaff. It is calculated that the conditions are no worse than in the Redox process which has already been tested with satisfactory results.

A sample of Al-clad Al-25 alloy has been exposed in a metal channel of the pile. No excess stack activity was noticed. This sample will be used for a small scale dissolver test.

The D_2O-UO_2F_2 solutions from the critical mass experiments are being distilled to replace D_2O by H_2O. This will require about two men for 1½ weeks. Some of the solutions have shown a black insoluble precipitate on drying, perhaps caused by material from the glyptal, which is being filtered out and analyzed.

II. 23 Production, Isolation, and Properties

CX9-1 - Isolation of U^{233} from Thorium and Its Compounds (E. G. Bohlmann)

The installation of the major items of equipment in the pretreatment cell has been completed. Connection of bubblers, manometers, etc., is now in progress.

Installation of the equipment in the extraction cell is under way. Some difficulty has been encountered in obtaining delivery of the necessary stainless steel packing for the column, but this now seems assured for the middle of August or perhaps a bit sooner. It is hoped that startup will be possible very soon after the arrival of the packing, but the very large demand on craft labor throughout the laboratory makes rapid progress difficult.

The survey of salting agents and solvents has run into the usual difficulties: non-reproducibility of results with different operators, batches of solvent, and so on. The present effort is devoted to definition and elimination of these difficulties.

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III. Radioisotope Research, Production, and Utilization

CX1-9 - The Preparation of Radioisotopes from Fission Materials

(W. E. Cohn, E. R. Tompkins, G. W. Parker)

Metal Dissolved and Extracted Dissolving for the "cross-sections" material has been completed and three new slugs have been processed through one stage of extraction and have been stored for accumulation for 61 and 43 separations. This metal is from a group of ten 533-day slugs pushed March 5, 1946 and represents about the best X metal available for long-lived components.

The Glass Solvent Extractor Installation is about one-third complete on the 12-liter batch extractor in Bank II, Cell I. The installation of the smaller extractor in Bank I has been delayed because of storage of high-level incompletely extracted material in the cell. A heavily shielded transfer line between the banks is contemplated for both the glass extractor and the new dissolver in Bank II.

Separations and Preparations The initial column separation of the combined superjuice from seven 14-month old slugs for the cross-section samples was attempted in the 6-foot, 100 ml resin column. The first sample, the anionic Ru, Te, etc., was taken off apparently successfully; however, the remaining separations were very poor probably due to the serious accumulation of cations both from the stainless dissolver and from the metal and fission-products.

The anionic cut contained considerable product (polymerized Pu(IV)) which must be removed, perhaps by boiling with HNO_3 and re-adsorbing the cations. The sample, it is hoped, should then be fairly free of extraneous solids and may be evaporated and mounted.

The other cuts may not be suitably pure for these samples and may be replaced with other material in storage.

During the processing of this total amount of material, and upon standing overnight, some few mls of gas accumulation were discovered in the column which it is conceived may have arisen from the heavy alpha or beta radiation. By allowing water or any reagent to move even slowly through the column at night the difficulty was overcome. Further observation will be made to attach the cause of gas formation to a type of radiation or to other difficulties.

Several semi-hot preparations were completed including 700 mc Y, 50-60 mc I, and 200 mc Sr.

The committed iodine preparations are being transferred next month to the Technical Division. They are duplicating the small-scale Te-source process in the 706-D hot lab with the help of 706-C personnel.

Electrolytic Purifications Using the standard mercury cathode, it has been established that Fe(II-III), Ni(II), Cr(III) and Cu(II) can be removed from a solution 0.1 N in HNO_3 to the extent of at least 98% when the original concentration of each is as much as 500 mg. Preliminary tracer investigations show

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that Ru and Te activity are both largely taken out of solution and deposited on the mercury. The precipitation is more nearly quantitative for Te than for Ru. The behavior of 43 is also being determined in the cell. The investigation is pointed toward shortcuts in purifications and separations.

W-10 Solution as Source of Ru and 43

A preliminary investigation of the W-10, Na_2CO_3-complexed solution of metal and some of the f.p's, has been found not too promising because of the very low concentration of activity, only 5% of which is ruthenium. The ratio of 43 to Ru is estimated in even 1 year old material to be of the order of 10^{-4}; therefore, unless this source becomes easier to extract than new metal, which is doubtful, it may be dropped until local ruthenium sources have been more thoroughly investigated.

Preparation of 61 Several small scale separations of the "61 fraction" of the rare earths from old material already available here have indicated that considerable success can be expected in the concentration of the soft beta components between yttrium and praseodymium with one cycle on a 4-6 foot exchange column. No attempt has been made to check contamination with Eu, stable Nd, or the alpha emitter. Soft to hard beta ratios of 10,000 have been obtained. Gamma contamination is much lower.

All-Column Fission Products Separations Apparatus The reassembly of the apparatus in a cell of building 706-C is nearing completion. Some additional equipment, including the storage and dispensing system and resin removal system has been designed and is now being constructed. The electronic recording instruments are nearing completion. It appears now that about another month will be required to complete the assembly.

Separations Chemistry (Ion Exchange Study) Construction of the flow-type counter tube was completed but, since it did not seem to operate successfully, it was returned to the shop for alterations. A counting pipette is also being constructed. It will consist of a thin-window cell in the form of a pipette which can be used for counting active solutions.

The study of Nalcite High Capacity Resin has been continued. The rate of movement of active, carrier-free, cerium down a column was tested with 5% citrate at pH 3.0. This rate is comparable to the rate of movement of Ce on IR-1 at pH 2.7-2.75. Macroscopic quantities of Y and Ce were separated nearly completely. The quantities that can be separated with a given bed volume of Nalcite are much larger than for an IR-1 column of equal size. Tests to determine the separation efficiency of the new resin for adjacent rare earths have been started.

The equilibrium experiments to determine which citrate ion or ions form coordination compounds with the rare earths are continuing. The results of the experiments so far are inconclusive. It appears that other tests such as electrochemical or solubility of known compounds in citrate solutions may be necessary to determine the nature of the citrate-rare earth complexes.

CX1-10 - The Preparation of Radio-isotopes Not Occurring in Fission
(W. E. Cohn, E. R. Tompkins, R. T. Overman, P. C. Tompkins, J. W. Irvine)

Sulfur Extractor The 15 gal. Hasteloy C reactor was inoperative about 75% of the time during the past month due to mechanical failures. During the remainder of the time a relatively large number of tests were made. The runs were made in triplicate with the time of extraction and the concentration of the HNO_3 being varied. The efficiency of extraction was determined by assaying the sulfur for P^{32} before and after extraction. The extract was analysed for sulfate and the P^{32} content determined. The results are not as yet complete but it was determined that (1) P^{32} may be almost completely (98%) extracted from the sulfur by extracting it for 5 minutes with about 20% of its volume of 1 M HNO_3; (2) lowering the concentration of HNO_3 reduces the efficiency of extraction but also reduces the quantity of sulfur oxidized; (3) the presence of air in the tank does not increase sulfur oxidation. The tests will be continued over a wider range of concentrations of HNO_3 and time of extraction to determine the optimum conditions for extraction of P^{32} with a minimum of sulfate as contaminant. The direction of this problem has been taken over by the Technical Division and its future progress will be described in the reports of that division.

Design of Shipping Container The device for closing the exposure cans has been completed and tested on some sample cans made by deep drawing. It proved to be satisfactory and easy to operate. A shipping container for the protective lead shield that holds the radioisotope has been designed and constructed. It has been approved for routine use in shipping radioisotopes. Illustrated directions for opening the exposure cans are being prepared. A short report describing the exposure can, shield and shipping container, will be issued soon.

C^{14} Process The basic chemistry of the C^{14} process has been completed. We are now setting up to do preliminary 1/10 scale runs in cooperation with Mr. Pressley of the Technical Division. The basic facts may be summarized as follows:

1) $Ca(NO_3)_2$ undergoes radiation decomposition in the pile by the reaction $Ca(NO_3)_2 \longrightarrow Ca(NO_2)_2 + O_2$.

2) C^{14} occurs entirely as $C^{14}O_2$.

3) Less than 1% of the $C^{14}O_2$ is lost from the dry $Ca(NO_3)_2$ by diffusion, only about 6% from the molten salt.

4) About 0.5% is lost by dissolving the $Ca(NO_3)_2$ in water.

5) The nuclear reaction $Ca^{40}(n,\alpha)A^{37}$ seems to occur to a significant extent. The radioactive gas evolved from $Ca(NO_3)_2$ has a half-life of close to 34.6 days which compares well with the half-life of 34.5 days reported for A^{37}.

6) The raw material gives about 0.7 mg C^{12} per can as CO_2 before it is bombarded. Cans that had received bombardment for 1 month in the center of the pile yielded about 4 to 5 mg C^{12} as CO_2, probably from the decomposition of stearic acid used as a lubricant during the canning process.

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7) The C^{14} yield is approximately three times the calculated value when based on specific activity measurements made by D. Norris.

8) The specific activity obtained from salt which had been bombarded one month in the center of the pile was 60 to 70 μc C^{14}/mg C.

9) The C^{14} as $Na_2C^{14}O_3$ in 1 to 5 M $Ca(NO_3)_2$ at pH >11 coprecipitated with $Ca(OH)_2$ to a slight extent (< 10%) under all conditions tried.

During the next month, three things should be accomplished:

1) Publication of the final report on the chemistry of the C^{14}-$Ca(NO_3)_2$ process.

2) The process should be well along on the pilot-plant stage.

3) A program to study the preparation of C^{14} from Be_3N_2 should be under way.

Investigation of Three Year Na^{22} Ballantine reports an (n, 2n) reaction on Na^{23} giving Na^{22}. The reaction would be $Na^{23}(n, 2n)^{2}Na^{22}$. This is an interesting activity since it has a 3 year half-life and a 0.58 Mev positron followed by a gamma ray. This would be quite important for biological work if it could be obtained in quantity since the only other Na activity has a 12.8 hour half-life. However, the preliminary work on the activity gives a yield of about 0.1 μc/gram Na at saturation. This is a specific activity which is probably much too low for utilization. The cross section for the (n, 2n) reaction is of the order of 10^{-5} barns.

Tentative Plans for Calibration Program Plans are being made for starting work on a program of calibrating the gamma ionization chamber. The plan is to make up standards of UX_1 and RaE and make accurate beta counting measurements on as many of the activities as possible. The gamma intensity will then be measured on large quantities of the activities. This will be calibrated then for each activity. We plan to calibrate it directly in disintegrations per second for those activities whose decay scheme is known. We plan to integrate this program with the standards program of the laboratory when this is set up.

Preparation of (n, γ) Phosphorus Work on a material and process for the preparation of (n, γ) phosphorus at Hanford has been under way. Several metal phosphides which will generate phosphine with water or acid have been looked into. Magnesium phosphide looks promising from the standpoint of ease of preparation, stability and suitability for recovery of the active phosphorus. Two types of recovery processes are being investigated. One consists of hydrolysis of Mg_2P_3 by water vapor and subsequent burning of the PH_3 to H_3PO_4 in oxygen. The other consists of oxidation of Mg_3P_2 to $MgCl_2$ and PCl_5 by Cl_2 followed by a separation of the products by sublimation. Phosphoric acid can then be obtained by hydrolysis of the PCl_5. Both methods show sufficient promise that the Technical Division is taking over the process design.

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Shipments - 6/15/46 - 7/15/46

Off Area: 4½# S (P^{32})
15 mc I^{131}
25 mc Sr^{89-90}
50 mc Sr^{89-90}
50 mc Y^{91}
50 mc $Ce^{141-143}$
100 mc $Zr-Cb^{95}$

To Clinton Lab: 500 mc "Super Juice" (F.P. Mix)

CX4-4 - Experimental Use of C^{14} (L. Spector, W. B. Leslie, O. K. Neville)

Following procedures previously worked out with dead material, 7.8 grams of radioactive acetic acid has been prepared. A yield of 87.5% was obtained in the carbonation step. After concentration, ether extraction and distillation the acetic acid was 78.5% (by volume) pure and represented a total over-all yield of 70%. The various residues, however, are easily re-cycled in subsequent runs. No figures are as yet available on the specific activity and radiochemical yield. Apparatus has been designed and assembled for use in the preparation of other organic intermediates containing C^{14}.

A progress report covering work completed on the counting of solid samples, synthesis of compounds containing C^{14}, and the investigation of bombarded NH_4NO_3 solutions is in preparation. The micro combustion apparatus has been modified, and a study of a procedure for the introduction of $C^{14}O_2$ (resulting from the combustion of organic compounds) into an ionization chamber is being made.

IV. Analytical Procedures

CX7-1 - Analytical Service (L. B. Rogers, J. E. Hudgens, W. M. Byerly)

The following analyses were requested during this period:

	Radiochemical	Gross Activity	Ionic	Spectrographic
Chemistry	174	59	145	66
Technical	100	666	565	15
Others	1	1	4	

CX7-2 - Research and Development Studies on Analytical Procedures (L. B. Rogers, J. E. Hudgens, W. M. Byerly)

Protoactinium Studies The 1300 area developmental program and process will place unusual requirements on the procedure for fission element analysis. The material used may be made up of as much as 99% Pa activity and only 1% gross

fission product activity. In order that the analytical results for the specific fission elements can be considered accurate, the fission product procedure must achieve a decontamination factor of 10^4. While some of the procedures as they now stand can achieve this goal, additional steps must be introduced in others. To test the Pa removal, the fission product procedures were run using Pa tracer prepared by pile bombardment of Th and allowing sufficient time for the Th^{233} to decay away. The Th used for this purpose was separated from decay products immediately before exposure. An aliquot containing 2×10^6 counts of Pa activity was used as a starting sample size, and the radiochemical activity analysis performed in the usual way. The activity found in the final mount of the fission element in question was then assumed to be made up entirely of Pa activity. The results of the analyses performed to date are shown in Table 2.

TABLE 2

CONTAMINATION OF THE FINAL FISSION ELEMENT PRECIPITATED BY Pa ACTIVITY

Fission Element Sought	% of Original Pa Activity Remaining after Usual Separations
Ba (HCl Ether Method)	0.010
Ba (Fuming HNO_3 Method)	0.004
Sr	0.002
Cb	0.033
Ru	0.003
Te	0.006
Cs	0.001
I_2	0.002
Total Rare Earths	0.014

Since elements commonly present in process solutions in macro amounts have a deleterious effect on the decontamination, experiments are in progress to minimize the effect on the accuracy of each fission product analysis by these elements.

Spectroscopists After visiting other plants on the area and consulting several spectroscopists, recommendations have been submitted for the expansion of the spectrographic laboratory and the purchase of additional equipment. The new equipment will also satisfy the needs of the Physics Division for the immediate future.

Rare Earths A sample of radioactive europium was obtained from R. T. Overman for electrolytic studies. The findings of J. A. Marinsky were supported in that two beta rays of 0.6 Mev and 1.6 Mev were found rather than the single 0.9 Mev beta reported in the literature. In addition, a soft beta or X-ray was noted together with a hard gamma of 1.5 Mev.

CX3-4 - Development of Radiochemical Procedures (R. W. Stoughton, J. Halperin)

Work is proceeding on the analysis of uranium in urine. During the last month an investigation of a number of variables in the electroplating step has been made. Conditions have been developed whereby 95% recovery of small amounts of uranium can be reproducibly obtained. It is of interest to note that tracer quantities of uranium cannot be recovered by electroplating under the same conditions as recommended for larger quantities by Scott and Hufford (CN-3328).

Work is proceeding on the identification of the radioactive contaminants of lanthanum salts. Difficulties have been encountered in interpreting data obtained from the range analyzer on relatively thick samples.

V. Basic Chemistry

CX3-2 - Basic Chemistry of Plutonium (K. A. Kraus)

The effect of acidity and iron concentration on the catalytic oxidation of Pu(V) by hydrogen peroxide and Fe^{+++} was investigated. It was found that practically complete catalytic oxidation can result in ca. 1 M $HClO_4$ in a very few minutes. Decreasing the acid concentration also decreases the extent of the catalytic oxidation, possibly due to the increased rate of reduction of Pu(V) by hydrogen peroxide, since after ca. 10 minutes a steady state seems to be reached. (No detailed comparison between the rates of reduction and the rates of oxidation have as yet been made.) The results are summarized in Table 3.

TABLE 3

CATALYTIC OXIDATION OF Pu(V) BY H_2O_2-Fe^{+++}
(ca. 0.05 M H_2O_2)

M H_3O^+	M Fe^{+++}		Per Cent Oxidized At Time (min.) 4		20	
0.98	0.0167		98		100	
0.98		0.00167		84		95
0.098	0.0167		79		87	
0.098		0.00167		33		40
0.026	0.0167		48		57	
0.0098		0.00167		(17)		20

The catalytic oxidation of Pu(III) to Pu(IV) by hydrogen peroxide (0.027 M H_2O_2, 1 M perchloric acid, 0.01 M Fe^{+3}) was found to be practically instantaneous. Simultaneous with the oxidation to Pu(IV), a large amount of oxidation to Pu(VI) occurred (9% Pu(VI) immediately + 15% Pu(VI) in 19 hours).

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Several experiments have been carried out on the rate of reduction of Pu(VI) by hydrogen peroxide in 1 M perchloric acid near 25° C. Over ca. the first hour of reduction a plot of 1/c vs. time (where c is the concentration of Pu(VI)) is a straight line (the amount of disproportionation of the resulting Pu(V) was found to be negligible in this time interval), with slopes of 15, 20, and 18 moles^{-1} min^{-1} for (a) 1.11 x 10^{-3} M Pu, ca. 0.05 M H_2O_2; (b) 1.19 x 10^{-3} M Pu, 0.05 M H_2O_2; and (c) 2.62 x 10^{-3} M Pu, 0.35 M H_2O_2, respectively.

An experiment comparing the rate of growth of Pu(VI) from a 9.12 x 10^{-4} M Pu(V) solution in the presence and absence of hydrogen peroxide (0.05 M H_2O_2 and 1 M $HClO_4$) showed that no appreciable oxidation of Pu(V) due to hydrogen peroxide occurs.

Summary reports on the topics are in preparation.

It has previously been indicated that the apparent deviations from the Beer's Law dependence of the 831 millimicron absorption band for Pu(VI) is purely an instrumental effect, depending upon the resolving power of the instrument (Beckman Quartz Spectrophotometer, model DU, were used). Experiments have been carried out to confirm this fact further, and at the same time show that the spectrum of Pu(VI) solutions is independent of its concentration, and therefore does not give evidence for either polymerization or depolymerization of PuO_2^{++} in 1 M $HClO_4$.

If the deviations from Beer's Law are due to the limited resolving power of the instrument, the same optical density readings should be obtained for the same instrument and any one product c x l (where c is the concentration and l is the cell length) irrespective of the ratio of c/l. Over a concentration range of 3.92 x 10^{-6} to 7.16 x 10^{-3} M Pu(VI) and the cell length range of 0.5 and 10 centimeters, this was found to be the case within experimental error for the two instruments, although the density readings differed for the two instruments. Low results were at first obtained in the most dilute solutions which, however, are believed due to reduction of Pu(VI) by impurities in the perchloric acid since the addition of ceric ions gave consistent results.

It has previously been observed that titration curves of plutonium (VI) with sodium hydroxide differ from back titration curves with perchloric acid after the plutonium solutions had reached a high pH. This hysteresis effect shows up most spectacularly in upward pH drifts after a basic solution of Pu(VI) has been acidified. Since it is felt that this hysteresis effect may be closely connected with the apparent hydrolytic discrepancies between uranium(VI) and plutonium(VI), a detailed study of this effect has been initiated. In this study it was thought desirable first to determine the pH region to which an acidic Pu(VI) solution has to be raised to exhibit the hysteresis effect. It was shown that a pH as low as pH 8 is sufficient to product on acidification pH drifts amounting to as much as 0.3 to 0.5 moles of hydroxide ions per mole of plutonium. Equilibrium values after acidification are being obtained by reducing the Pu(VI) solutions to Pu(V) solutions and measuring the number of moles of hydroxide ions liberated in this reduction, as well as the pH drifts occurring when the Pu is still Pu(VI).

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The latest set of acid-base titrations of "barium plutonate" seem to give relatively consistent results and indicate that ca. 2.5 moles of hydroxide ions are in the compound per mole of plutonium. The titrations have been carried out in the absence of carbon dioxide, and the final solutions of Pu(VI) have been reduced to Pu(V) to avoid difficulties due to the hysteresis effect occurring with Pu(VI). Experiments are now under way to determine the barium-plutonium ratio of the same compound, using a combined barium tracer-weighing technique. Uncertainties in the extent of hydration of the final compound (barium chloride) make the barium-plutonium ratio somewhat uncertain. Experiments are now under way to establish the extent of hydration of the barium chloride prepared under the conditions of the analysis.

Experiments are under way to prepare aqueous solutions of uranium(V) at reasonably high concentrations to permit study of such a valence state. Uranium(V) would be expected to exist with a reasonable stability in view of the analogy of uranium to plutonium and neptunium.

Experiments are being undertaken to determine the extent of carbonate complexing of Pu(VI).

CX3-5 - Basic Studies of Separation Processes (G. E. Boyd)

Radiochemistry of the Rare Earths (B. H. Ketelle) The activity produced by the bombardment of pure erbium oxide in the pile is being investigated. No evidence has been found for the seven minute activity assigned to $Er^{169,71}$. The twelve hour activity and activities of longer half life have been produced. The properties of the twelve hour activity are being studied so that it may be used to follow the separation of erbium from holmium and thulium.

The column separation of Ce^{141} (28 day) from Pr^{143} (13.5 day) has been begun. Difficulty has been encountered in continuously measuring the soft cerium radiation in the effluent solution from the column. A new solution counting cell has been designed and is ready to be tested for counting soft radiations in solution. Some studies of the separation of cerium and praseodymium will be made so that the results may be used in designing experiments for the separation of the less available heavier rare earths.

Ion-exchange Theory (L. S. Myers, Q. V. Larson) Two sets of experiments have been carried out to study the application of the Mass Transfer (Schumann) Theory to the adsorption and desorption of radioactive tracer ions by Amberlite IR-1.

These studies were made by measuring the adsorption of Na^{24} ion on Cs resin from 0.001 M CsCl solution. Five columns were employed to determine the effects of bed height, flow rate, concentration of CsCl, and the reproducibility of the adsorption process.

The desorption studies were made studying the same effects but desorbing Rb* ion from hydrogen resin with 0.001 M $HClO_4$ solution.

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Results of these experiments will be reported next month.

Experiments have been finished using the shallow bed adsorption column technique. These studies have included an investigation of the effect of change in solution concentration, in flow rate, and in direction of passage of the absorbate through the resin bed. These results will be analyzed to determine the role of mass action and diffusion rate processes in adsorption.

Adsorption Studies with Be (L. S. Myers) One experiment has been made in an attempt to separate the Be^7 and Be^9 isotopes by adsorption and desorption using Amberlite IR-1. Results will be given next month.

Thermodynamics of Coprecipitation (F. Vaslow) The value of ΔF of transfer of a substance from a perfect solid solution to an actual solution was measured at 70° C. and a value computed from Kolthoff's data at 98°. The values for these and previous results (MonN-131) are as follows: 30°, 419 cal/mole; 50°, 392 cal/mole; 70°, 190 cal/mole; 98°, -230 cal/mole. Since the entropy change would correspond to from 1.5 cal/mole deg to 14 cal/mole deg for the range, errors in either the experimental data or the solubility products used are indicated.

Rate studies indicated that at 30° C. equilibrium is reached in about four hours.

NaBr free of Cl has been prepared for use in experiments with AgBr as the host crystal.

Szilard-Chalmers Reactions (S. Wexler) Work has begun on experiments designed to verify or disprove the predictions given by simple equations describing the irradiation decomposition of compounds bombarded in the pile (CN-2833). A few improvements have been made in the definitions used in the theory. An iron compound, hemin, and a bromine compound, potassium bromate, are being used. A method of separating the inactive iron from the iron complexed in the hemin has been worked out and is being refined. A method of separating active bromine as bromide from bromine in irradiated potassium bromate using molecular bromine as carrier has been worked out. The separation of bromide from bromate without carrier by oxidation and extraction into carbon tetrachloride has been found not to be quantitative, the efficiency of the extraction being dependent on the amount of bromide present. Re-extraction into 6% sulfurous acid has also been found not to be quantitative when microgram quantities of bromide are present. Preliminary results on the direct determination of bromide without separating from bromate have given encouraging results on controls.

Study of "43" Activities (E. E. Motta, G. E. Boyd) The characterization of a long-lived 43 activity produced by decay from pile neutron bombardment of $Ru(OH)_3$ has been described in a current report, MonC-132. This 92 d 43^{97} activity was observed to emit 1.5 mg Al/cm^2 conversion electrons along with some unconverted gamma radiation. Additional tentative evidence of the presence of X-rays was obtained, but it was not possible to determine whether these could be attributed to element 43 or to Mo.

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Studies of the coprecipitation of 43 with rhenium sulfide, platinum sulfide, tetraphenyl arsonium perrhenate and with nitron perrhenate have been completed. In these studies, the effects of changes in acidity, amount of Re (or Pt) carrier and temperature were determined, and the optimum conditions for the analytical use of these precipitates were found. A progress report (MonC-99) summarizing these and other studies on the chemistry of element 43 will be issued in the coming period.

The fast neutron bombardment of Rh in the uranium donut has indicated the production of a new 43 activity presumably by an (n, γ) reaction.

The properties of the radiations from the ground state of the 43^{99} nucleus are being determined, and an estimate of its half-life based on its yield from the slow neutron bombardment of Mo has been attempted.

CX4-1 - Study of the Distribution of Half-lives and Energies Among the Fission Products (R. Livingston)

Several fluorocarbons have been tried in the cloud chamber. Chemicals 816 and 716, completely fluorinated dimethyl cyclohexane and completely fluorinated n-heptane, showed alpha tracks when used with argon at expansion ratios of 1.66 and 1.77. The background was very heavy and could not be cleared by increasing the sweep field voltage. Carbon tetrachloride in argon gave tracks at 1.65. Chemicals 714 and 816 low boilers would not show tracks with expansion ratios up to 1.95. Freon 113 was also unsatisfactory. Attempts are now being made to obtain more fluorocarbons.

CX4-3 - Fission Product Radiochemistry (H. A. Levy)

An investigation of the mass-assignment and genetic relationship of the 10 h Y fission activity is under way.

CX10-21 - Experiments with Molecular Beams of Radioactive Isotopes (E. H. Taylor)

Design and construction of apparatus is proceeding.

CX15-1 - Effect of Radiation on Organic Compounds (A. O. Allen, E. C. Coyner)

Carbon tetrachloride has been purified and samples sealed under vacuum in glass ampoules preparatory to exposure in the pile.

Calorimetric Studies (C. V. Cannon)

Preliminary work on a gamma calorimeter has continued. In this calorimeter the volume of gas evolved from liquid nitrogen at constant pressure is the measure of the heat input.

In order to study the sensitivity of this type of calorimeter, a liquid nitrogen container of the Dewar flask type was constructed and a small electrical resistance suspended at the center of the inner flask. Measurements of gas evolution were made with the inner flask filled with liquid nitrogen and with the outer flask immersed in liquid nitrogen.

The rate of evolution of nitrogen was measured for several energy inputs ranging from 0.4×10^{-2} to 2.8×10^{-2} watts and was found to be linear with energy input. The reproducibility of the rate measurements was ±1.2%. The background evolution of nitrogen was about 0.35 cc per minute.

CX10-22 - Chemical, Physical, and Nuclear Properties of Heavy Isotopes (R. W. Stoughton, J. Halperin)

A 1.5 millicurie sample of Th^{234} (UX_1) has been prepared free from uranium and been given to L. B. Borst for fissionability measurements. It is estimated that the sample contains less than one part U^{235} in 10^5 Th^{234}. Preliminary fission measurements indicate (1) that the thermal neutron fission cross-section of Th^{234} is considerably less than one barn and (2) the growth of U^{234} with possibly a higher fission cross-section than Th^{234}. These results are quite tentative, and it is hoped that more precise data will be obtained within the next month. Work is proceeding on the development of the purification procedure to separate Th^{234}(UX_1) from uranium.

In order to isolate and measure the amount of Ac^{227} formed during a neutron bombardment of Ra^{226}, an IR-1 resin adsorption column has been set up and a number of preliminary experiments have been run. It is desired to obtain more exact data concerning the capture cross-section of Ra^{226} than is now available.

Theory of Solvent Extraction (F. J. Leitz, J. P. McBride)

J. P. McBride has gone to Chicago to test radiation effects on the various solvents of interest to the several extraction processes being studied at Clinton Laboratories.

The absorption spectrum of uranyl nitrate has been determined in a variety of organic solvents and as a function of concentration, pH, and concentration of salting agent in aqueous solution. Structure in the spectrum occurs in the wavelength region from 350 to 500 millimicrons in all cases; the absorption increasing at shorter wavelength and decreasing at longer without apparent limit.

The observed location and height of the density maxima and minima for 0.1 M UNH at pH 2 are in good agreement with those reported by Goldring and Brady in MonC-106. The characteristic linear increase of density with concentration indicates compliance with Beer's Law from 0 to 0.1 molar uranyl nitrate at pH 2. At higher concentrations (0.1 to 1.0 molar) the molar extinction coefficient increases slightly.

From 340 to 500 millimicrons the absorption by 0.1 M UNH is essentially unchanged (maximum deviation of 7%) by variations in pH over the range 0.5 to 2.0. Similarly the absorption by 0.1 M UNH in 5.8 N NH_4NO_3 was found unaltered by more than 3% in the pH range 0.to 2.0.

The absorption of dibutyl cellosolve, diethyl ether, and diethyl cellosolve is less than 10% that of 0.1 M UNH over the spectral range from 340 to 500 millimicrons. Absorption by the solvent is likewise suitably low over most of this range for the other solvents investigated, being more than 10% that of 0.1 M UNH

for hexone only below 395 millimicrons, for diisopropyl ether from 335 to 390 millimicrons, and for dibutyl carbitol from 345 to 365 millimicrons. Ca. 0.1 M UNH salted by 6 N $Al(NO_3)_3$ into hexone, diethyl cellosolve, and dibutyl carbitol gives spectra similar in shape in the various solvents which are greater in density than aqueous solution, particularly in the ranges 350-390 millimicrons and 420-500 millimicrons with a pronounced delineation in structure in the latter range. Similar results are observed in diethyl ether and dibutyl cellosolve, somewhat obscured by what is apparently a fairly rapid photo-decomposition of uranyl nitrate in these media.

As expected, the molar extinction coefficients of the salting agents, Al, Be, Ca, La, Li, Mg, NH_4^+, and Th nitrates were observed to be suitably low for studies of variations in the uranyl nitrate spectrum at high salting agent concentrations, being less than 0.1 above 350 millimicrons. In 1.8 to 8.6 N $Ca(NO_3)_2$ at pH 1 the structure of the 0.1 M UNH spectrum remained essentially unchanged, but the density increased with increasing salting agent concentration, particularly in the region 420-500 millimicrons where the increase was by a factor of 3 to 4 for 8.6 N $Ca(NO_3)_2$. For 0.1 M UNH at pH 1 in 1.8-8.6 N NH_4NO_3 the absorption curves were almost identical with those for $Ca(NO_3)_2$ except that the increase in density was slightly (up to 20%) greater for equivalent NH_4NO_3 concentrations. Correlation of the absorption spectra data with the batch extraction data will be attempted as soon as the latter results are available.

Radiochemical Studies with Enriched Fe Isotopes (J. A. Swartout)

Work with the enriched Fe isotopes obtained from Y-12 has been initiated with the primary objective of studying Mn activities produced by (n, p) reactions. Chemical procedures for separating Mn from Fe quantitatively were tested using Fe^{59} and Mn^{56} tracers. Results of preliminary bombardments of about 1 mg of the enriched Fe^{54}, Fe^{56}, and Fe^{58} samples indicated that these are contaminated by impurities. From the amount of 2.6 h activity produced during bombardment of the Fe^{58} sample, it appeared that about 1% Mn was initially present in the iron. Because of the bearing which this would have upon cross-section measurements made by the Physics Division, more detailed study of impurities is in progress.

Activities Induced in Ni by Neutron Bombardment (E. E. Conn)

In the study of long lived Ni^{59} activity and search for Ni^{63}, rapid separations of nickel from cobalt carriers by precipitation of the nickel salt of dimethylglyoxime have been made. Using the 177 day pile bombarded nickel and measuring the activity in the nickel precipitate with an ionization chamber, a growth of a short lived activity has been found. Further work is being done to identify and characterize the radiations of this new radioisotope.

There is strong evidence for a new activity of cobalt with half-life of 11.5 hours and a beta of approximately 0.7 Mev produced by (n, p) reaction on highly purified nickel oxide. Another experiment to check these values for half life and beta energy as well as gamma radiation has been completed and the results are being studied.

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Activities Induced in Pd by Neutron Bombardment (A. R. Brosi)

The identification and characterization of 17 d Pd^{103} has been completed and a report is being written. Study of the radiochemistry of Pd is being continued in a search for a possible long-lived Pd^{107}. An attempt is also being made to verify evidence of new radioisotopes formed by (n, 2n) and (n, p) reactions on Pd.

A study of the radiochemistry of Pt has been started with a search for Pt^{193}.

VI. Special Instrument Development

CX11-1 - Geiger Tube Development (C. J. Borkowski)

An alpha source mounted on a micrometer caliper head has been constructed for the measurement of mica window thickness on G-M counters. Preliminary measurements indicate that the mica window thickness can be measured by this method with a precision of ± 0.1 mg/cm^2.

The low absorption counter with a cylindrical absorber arrangement has been completed and is now in operation. The geometry of the counter is about 23%, and the operating voltage plateau is 100 volts long. Seven absorbers ranging from 0.1 mg/cm^2 to 7.2 mg/cm^2 are available for obtaining absorption curves. The counter can be evacuated and filled in less than ten minutes.

CX11-4 - Development and Construction of Alpha-counting Equipment (C. J. Borkowski)

The alpha range analyser was moved to a new room, and permanent facilities have been made for it.

CX11-5 - Development and Construction of Special Electronic Equipment (C. J. Borkowski)

The ionization chambers previously described for measuring $C^{14}O_2$ in the gas phase have been used for C^{14} assay with excellent results. The background current of the chambers is 3×10^{-16} amperes. Because of the special design of the insulators the insulator currents which develop when the chamber is evacuated decay within five minutes, thus making possible rapid measurement of ionization currents.

It is interesting to know that a half-life of 32 days was obtained on an unknown radioactive gas suspected to be A^{37}. This half-life was calculated from a decay which was observed on the vibrating reed electrometer over a three hour period. Over a two week period the half-life was found to be 34.5 days--identifying A^{37}.

A second vibrating reed electrometer is being assembled for use by the Chemistry Division.

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Distribution of Technical Personnel

P.A. No.	Title	No. of Men Past Month	No. of Men Next Month
	Work Relating to New Piles		
CX5-7	The Chemistry of Gas & Peroxide Formation Induced by Radiation in Water Solutions	2	2
CX5-9	The Recovery of Pu and U from Chain Reacting Solutions	6	6
CX5-20	Effects of Heavy Particles on Water and Aqueous Solutions	5½	6
	23 Production, Isolation, and Properties		
CX9-1	Isolation of U^{233} from Thorium and Its Compounds	6	6
	Radio-isotope Research, Production, and Utilization		
CX1-9	The Preparation of Radio-isotopes from Fission Materials	10½	11
CX1-10	The Preparation of Radio-isotopes Not Occurring in Fission	8½	8
CX4-4	Experimental Use of C^{14}	3	3
	Analytical Procedures		
CX7-1	Analytical Service	9	10½
CX7-2	Research and Development Studies on Analytical Procedures	16	20
CX3-4	Development of Radiochemical Procedures	1	1
	Basic Chemistry		
CX3-2	Basic Chemistry of Plutonium	7	7
CX3-5	Basic Studies of Separation Processes	6½	7
CX4-1	Study of the Distribution of Half-lives and Energies Among the Fission Products	1	1
CX4-3	Fission Product Radiochemistry	1	1
CX10-21	Experiments with Molecular Beams of Radioactive Isotopes	1½	1½
CX15-1	Effect of Radiation on Organic Compounds	½	½
	Calorimetric Studies	2	2
CX10-22	Chemical, Physical, and Nuclear Properties of Heavy Isotopes	2	2
	Theory of Solvent Extraction	2	2
	Radiochemical Studies with Enriched Fe Isotopes	1	1
	Activities Induced in Ni by Neutron Bombardment	1	1
	Activities Induced in Pd by Neutron Bombardment	1	1
	Special Instrument Development		
CX11-1	Geiger Tube Development	2	2
CX11-4	Development & Construction of Alpha Counting Equipment	1½	1
CX11-5	Development & Construction of Special Electronic Equipment	2½	2
	Plutonium Project Record	10	8
	On Leave	1	1
	Supervision	5	4
	Total Number of Technical Personnel in the Division	116	118½

Number of technical personnel added: 8
Number of technical personnel terminated: 4
Number of non-technical personnel: 29

Y 12 OPERATIONS DIVISION
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