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A.E.C. RESEARCH AND DEVELOPMENT REPORT

ISC-643

**AMES
LABORATORY
IOWA STATE
COLLEGE**

CHEMISTRY. QUARTERLY SUMMARY RESEARCH REPORT.
APRIL, MAY, JUNE, -- 1955

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1
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ISC-643

UNITED STATES ATOMIC ENERGY COMMISSION

QUARTERLY SUMMARY RESEARCH REPORT IN CHEMISTRY

For April, May, June, 1955

by

Ames Laboratory Staff

October 24, 1955

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
Contract W-7405 eng-82

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2

ISC-643

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TABLE OF CONTENTS

Page

CHEMISTRY

Physical and Inorganic Chemistry

1. Separation of Rare Earths by Ion-Exchange	7
1.1 Production of Heavy Rare Earths and Yttrium	7
2. Separation of Isotopes by Ion-Exchange	9
3. Rare Earth Metallurgy	9
3.1 Structures of Rare Earth Metals	9
3.2 Vapor Pressure Studies	10
4. Transport Numbers in Fused Salts	10
5. The Chemistry of Gallium(II) Halides in Aqueous Base	12
6. Metal-Metal Salt Solubilities	12
7. Adsorption Studies	13
8. Hafnium-Zirconium Studies	13
9. Reaction Kinetics	14

Pyrometallurgy

1. Metallurgical Separation of Fuel and Fission Products	15
2. Uranium-Samarium Studies	15
3. Ruthenium Studies	16

Analytical Chemistry

1. Titration of Mercuric Ion	16
2. Sulfur in Organic Compounds	16
3. Yttrium	16
4. Analytical Procedures	16
5. Service Analyses	17

Spectrochemistry

1. Spectrometer Development	17
2. Development of Spectrometric Methods of Analysis	17
3. Spectroscopic Service Analyses	17

Radiochemistry

1. Hot Atom Chemistry	18
2. Photuclear Processes	18
2.1 Gallium	18
2.2 Iron	18

TABLE OF CONTENTS (Continued)

	<u>Page</u>
3. Szilard-Chalmers Reactions.	19
4. Solubilities by Radioassay.	19
APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY . .	20
1. Reports for Cooperating Laboratories.	20
2. Papers Published in Scientific Journals	20
APPENDIX II: LIST OF SHIPMENTS	22

Quarterly Summary Research Report in Chemistry

For the period April, May, and June, 1955

This report is prepared from material
submitted by the group leaders of
the Laboratory

Previous quarterly research reports in this series are:

ISC-35
ISC-41
ISC-56
ISC-69
ISC-74
ISC-76
ISC-79
ISC-113
ISC-130
ISC-133
ISC-137
ISC-171
ISC-193
ISC-220
ISC-245
ISC-285
ISC-299
ISC-321
ISC-337
ISC-394
ISC-421
ISC-450
ISC-484
ISC-505
ISC-530
ISC-574
ISC-606

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Under the direction of F. H. Spedding, C. A. Goetz, C. V. Banks, J. Corbett, A. H. Daane, F. R. Duke, V. A. Fassel, J. S. Fritz, M. Griffel, R. S. Hansen, G. Hammond, D. S. Martin, J. Powell, R. E. Rundle, H. J. Svec and A. F. Voigt

Physical and Inorganic Chemistry

1. Separation of Rare Earths by Ion-Exchange (F. H. Spedding and J. E. Powell)*

1.1 Production of Heavy Rare Earths and Yttrium

Pilot plant scale production of pure rare earths was continued during this period with special emphasis on the purification of yttrium.

A paper (ISC-604) entitled "The Stability of the Rare Earth Complexes with N-Hydroxyethylethylenediaminetriacetic Acid" by F. H. Spedding, J. E. Powell and E. J. Wheelwright was submitted to J. Am. Chem. Soc. for publication.

Abstract

The stability constants of the complexes formed between the rare earth metal ions and the anion of N-hydroxyethylethylenediaminetriacetic acid, abbreviated HEDTA, have been measured at a temperature of 25°C and an ionic strength of $\mu = 0.1$ by two independent methods. In the first method, the rare earth-HEDTA stability constants were calculated from measurements of the equilibrium constants of reactions involving competition between HEDTA and a polyamine chelating agent, triaminotriethylamine, for the rare earth ions. The equilibrium constants were calculated from pH measurements of the various reaction mixtures. The second method involved the polarographic measurement of the amount of free copper ions liberated when equal molar quantities of the copper II-HEDTA complex and rare earth ions are mixed together.

A report (ISC-637), entitled "The Use of Chelating Agents in the Separation of the Rare Earth Elements by Ion-Exchange Methods" by E. J. Wheelwright and F. H. Spedding was distributed.

Abstract

The research described in this report was undertaken in order to accomplish two main objectives. The first was to measure the stability of the complexes formed by each of the trivalent rare earth cations with ethylenediaminetetraacetic acid, abbreviated EDTA, and with N-hydroxyethylethylenediaminetriacetic acid, abbreviated HEDTA. The second objective was to find methods for using the two chelating agents in conjunction with an ion-exchange resin for separating the rare earths.

*Names indicate group leaders in charge of work.

The stability constants of the complexes formed between the rare earth metal ions and the anion of EDTA have been measured at a temperature of 20.0°C and an ionic strength of 0.10 by two independent methods. The two methods are shown to supplement each other, one being more accurate for the lighter rare earths and the second method more accurate for the heavy rare earths.

In the first method, the rare earth-EDTA stability constants were calculated from measurements of the equilibrium constants of reactions involving competition between EDTA and a polyamine chelating agent, triamino-triethylamine, for the rare earth ions and copper ions. The equilibrium constants were calculated from pH measurements upon the various reaction mixtures.

The second method is based upon the fact that it is possible to measure the concentration of free uncomplexed copper II ions in the presence of the copper complex, CuY^{-2} , by polarographic means. The rare earth-EDTA stability constants were determined by measuring the amount of copper II ions liberated when equal molar amounts of the copper-EDTA complex and a rare earth salt are mixed together.

The acid association constants of HEDTA were calculated from pH titration curves obtained by potentiometrically titrating the acid with standard KOH at 25.0°C and an ionic strength of 0.10.

The stability constants of the complexes formed between the rare earths and the anion of HEDTA were measured at a temperature of 25.0°C and an ionic strength of 0.10. The methods used were the same as those described for measuring the rare earth-EDTA stability constants. In this case, the potentiometric method is shown to give more accurate constants.

A rapid method for separating the individual rare earths into enriched fractions has been developed. The process consists of complexing part of the rare earths in a mixture--those rare earths which form the more stable complexes--with EDTA and separating the complexed rare earth ions from the uncomplexed ions by passing the mixture through an ion exchange column in the ammonium cycle. The complexed ions pass through the resin bed, but the uncomplexed ions are adsorbed.

A method has been found for separating pure rare earths in macro quantities from rare earth mixtures. The method consists of eluting a band of mixed rare earths, adsorbed on a cation-exchange resin, through a second cation-exchange resin bed in the copper II or iron III state. Copper was found to be far superior to iron. The eluant consists of an ammonia-buffered solution of EDTA.

The elution of a mixture of all of the rare earths down an ion exchange bed with an ammonia-buffered solution of HEDTA indicated that this chelating agent is not as effective for separating the heavy rare earths as the EDTA-copper II system under the conditions tested.

2. Separation of Isotopes by Ion-Exchange (F. H. Spedding and J. E. Powell)

N¹⁵ was enriched to greater than 98% by continuing the separation described last quarter (ISC-606) on a series of 1-cm columns. The decreased diameter improved the separation, but not as much as might be expected. The HETP was only fair in this experiment.

A paper (ISC-611) entitled "A Laboratory Method for Separating Nitrogen Isotopes by Ion-Exchange" by F. H. Spedding and J. E. Powell was submitted to J. Am. Chem. Soc. for publication.

Abstract

Various aspects of the separation of N¹⁵ and N¹⁴ isotopes from each other by an ion-exchange process have been discussed. A number of experiments have been performed to establish the feasibility of using the process and to check the counter-current theory of separation which has been developed. The separation factor for the exchange of N¹⁵ and N¹⁴ between a solution of dilute ammonium hydroxide and the ammonium form of Dowex 50-X12 was measured and found to be 1.0257 ± 0.0002 . It was shown that an adsorbed band of ammonium ion must be eluted about 39 times its length in order to achieve separation of the isotopes. A method of continuous operation using a series of ion-exchange beds has been described and factors which influence the HETP at a steady state have been investigated.

3. Rare Earth Metallurgy (F. H. Spedding and A. H. Daane)

3.1 Structures of Rare Earth Metals

Precision lattice determinations have been made on extremely pure specimens of all of the rare earth metals. A transformation in lanthanum metal at about 300°C was observed in studies of the resistivity as a function of temperature, indicated by a small inflection in the plot of the data. High temperature x-ray studies on lanthanum have shown this to correspond to a transformation from the hexagonal closest packed structure, stable at room temperature, to a face centered cubic structure with $a = 5.306 \text{ \AA}$, which has sometimes been reported as the normal room temperature form of this metal. The x-ray studies indicate another transformation slightly below 900°C.

In the same high temperature x-ray equipment, a transformation in praseodymium metal at about 800°C has been observed, and although a complete diffraction pattern has not been observed, this transformation appears to be from the hexagonal form to a body-centered cubic structure with $a = 4.13 \text{ \AA}$.

In an effort to stabilize the face centered cubic structure of lanthanum at room temperature, an 85% lanthanum-15% cerium alloy was prepared, but at room temperature it was found to have the hexagonal lanthanum structure.

X-ray diffraction studies on a series of lanthanum-carbon alloys indicate that there are two carbides of lanthanum, stable at room temperature; LaC , body centered cubic with $a = 8.80 \text{ \AA}$, and LaC_2 , tetragonal with $a = 5.56 \text{ \AA}$ and $c = 6.59 \text{ \AA}$.

3.2 Vapor Pressure Studies

The vapor pressure of cerium has been remeasured, and the data indicate that cerium has a volatility and a heat of vaporization that place it between lanthanum and praseodymium in these respects. This is believed to be more accurate data for cerium than that previously reported by this Laboratory which indicated a distinctly anomalous situation for cerium compared with the adjacent rare earth metals.

4. Transport Numbers in Fused Salts (F. R. Duke)

Work on transport numbers in mixtures of fused salts disclosed the significant fact that the minor constituent conducts the major portion of the current. This is interpreted in terms of the liquid structure being a combination of ordered and disordered regions, the conductivity and the minor constituent being concentrated in the disordered regions.

Work was continued on transport numbers, using a new technique. A porous porcelain plate is partially saturated with the salt and a known amount of electricity is passed through. Since the salt can accumulate near one electrode in the capillaries of the porous plate, an analysis of the plate in the electrode regions serves to yield data from which transport numbers can be calculated. This method agrees with the moving bubble cell for transport numbers of the silver nitrate; the method is now being tried with sodium chloride.

A paper (ISC-654) entitled "Measurement and Significance of Transport Numbers in Fused Salts" by Richard W. Laity and F. R. Duke was distributed.

Abstract

The concept of transport numbers in fused salts is discussed in the light of the inapplicability of the usual definition applied to electrolytic solutions. The lack of

a solvent reference frame, with respect to which the mobilities of the ions are normally compared, necessitates employment of a microscopic definition, if the conductance of a molten electrolyte is to be divided into a sum of meaningful ionic conductances. Thus, the reference frame selected here consists of the large bulk of ions not involved in the conductivity process at any given instant, i.e., those ions which lack the necessary energy of activation for migration. The transport numbers are therefore the fractions of current carried by the migrating ions during electrolysis as measured with respect to this frame.

Attempts of previous workers to measure transport numbers in fused salts are reviewed with respect to their validity and significance. It is shown that, while a few of the papers present significant data, the failure of any previous investigators adequately to consider the nature of the quantities they were measuring has led in other cases to publication of completely useless or uninterpretable experimental results.

A cell for measuring the transport numbers of the ions in pure molten salts is described. It has two vertical electrode compartments separated by a porous glass membrane. The displacement during electrolysis of an air bubble in a capillary tube connecting the two compartments yields data which can be combined with known density data to calculate the transport numbers, assuming the simplest formulas for the current-carrying ions. The validity of the use of this cell is verified for PbCl_2 by showing the lack of dependence of the measured transport numbers on the chemical nature of the membrane, as well as by other experiments and theoretical considerations. A criterion for indicating the applicability of the method to other pure salts, based on the possible influence of the membrane on the experimental activation energy of conductivity, is proposed and its use demonstrated.

A cell for measuring transport numbers in mixtures of fused salts is described. The electrode compartments are again separated by a porous glass membrane. Results with this cell are found by using a suitable analytical procedure to determine the actual quantity of each ion transferred from one compartment to the other on electrolysis.

Application of the former cell to a number of pure fused salts is shown to yield the following experimental transport numbers for the negative ions: PbCl_2 -0.76 at 565 and at 635°C; PbBr_2 -0.65 at 500 and 0.67 at 600°C; TlCl -0.49+ at 475, at 505 and at 525°C; AgNO_3 -about 0.24 at 225 and at 275°C. In a nearly equimolar AgNO_3 - NaNO_3 mixture use of the latter cell is shown to indicate that the nitrate ion carries a negligible fraction of the current, while the maximum transport number of the silver ion is less than 0.67.

An experiment is proposed by which the latter cell might also be used to determine the extent to which complex ions carry current in molten salts. The procedure would involve placing labeled cation or anion in the appropriate compartment and measuring the quantity of labeled ion that moves in the opposite direction from the corresponding electrode. It is shown how such information, combined with that of the type assembled in the present work, may be of considerable use in the development of a theory of the liquid state.

5. The Chemistry of Gallium(II) Halides in Aqueous Base (J. D. Corbett)

The remarkable observation has been made that gallium(II) halides can be dissolved in aqueous base to yield rather stable solutions. These solutions slowly evolve hydrogen homogeneously, and in the absence of stirring become highly supersaturated with gas. The kinetics of the hydrogen evolution in well-stirred solutions are being measured. The rate is first order in reduced gallium, zero order in Ga(III) , and approximately first order in hydroxide for 1 to 2 M OH^- . The half life for the decomposition in 2 and 4 molar base is about 2.3 and 1 hours, respectively.

The compound containing the reducing strength is completely precipitated upon neutralization of the solution; further acidification results in rapid decomposition. This amphoteric behavior of the solute appears to favor the symmetrical structure involving gallium-gallium bonds for the gallium(II) oxidation state, since gallium(I) would not be expected to be amphoteric.

The reducing properties of these solutions are shown by the ready reduction of Cd(OH)_2 , PbO_2^- and AsO_3^- to the metals, Fe_2O_3 to Fe_3O_4 , and CrO_4^- to CrO_2 . In acid, Sn(II) is reduced to the metal, and SeO_4^- rapidly to Se.

6. Metal-Metal Salt Solubilities (J. D. Corbett)

Examination of diverse metal-metal salt systems has been under way in an effort to correlate this sort of interaction. It now appears that at least in a number of instances, the larger metal solubilities in their molten halides occur in systems where the formation of subhalide of borderline stability might be expected, such as already reported for gallium and aluminum. (This concept, however, has an uncertain relation to the unusual solubilities reported for the alkali metal systems.)

Zinc chloride dissolves 1.8 mole per cent metal at 400°C , as shown by both loss in weight of the metal and direct analysis of the quenched salt. The colorless metal-saturated liquid can be rapidly quenched to a clear glass, which blackens only when heated sufficiently to allow the ZnCl_2 to crystallize. Zinc iodide dissolved 3.69 per cent metal at 500°C , and behaves similarly on cooling.

Antimony(III) chloride does not appear to dissolve a significant amount of metal at 275°C, the weight loss of the metal corresponding to 0.02% solubility. However, at the higher temperature of 475°C, where the vapor pressure of the metal is still negligible, metal is transported by SbCl_3 vapor, indicating a lower chloride that is stable only in the gas phase. In contrast, antimony(III) iodide "dissolves" about 6% metal at 400°C; the quenched salt is black.

7. Adsorption Studies (R. S. Hansen)

Experimental work on inference of adsorption from double layer capacitance measurements was completed and results tabulated for analysis. The final portion of this work was devoted to a study of the dependence of differential capacitance on polarizing potential and concentration of adsorbable electrolyte. It was found that meaningful surface coverages could be calculated from observed differential capacitances according to the method of Hansen and Clampitt* only in the neighborhood of the electrocapillary maximum. At polarizing potentials greater than a few tenths of a volt, desorption occurs due to concentration of component of higher dielectric constant in the high field region displacing adsorbate, and this not only reduces actual surface coverage, but leads to a pseudocapitance of sufficient magnitude to indicate a negative "apparent adsorption". A theory has been developed representing the observed data qualitatively and semi-quantitatively.

Surface tensions were determined as functions of concentration over the entire concentration range at 25°C for the following two binary pairs: acetic acid-perfluoroacetic acid and propionic acid-perfluoropropionic acid. These systems have both a theoretical and a practical interest; the theoretical interest stems from the significant variation in surface tension in binary systems which are otherwise nearly ideal, and the practical interest stems from the status of the fluorocarbons as one of the few classes of compounds showing promise as wetting agents in non-aqueous media.

8. Hafnium-Zirconium Studies (R. S. Hansen)

A paper (ISC-590), entitled "Solvolytic of Hafnium and Zirconium Tetrachlorides in Methyl and Ethyl Alcohols" by C. R. Simmons and R. S. Hansen was distributed.

Abstract

Equilibrium constants $\bar{K}_n$ for the reactions

where M is Zr^{IV} or Hf^{IV} , ROH is methanol or ethanol, and $n = 1, 2, 3, 4$, were obtained at 25°C by potentiometric

*ISC-536

dilution measurements and, independently, by conductimetric dilution measurements. Results obtained by the two different methods were found to be in good agreement.

Solvolysis of both tetrachlorides was more extensive in methanol than in ethanol. Solvolysis of HfCl_4 was more extensive than that of ZrCl_4 in both solvents, the difference being greater in methanol than in ethanol.

9. Reaction Kinetics (H. J. Svec)

A report (ISC-653) entitled "Kinetics of the Reaction between Thorium and Water Vapor" by B. E. Deal and H. J. Svec was distributed.

Abstract

An examination of the reaction between thorium metal and water vapor has been made between the temperatures of 200° to 600°C and at water vapor pressures of 40, 70 and 100 mm Hg. Analyses of the products have indicated that ThO_2 and H_2 are the main species formed during the reaction with thorium hydride as a possible side-reaction product. Two methods, gravimetric and manometric, were used successfully to determine the rates of reaction. During these rate studies three variables were examined: time, temperature and pressure. The reaction data were found to obey the logarithmic rate law $w = k \log(1 + 0.45t)$, where w = weight of water reacted per unit area of thorium surface, t = time and k is the rate constant.

Three temperature regions have been examined in which different-appearing oxides were observed: 200° to 275° , black; 300° to 450° , gray or white; and 450° to 550° , metallic. The rate constants were found to be first order in dependence on water vapor pressure. The Arrhenius equation $\ln k = -E/RT + C$, where k = rate constant, E = activation energy, T = absolute temperature and R and C are constants, has been used to determine the activation energy. An average value of 6.44 ± 0.75 kcal/mole was calculated for the activation energy of the thorium-water vapor reactions. Several experiments were carried out in order to determine the reaction mechanism, and it has been postulated that inward diffusion of water molecules or a species thereof is the rate-determining step of the reaction. A value for the diffusion coefficient of water in ThO_2 was estimated to be approximately 10^{-7} cm^2/sec . Other experiments have shown hydrogen, produced by the reaction, to have diffused into the metal at the higher temperatures and lower pressures, thus causing erroneous results for rate constant values at those temperatures.

Pyrometallurgy

1. Metallurgical Separation of Fuel and Fission Products (A. F. Voigt)

Experiments on liquid metal extraction of fission products from uranium have been confined to work on artificial mixtures of "Fissium". Samples of uranium alloy were made up with radioactive forms of the most abundant non-volatile fission products, Zr, Mo, Ru and Nd (the last as a representative of all the rare earths) at concentrations corresponding to burnup of about 2% of the uranium atoms.

A number of problems were encountered in the preparation of this material since it was found difficult to prepare a homogeneous mixture. Methods of testing for homogeneity were developed using the added tracers and making use of radioautography and scintillation counter scanning to determine the location of particular elements in the melts. It was especially difficult to get zirconium equally distributed lengthwise throughout the sample. The scintigram was useful in deciding what portions of the sample were sufficiently homogeneous to use.

Results were in essential agreement with those obtained at lower fission concentrations with the exception that better extraction of ruthenium by rare earth extractants as obtained at this level than at tracer level ruthenium concentrations. In a single equal volume extraction, cerium removes 50% of the ruthenium, a similar fraction of the zirconium, 95% of the rare earths and essentially no molybdenum. Lanthanum removes 25% of the ruthenium, half of the zirconium and about 10% of the molybdenum. Similarly, silver removes about 90% of the rare earths, 65% of the zirconium and none of the molybdenum or ruthenium.

2. Uranium-Samarium Studies (A. H. Daane)

Samarium is one of the more important rare earth fission products, and its metallurgical behavior with uranium has not been studied in detail. Several experiments are being conducted in this Laboratory on this alloy.

The solubility curves of uranium and samarium in each other have been studied by co-melting specimens of these metals and quenching them from various temperatures.

To determine the extent of removal of samarium metal from uranium metal in a vacuum melting operation, a 1 weight per cent samarium in uranium alloy was prepared and heated in a vacuum for 12 minutes at 1200°C. It was found that the samarium content was reduced to less than 0.01 weight per cent (the limit of detection by our present analytical method).

3. Ruthenium Studies (A. H. Daane)

The lanthanum-rich end of the lanthanum-ruthenium alloy system has been examined briefly to see what intermetallic compound is responsible for the extraction of ruthenium from uranium by lanthanum. It has been found that this compound probably has the composition La_5Ru , with an eutectic between this compound and pure lanthanum. At least two more compounds appear to be present in this system.

Analytical Chemistry

1. Titration of Mercuric Ion (J. S. Fritz)

It has been found that mercury(II) can be titrated with diethanolaminedithiocarbamate in 30% acetone-70% water using copper(II) and EDTA (ethylenediaminetetraacetate) as the indicator. When all of the mercury(II) has been complexed with the dithiocarbamate, the first excess of titrant reacts with copper(II), forming a highly colored complex. The appearance of this yellow color indicates the end point. The function of the EDTA is to complex the copper(II) and thus cause all of the mercury to react with the dithiocarbamate titrant first. This method is very selective for mercury(II) and has the additional advantage that mercury(II) can be titrated in the presence of chloride and bromide.

2. Sulfur in Organic Compounds (J. S. Fritz)

A fairly rapid method for determining sulfur in organic compounds has been devised. The sample is decomposed in a sodium peroxide bomb. The bomb contents is dissolved in water, acidified and the sulfate is adsorbed on a small alumina column. This concentrates the sulfate and separates it from the bulk of the foreign salts. The sulfate is then eluted from the alumina column with dilute ammonia and then passed through a small cation exchange column to remove ammonia. The sulfate is then titrated by the method of Fritz and Yamamura (ISC-540, Nov., 1954). Numerous organic compounds have been successfully analyzed for sulfur by this procedure.

3. Yttrium (C. V. Banks)

A polarographic method for the determination of zinc in yttrium metal was developed using cadmium as an internal standard.

4. Analytical Procedures (C. V. Banks)

A manual (ISC-584) was distributed which describes analytical procedures for the determination of aluminum, chromium, iron, manganese, nickel, nitrogen and silicon in calcium metal.

5. Service Analyses (C. V. Banks)

A total of 2585 service analyses were made during the period of this report.

Spectrochemistry

1. Spectrometer Development (V. A. Fassel)

A paper (ISC-602), entitled "A Rotating Step Sector for Use with AC or Other Intermittent Spectrographic Light Sources" by R. N. Kniseley and V. A. Fassel was submitted for publication in J. Opt. Soc.

Abstract

The calibration of the response of photographic emulsions using rotating step-sectors may lead to erroneous results when intermittent spectrographic light sources are used. These errors arise through partial synchronization between the periodicity of the light pulses and the passage of sector apertures in front of the spectrograph slit. A design for a rotating step sector which should overcome synchronization possibilities has been conceived and some actual sectors have been tested. This sector essentially consists of a series of stepped apertures randomly spaced about the periphery of a rotating disc. Data are presented to show that the random spacing of the sector apertures eliminates the possibilities of introducing errors through synchronization effects when conventional intermittent discharges are used.

2. Development of Spectrometric Methods of Analysis (V. A. Fassel)

The following spectrometric analytical methods were completed during this quarter:

1. Determination of small amounts of gadolinium in purified samarium (emission spectrometric).
2. Determination of low percentages (0.05 to 2%) of samarium in uranium (emission spectrometric).
3. Analysis of Ta-Zr binary alloys in the concentration range of 3 to 50% Ta (X-ray fluorescence).

3. Spectroscopic Service Analyses (V. A. Fassel)

2,029 samples were analyzed or examined by emission, fluorescence, or infra spectroscopic techniques during this period.

Radiochemistry1. Hot Atom Chemistry (A. F. Voigt)

Studies of the nature of the recoil products after activation of bromine in n-propyl and iso-propyl bromides appears to be very much the same regardless of the extent of the recoil energy. Studies using photonuclear reactions making use of the synchrotron x-ray beam and producing 57h Br⁷⁷ by (γ ,2n) as well as 4.6h Br^{80m} and 18 min. Br⁵⁰ by (γ ,n) reactions give results that are very similar to those obtained by (n, γ) reactions producing the Br⁸⁰ isomers and 36h Br⁸².

2. Photonuclear Processes (D. S. Martin)2.1 Gallium

Samples of gallium activities were prepared by the irradiation of reagent grade arsenic oxide by the 70 Mev bremsstrahlung x-rays from the Iowa State College synchrotron. The chemical separation involved ether extractions from hydrochloric acid solutions and precautions were taken to insure that the gallium was separated cleanly from possible zinc and germanium tracers. A resolution of the counting decay curve gave expected components with half-lives of 20 min., 5 hr. and 14 hrs. corresponding to the nuclides Ga⁷⁰, Ga⁷³, and Ga⁷², respectively. In addition, a component of moderately high intensity with the unexpected half-life of 60-70 min. was noted. The only known nuclide with this activity is Ga⁶⁸. However an As⁷⁵(γ ,2p,5n)Ga⁶⁸ is required for its formation which has a threshold (from isotopic masses) of 50 Mev. The identity of this product was supported by an experiment in which the positron component was separated from the electron fraction by a magnetic field. A pure 68 min. half-life was observed in the positron fraction consistent with the assignment to Ga⁶⁹. Experiments are under way to evaluate the yields of the gallium activities.

2.2 Iron

Final values of yields for photonuclear reactions observed in iron have been computed and included in the following table.

Photonuclear Yields for 70 Mev Bremsstrahlung
N¹⁴(γ ,n)N¹³ = 1

<u>Process</u>	<u>Yield</u>
Fe ⁵⁴ (γ ,pn)Mn ^{52m}	3.9
Fe ⁵⁴ (γ ,pn)Mn ⁵²	0.58
Fe ⁵⁴ (γ ,2n)Fe ⁵²	0.23
Fe ⁵⁷ (γ ,p)Mn ⁵⁶	9.2*

*Assuming Mn⁵⁶ to be formed only by this process.

It is now possible to make an interesting comparison of the yields of photonuclear reactions of Fe^{54} with the yields of the same nuclides formed by high-energy bombardments of Cr^{50} . The differences in the yields of the isomeric pair reflect the differences between photonuclear reactions and heavy particle induced reactions.

3. Szilard-Chalmers Reactions (D. S. Martin)

Crystals of tris(ethylenediamine)cobalt(III) nitrate have been irradiated by the 70 Mev bremsstrahlung beam to produce the 9 hr.- $\text{Co}^{58\text{m}}$. It has been found that 52% of the activity is carried by a precipitation of Co^{II} carrier as $\text{Co}(\text{OH})_2$, 22% of the activity was retained as the original complex which was separated by a fractional crystallization of the bromide, and 26% as an unidentified third fraction. When the solution of the irradiated crystals was allowed to stand at 22°C for 5 hours, there was little change in the retention of activity by the complex but the unidentified fraction increased from 27% to 35%, primarily at the expense of the fraction carried by Co^{II} . When the solutions stood 12.5 hrs. at 98°C, the retention was scarcely changed but the unidentified fraction was converted completely to the Co^{++} fraction.

When irradiated crystals were aged at 108°C, the retention increased and, in about half a day, approached a limiting value of 67%. The unidentified fraction possibly passed through a maximum within 1-2 hours of aging but then approached a limiting value of about 9% with the aging. In the aging process radioactive cobalt atoms, which originally were carried by the Co^{++} fraction, were incorporated into the crystals, apparently by a heating of the crystals in which the complex species were reformed from the fragments produced in stopping the recoiling atoms.

4. Solubilities by Radioassay (D. S. Martin)

By utilizing Ag^{110} the solubility of AgIO_3 has been determined by means of radioassays at different temperatures in solutions of LiIO_3 and in solutions of $\text{LiIO}_3\text{-LiClO}_4$ with an ionic strength of 1.00. The system has been described by means of the equilibria:

Values of the equilibrium constants are:

	25°	35°	50°
K_{SP}	$(3.0 \pm 0.15) \times 10^{-8}$	4.3 ± 2.6	$7.9 \pm 5 \times 10$
K_1	$(6.3 \pm 0.3) \times 10^{-8}$	6.3 ± 1.9	$6.6 \pm 4 \times 10$
K_2	$(17.4 \pm 1.0) \times 10^{-8}$	9.1 ± 1.2	$4.1 \pm 3 \times 10$

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-531 Ames Laboratory Staff. Metallurgy. Quarterly Summary Research Report. July, August, September, 1954.
- ISC-574 Ames Laboratory Staff. Chemistry. Quarterly Summary Research Report. October, November, December, 1954.
- ISC-576 Compiled by P. Chiotti and O. N. Carlson. Hanford Slug Program. Quarterly Summary Research Report. October, November, December, 1954.
- ISC-577 Ames Laboratory Staff. Physics, Quarterly Summary Research Report. October, November, December, 1954.
- ISC-598 W. A. Rhinehart and D. J. Zaffarano. A Voltage Calibration System for Accurate Pulse Height Measurement.
- ISC-599 R. A. Lowry, J. E. Osher and G. H. Miller. A Pressure Regulator for a Low Pressure Continuous Flow Ionization Chamber.
- ISC-601 R. W. Fisher. Comprehensive Report on Production of Thorium IA. Thorium Fluoride Preparation.
- ISC-602 R. N. Kniseley and V. A. Fassel. A Rotating Step Sector for Use with AC or Other Intermittent Spectrographic Light Sources.

2. Papers Published in Scientific Journals

- Banks, C. V. and R. J. Davis
Analytical Applications of the Reaction of Thorium with Benzenephosphoric Acid. Anal. Chem. Acta 12, 418-31, (May, 1955).
- Banks, C. V. and R. E. Edwards. Separation and Determination of Thorium and Aluminum. Anal. Chem. 27, 947-49 (June, 1955).
- Dooley, M. E. and D. F. Atkins
A New Electronic Vacuum Dilatometer. Rev. Sci. Instr., 26, 568-71 (June, 1955).
- Duke, F. R. and R. W. Laity
The Measurement of Transport Numbers in Pure Fused Salts. J. Phys. Chem., 59, 549-52 (June, 1955)
- Duke, F. R. and F. R. Parchen
Kinetics of the Reduction of Ferric Ion by Hydroquinone in the Presence of 1,10-Phenanthroline. J. Am. Chem. Soc. 77, 3198-99 (June, 1955).

- Fassel, V. A., B. Quinney, L. C. Krotz and C. F. Lentz
Quantitative Spectrographic Analysis of the Rare Earth Elements. Anal. Chem., 27, 1010-14 (June, 1955).
- Fassel, V. A. and H. J. Hettel
Isotopic Assay of Lithium by Means of Hydride Band Emission Spectra. Spectrochim. Acta, 7, #3, 175-78 (May-June, 1955)
- Grantham, L. F., T. S. Elleman and D. S. Martin, Jr.
Exchange of Chlorine in Aqueous Systems Containing Chloride and Tetrachloroplatinate. II. J. Am. Chem. Soc., 77, 2965-71 (June, 1955).
- Hammer, C. L. and A. J. Bureau
A Method for the Prompt Destruction of the Electron Beam in a Conventional Synchrotron. Rev. Sci. Instr., 26, 594-98 (June, 1955).
- Hammer, C. L. and A. J. Bureau
A Method for the Prompt Destruction of the Electron Beam in a Conventional Synchrotron. II. Rev. Sci. Instr., 26, 598-600 (June, 1955).
- Hansen, R. S. and R. D. Hansen
The Adsorption of Hydrocarbons for Menthanol and Ethanol Solutions by Non-Porous Carbons. J. Phys. Chem., 59, 496-498 (June, 1955).
- Hansen, R. S., F. A. Miller and S. D. Christian
Activity Coefficients of Components in the System Water-Acetic Acid, Water-Propionic Acid, and Water-n-Butyric Acid at 25°C. J. Phys. Chem., 59, 391-95 (May, 1955).
- Hughes, F. J. and D. S. Martin, Jr.
Kinetics of the Oxidation of Selenious Acid by Hydrogen Peroxide. J. Phys. Chem., 59, 410-15 (May, 1955).
- Klingman, D. W., D. T. Hooker and C. V. Banks
Photometric Titration Assembly for Beckman Model DU Spectrophotometer. Anal. Chem., 27, 572 (April, 1955).
- Nadler, M. R. and E. S. Fitzsimmons
Preparation and Properties of Calcium Zirconate. J. Am. Ceram. Soc., 38, 214-17 (June, 1955).
- Nichols, R. T., A. V. Pohm, J. H. Talboy, Jr. and E. N. Jensen
A Beta-Ray Spectrometer for Coincidence Measurements. Rev. Sci. Instr., 26, 580-83 (June, 1955).

APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
Mallinckrodt Chemical Works 3600 North 2nd Street St. Louis, Missouri	50 mg thulium oxide 50 mg lutetium oxide
Dr. Daniel Laszlo, Chief Div. of Neoplastic Diseases Montefiore Hospital New York 67, N. Y.	25 gm yttrium oxide 99.9%
Dr. S. Jaffe Air Reduction Co., Inc. Research Laboratory Murray Hill, New Jersey	2 gm pure thulium oxide
U. S. Bureau of Mines Rare and Precious Metals Experiment Station Reno, Nevada	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 1 gm erbium oxide 1 gm ytterbium oxide 100 mg holmium oxide 100 mg thulium oxide 100 mg lutetium oxide 100 mg terbium oxide
Dr. Charles E. Holley, Jr. Los Alamos Scientific Laboratory Los Alamos, New Mexico	20 gm yttrium metal 20 gm dysprosium metal 20 gm erbium metal 20 gm ytterbium metal
Brookhaven National Laboratory Upton, Long Island, New York	50 gm cerium metal
Supply Officer Naval Research Laboratory Washington, D. C.	100 gm thorium metal
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	100 gm ytterbium oxide 100 gm erbium oxide 100 gm dysprosium oxide
Litton Industries Beverly Hills, California	3 thulium buttons

<u>Destination</u>	<u>Item</u>
Dr. LeRoy Eyring Department of Chemistry State University of Iowa Iowa City, Iowa	20 gm lanthanum oxide 20 gm cerium oxide 20 gm neodymium oxide 20 gm praseodymium oxide 20 gm samarium oxide 20 gm ytterbium oxide 10 gm gadolinium oxide 5 gm terbium oxide 5 gm thulium oxide
General Electric Co. A. N. P. Department Cincinnati, Ohio	30 gm yttrium oxide 50 lb yttrium oxide (highest purity) 1 lb samarium metal 10 lb yttrium metal 1 lb gadolinium metal
Dr. Howard E. Kremers Lindsay Chemical Co. West Chicago, Illinois	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Supply Officer Naval Research Laboratory Washington 25, D. C.	0.5 gm erbium metal 0.5 gm dysprosium metal
Research Laboratories of Colorado, Inc. Newtown, Ohio	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide

<u>Destination</u>	<u>Item</u>
Battelle Memorial Institute Columbus, Ohio	2 gm neodymium oxide 2 gm gadolinium oxide
State University of Iowa Purchasing Department Iowa City, Iowa	5 gm lanthanum metal 5 gm praseodymium metal 5 gm samarium metal 5 gm ytterbium metal
Trans World Airlines, Inc. Kansas City 15, Kansas	2 thulium buttons
M. I. T. Lincoln Laboratory Lexington, Massachusetts	1 gm gadolinium metal 1 gm dysprosium metal 1 gm erbium metal
Argonne National Laboratory Lemont, Illinois	30 mg thulium oxide 30 mg holmium oxide
Dr. Paul V. Harper Chicago, Illinois	20 gm yttrium oxide 99.8%
Dr. Nathan Sugarman Chicago, Illinois	2 gm praseodymium metal 2 gm holmium metal
National Bureau of Standards Washington, D. C.	1 lb lanthanum metal 1 lb cerium metal
Mallinckrodt Chemical Works 65 Destrehan Street St. Louis, Missouri	50 mg terbium oxide 50 mg dysprosium oxide 50 mg erbium oxide 50 mg lutetium oxide 50 mg thulium oxide
Argonne National Laboratory Lemont, Illinois	1 sample samarium metal 1 sample neodymium metal
Commanding Officer U. S. Naval Hospital St. Albans, New York	5 gm Y_2O_3 99.9%
Florida State University Tallahassee, Florida	2 gm ytterbium oxide
Carbide and Carbon Chemicals Co. X-10 Plant Oak Ridge, Tennessee	200 gm erbium oxide 500 gm neodymium oxide 200 gm holmium oxide 400 gm yttrium oxide 400 gm neodymium oxide
American Metallurgical Prod. Co. New Castle, Pennsylvania	1 lb lanthanum metal (99% pure)