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ISC-1116

Chemistry-General (UC-4)  
TID 4500, Oct. 1, 1958

UNITED STATES ATOMIC ENERGY COMMISSION

Research and Development Report

CHEMISTRY SEMI-ANNUAL SUMMARY  
RESEARCH REPORT

for  
JULY-DECEMBER, 1958

by  
Ames Laboratory Staff

Date of Issuance

April 15, 1959

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

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Printed in USA. Price \$ 2.00 . Available from the

Office of Technical Services  
U. S. Department of Commerce  
Washington 25, D. C.

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## SEMI-ANNUAL SUMMARY RESEARCH REPORT IN CHEMISTRY

For the Period July through December, 1958

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

Previous research reports in this series are:

ISC-35	ISC-321
ISC-41	ISC-337
ISC-56	ISC-394
ISC-69	ISC-421
ISC-74	ISC-450
ISC-76	ISC-484
ISC-113	ISC-505
ISC-130	ISC-530
ISC-133	ISC-574
ISC-137	ISC-606
ISC-171	ISC-643
ISC-193	ISC-706
ISC-220	ISC-757
ISC-245	ISC-834
ISC-285	ISC-902
ISC-299	ISC-976
	ISC-1049



## CHEMISTRY

(Semi-Annual Report, July-December, 1958)

Under the direction of F. H. Spedding, C. A. Goetz, C. V. Banks, L. S. Bartell, J. Corbett, A. H. Daane, F. R. Duke, V. A. Fassel, J. S. Fritz, R. S. Hansen, L. D. Jennings, D. S. Martin, J. E. Powell, K. Ruedenberg, 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 Pilot Plant Separations

Both EDTA and HEDTA have found continued usage in resolving rare-earth mixtures in the 6-inch-column and 4-inch-column pilot plants. HEDTA is superior for the resolution of Lu-Yb-Tm-Er mixtures while EDTA is best for Er-Ho-Dy-Y-Tb-Gd-Eu-Sm mixtures. Both EDTA and HEDTA are satisfactory for resolving Nd-Pr-Ce-La mixtures. Due to its greater solubility in water and the fact that it can be more readily recovered and recycled, HEDTA appears to be more practical than EDTA for resolving the latter group of elements. During the last six months the following noteworthy rare-earth fractions have been prepared in the pilot plants.

Table I

Noteworthy Quantities of Pure Rare Earths  
Produced During July - December 1958

<u>Material</u>	<u>Wt. in Grams</u>
Tm <sub>2</sub> O <sub>3</sub>	6,284
Ho <sub>2</sub> O <sub>3</sub>	10,923
Dy <sub>2</sub> O <sub>3</sub>	10,157
Gd <sub>2</sub> O <sub>3</sub>	11,191
Sm <sub>2</sub> O <sub>3</sub>	38,678
Nd <sub>2</sub> O <sub>3</sub>	228,897
Pr <sub>6</sub> O <sub>11</sub>	32,369
Y <sub>2</sub> O <sub>3</sub>	<u>1,499</u>
Total	339,998

### 1.2 The Order of Elution in Rare Earths and Common Elements with EDTA

In the report for the previous period (ISC-1049), Zn<sup>+2</sup> was reported to fall between Yb<sup>+3</sup> and Tm<sup>+3</sup>. In a large scale run with EDTA, Zn<sup>+2</sup> has recently been found between Er<sup>+3</sup> and Ho<sup>+3</sup>. It appears that perhaps Zn<sup>+2</sup> can shift along the series with changing pH of the eluant or perhaps with temperature.

### 1.3 Small Scale Investigations of New Chelating Agents

Investigation of the performance of  $\beta$ ,  $\beta'$ -diaminodiethylether-N, N, N, N-tetraacetic acid in eluting rare earths was continued. A reversal in the usual elution sequence of the heavy rare earths has been noted which is much like that observed with diethylenetriamine pentaacetic acid (DTPA) elutions. As a result of this the middle rare earths, Sm-Er, elute first. Although this group is poorly resolved, the leading elements appear to be Tb and Dy. Gd and Ho elute at about the same position and Sm and Er tend to overlap badly. After Sm and Er, the heavy rare earths Tm, Yb and Lu appear, well separated, but in the opposite order generally observed with ion-exchange elutions. Yttrium elutes next, followed by Nd, Pr, Ce and La. It appears, therefore, that the stability constant of the rare-earth-chelate species increases from La to Tb and then decreases from Dy to Lu. Yttrium falls between Sm and Nd as is the case with HEDTA and DTPA. The stability constants for Sm and Nd must be fairly far apart to allow the resolution of Tm, Yb, Lu and Y in the gap between Sm and Nd. Apparently the stability constants of the Sm, Eu, Gd, Tb, Dy, Ho, Er-chelates of  $\beta$ ,  $\beta'$ -diaminodiethylether-N, N, N, N-tetraacetic acid do not differ greatly from one element to the next. They just rise gradually from Sm to Tb and then decrease slightly from Dy to Er. It now appears doubtful that

this chelating agent will be of much practical value for separating rare earths.

## 2. Rare-Earth Metallurgy

### 2.1 Preparation of Rare-Earth Metals (F. H. Spedding and A. H. Daane)

From vapor pressure studies on scandium and yttrium described previously, it appeared likely that these metals could be distilled to obtain very pure metal, if only on a small scale. This has been done, requiring a temperature of  $1800^{\circ}\text{C}$  for scandium and a temperature of  $2000^{\circ}\text{C}$  for yttrium. The distillates seemed to be significantly more ductile than the starting metal. In the case of yttrium, the metal was found to contain less than 300 ppm oxygen, the tantalum content being below the limit of detection. Although only small quantities of metal have been prepared by this technique, it is hoped to extend it to some of the rare-earth metals of low volatility (lanthanum, cerium, praseodymium and neodymium) to obtain massive samples of these metals.

A tungsten filtering device has been constructed, through which samples of molten rare-earth metals have been filtered at temperatures slightly above their melting points. Some reduction in oxygen content has been observed, but the main effect has been the lowering of the tantalum content to very low levels, while adding only a small amount

of tungsten. Quantitative data on these impurities are not yet available.

A furnace large enough to prepare ten pounds of a rare-earth metal by the calcium reduction of the rare-earth fluoride has been placed in operation, and has been found to work satisfactorily. It is very similar to the semi-continuous furnace used for the preparation of yttrium metal on a larger scale, described in previous reports (see ISC-706, ISC-757 and ISC-902). The furnace utilizes a tantalum reaction chamber, with a bottom pour spout and a water-cooled copper mold.

## 2.2 Properties of Rare-Earth Metals

### 2.2.1 Melting Point Determinations (F. H. Spedding and A. H. Daane)

New melting point data have been observed for some of the rare-earth metals. These data represent refinements in that either the metal itself is purer than that used previously, or the measuring techniques have been improved to give more accurate data than those previously obtained at this Laboratory. The data are:

<u>Metal</u>	<u>Melting Point</u>
Scandium	1538°C
Gadolinium	1312°C
Lutetium	1680°C

X-ray studies of the allotropic modifications of the rare earths have shown a body-centered cubic structure to occur in yttrium ( $a = 3.91\text{\AA}$ ) in a temperature region just below the melting point of the metal, and a body-centered cubic structure to exist in samarium above  $917^{\circ}\text{C}$  ( $a = 4.07\text{\AA}$ ). Resistivity measurements on ytterbium in this Laboratory have indicated a transformation in ytterbium near  $280^{\circ}\text{C}$ . X-ray diffraction patterns taken on a sample of ytterbium as it was heated up to  $600^{\circ}\text{C}$  showed only the face-centered cubic structure of the metal. However, if a small amount of air is in the X-ray capillary, a skin forms over the sample so that it can be heated to  $800^{\circ}\text{C}$  without serious volatilization of the metal, and, on cooling, a hexagonal phase appears at  $710^{\circ}\text{C}$ , and exists to  $260^{\circ}\text{C}$ , below which the face-centered cubic form is present. The transformation at  $710^{\circ}$  is  $90^{\circ}$  below the temperature observed in the pure metal, so it is possible that the hexagonal form is characteristic of metal containing a small amount of oxygen or nitrogen in solid solution.

### 2.2.2 Thermal Properties (F. H. Spedding and L. D. Jennings)

We have re-examined our heat capacity results for thulium and find that there are scarcely noticeable, rapid changes of slope of the heat capacity versus temperature curve near  $87^{\circ}$  and near  $175^{\circ}\text{K}$ . There

is thus some anomalous behavior at temperatures above the main peak arising from magnetic ordering. (This peak is at  $54.8^{\circ}\text{K}$  and displays thermal hysteresis to the extent of 0.4 per cent). Thus, in a certain sense, not even in thulium is there thermal hysteresis at the highest temperature anomaly as suggested in report ISC-1049.

The heat capacity of  $\text{CrBr}_3$  has been measured in the temperature region from  $15^{\circ}$  to  $350^{\circ}\text{K}$ . There is an anomaly at  $32.5^{\circ}\text{K}$ . It appears to be more difficult to reconcile the data with the assumption that the magnetic entropy under the anomaly is  $R \ln 4$  than in the case of the fluoride and chloride, although the complexity of the calculation is such that one cannot have great confidence. This result may be related to our observation that the bromide does not show any magnetic hysteresis at helium temperatures as do the other halides; these results then indicate that there may be additional magnetic ordering below the lowest temperatures we have investigated.

### 2.3 Rare-Earth Halides (F. H. Spedding and A. H. Daane)

In a study of rare-earth halides, the following data have been obtained:

$\text{YbCl}_3$  melts at  $865^{\circ}\text{C}$ .

$\text{SmCl}_3$  melts at  $682^{\circ}\text{C}$ .

$\text{CeCl}_3$  melted under one atmosphere of  $\text{Cl}_2$  and did not form a detectable amount of  $\text{CeCl}_4$ .

$\text{YbCl}_3$  does not appear to be reduced to  $\text{YbCl}_2$  by zinc metal at temperatures below about  $800^\circ\text{C}$ .

When  $\text{YF}_3$ ,  $\text{YOF}$  or mixtures of  $\text{YF}_3$  and  $\text{Y}_2\text{O}_3$  are heated in a graphite crucible in a vacuum,  $\text{YF}_3$  distills out of the mixture, although traces of oxygen are found in the condensate.

## 2.4 Rare-Earth Alloys (F. H. Spedding and A. H. Daane)

### 2.4.1 La-B System

When  $\text{LaB}_6$  is heated in a vacuum to about  $2000^\circ\text{C}$ , some lanthanum is distilled from the compound to give a  $\text{LaB}_{12}$  composition that is blue instead of purple, and yet has essentially the same lattice constants as  $\text{LaB}_6$ . Boron does not change the melting point or transformation temperatures of lanthanum.

### 2.4.2 La-Y System

From 52 to 58 atomic per cent yttrium, there appears to be a single phase area in this system that possesses the samarium structure with  $a = 6.687\text{A}$  and  $c = 27.10\text{A}$ , indexed on a hexagonal cell. This phase appears to decompose at  $625^\circ\text{C}$ .

This samarium-structured phase has been observed in the Ce-Y, Pr-Y and Nd-Y systems. It is interesting to note that the  $c/a$  ratio of these hexagonal phases, corrected to that of simple hexagonal close packed structures by dividing by 4.5, are all about 1.63, which is that of hexagonal packing of perfect spheres.

### 2.4.3 Rare-Earth-Tantalum Systems

The amount of tantalum that dissolves in molten rare-earth metals appears to be more of a function of time at temperature than was previously supposed. The following data indicates this:

<u>Metal</u>	<u>Time</u>	<u>Temperature</u>	<u>%Ta</u>
Dy	5 min.	1500°C	0.27
Dy	60 min.	1500°C	0.67
Tm	5 min.	1600°C	1.02
Tm	60 min.	1600°C	1.51

When samples of dysprosium and thulium were held for 15 minutes at 1600°C, they were found to contain 0.74 and 1.50 per cent Ta, respectively.

### 2.4.4 Y-Ni System

This system appears to be similar to the Ce-Ni and Pu-Ni system in many respects.

### 2.4.5 Y-Cu System

Since yttrium is clad with copper for extrusion and other fabrication operations, a study of the yttrium-copper system was initiated. The compounds YCu (bcc,  $a = 3.54\text{\AA}$ ), YCu<sub>2</sub> (Hex.  $a = 7.41\text{\AA}$ ,  $c = 5.84\text{\AA}$ ), YCu<sub>4</sub> (Hex.  $a = 9.99$ ,  $c = 8.55\text{\AA}$ ) and YCu<sub>6</sub> (Hex.  $a = 6.83\text{\AA}$ ,  $c = 4.07\text{\AA}$ ) have been observed.

### 3. Ion Mobilities (F. R. Duke)

The mobilities of the ions in fused silver chloride were determined. At 550°C, the silver ion carries all of the current. However, the silver ion carries about four-fifths of the current at 850°C. Further studies on the ion mobilities as a function of temperature are under way.

It was found that the mobility of chloride ion in low concentration in fused sodium nitrate was constant as concentration varied, and a little larger than that of the nitrate ion.

A paper (ISC-1086), "Transport Numbers in Pure Fused Salts. The Alkali Metal Chlorides" by Frederick R. Duke and Allen L. Bowman, was submitted for publication in J. ELECTROCHEM. SOC.

Abstract--The transport numbers of the ions in the pure fused alkali chlorides were determined and found to be, for the cation,  $0.25 \pm .03$ ,  $0.38 \pm .04$ ,  $0.38 \pm .04$ ,  $0.42 \pm .04$  and  $0.36 \pm .04$  for Li, Na, K, Rb and Cs, respectively. The radius ratio equation,  $t_+ = \frac{r_-}{r_+ + r_-}$  fits with the exception of CsCl. In general, radio-chloride and quartz membrane cells were used to estimate the ion mobility.

A report (ISC-1071), "Transport Numbers in Fused Silver Chloride-Alkali Metal Chloride Systems" by Allen L. Bowman and F. R. Duke, is being distributed.

Abstract--The ionic transport numbers are determined in the fused alkali metal chlorides, silver chloride, and mixtures of silver chloride with lithium, sodium, and potassium chlorides. The variation of the ionic mobilities with composition was determined for the fused system KCl-AgCl. The anion transport numbers were determined by following the migration of  $\text{Cl}^{36}$  through a fine porosity membrane. The transport numbers of the cations in the mixtures were determined by following the migration of  $\text{Ag}^{110\text{m}}$  or by the measurement of  $\theta$  in a Hittorf-type experiment.

The chloride ion carries from 25 to 45 per cent of the current in the pure alkali metal chlorides. With the exception of cesium chloride, the transport numbers obey the relation

$$t_- = r_+ / (r_+ + r_-)$$

where the  $r$ 's are the ionic radii. The mobilities of the chloride ion are not constant, either at constant absolute temperature or at a corresponding temperature of five per cent above the absolute melting point. The chloride ion is almost completely immobile in fused silver chloride. Thus, it is suggested that this salt contains a fairly rigid chloride lattice, through which the silver ions move easily.

The transport numbers in the mixtures of silver chloride with sodium and potassium chlorides are essentially the same. With

lithium chloride, the general character of the curves is the same, but the lithium transport number is greater than that of sodium or potassium. Since conductivity data are not available for the AgCl-LiCl and AgCl-NaCl systems, the mobilities of the ions in these systems cannot be calculated.

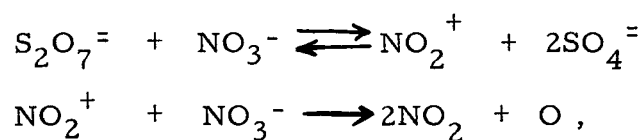
When potassium chloride is added to silver chloride, the mobility of the chloride ion remains essentially zero until the concentration of potassium chloride becomes greater than 25 mole per cent, while the silver ion mobility decreases rapidly. When small amounts of silver chloride are added to potassium chloride, the mobility-composition curves indicate the presence of AgCl and  $\text{AgCl}_2^-$  complex species, with formation constants of 3 and  $10^{-2}$ , respectively. The assumption is made that the mobilities of the potassium and chloride ions should remain constant.

A set of equations with seven adjustable parameters is proposed to describe the conductivity, fluidity, self-diffusion coefficients, and transport numbers in a pure fused salt. The correlation of sodium nitrate data is far from satisfactory, but may be within experimental error.

#### 4. Reaction Kinetics (F. R. Duke)

##### 4.1 Acid-Base Reactions

The work on the acid-base reactions discussed in the previous semi-annual report (ISC-1049) was continued. Instead of the reaction sequence reported there, ( $\text{Cr}_2\text{O}_7^{=}$  +  $\text{NO}_3^- \rightleftharpoons \text{NO}_2^+$  +  $2\text{CrO}_4^{=}$ ) followed by  $\text{NO}_2^+$  +  $\text{NO}_3^- \rightleftharpoons 2\text{NO}_2$  + O, the reaction sequence



was studied. It was considered possible that  $\text{S}_2\text{O}_7^{=}$  is sufficiently stronger as an acid than  $\text{Cr}_2\text{O}_7^{=}$  so that a larger equilibrium constant would be found for the reaction producing the  $\text{NO}_2^+$ . This is indeed the case; in fact, the equilibrium constant in the case of the  $\text{S}_2\text{O}_7^{=}$  reaction is large enough that it can be separated from the rate constant for the decomposition of  $\text{NO}_2^+$ . The data are now being worked up, and will allow calculation of the equilibrium constants separate from the rate constant in all other cases, for example, the  $\text{Cr}_2\text{O}_7^{=}$  case. Thus, it is now known that it will be possible to calculate actual concentrations of  $\text{NO}_2^+$  in all of these acidic mixtures.

Experiments on the decomposition of  $\text{ClO}_3^-$  and  $\text{BrO}_3^-$  indicate that possibly the paramagnetic metal ions catalyze the reaction and others do not. This hypothesis is being tested presently using rare-earth ions as catalysts.

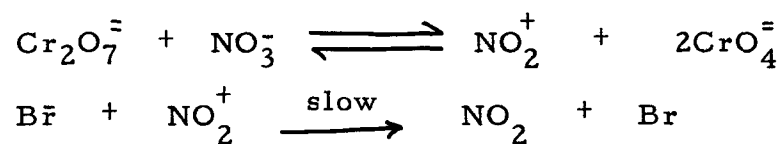
A paper (ISC-1042), "Acid-Base Reactions in Oxidation Mechanisms" by F. R. Duke, was submitted for publication in ANAL. CHEM.

Abstract--The hypothesis is advanced that in general, oxidation-reduction reactions are preceded by, or are simultaneous with, an acid-base step. Application of the hypothesis allows the research analytical chemist to decide such things as when a reaction might be slow and what catalyst might be effective for a given reaction.

#### 4.2 Oxidation of Bromide Ion

A paper (ISC-1077), "Kinetics of the Oxidation of Bromide Ion in Fused Alkali Nitrate Solutions of Dichromate" by F. R. Duke and M. L. Iverson, was submitted for publication in ANAL. CHEM.

Abstract--The oxidation of bromide ion by dichromate in fused sodium nitrate-potassium nitrate eutectic is found to proceed through the steps:



Lead ion is added to precipitate  $\text{CrO}_4^=$  and drive the first equilibrium equation. Corrections need to be made for the complexation of lead ion by dichromate and bromide ions.

#### 5. Aqueous Chemistry (F. R. Duke)

Benzoquinone and pyrazine were found not to catalyze the Fe(III)-Fe(II) electron exchange. Paraphthalic acid is a catalyst for the exchange.

We judge, therefore, that under the conditions of the experiment, either Fe(III) or Fe(II) or both do not form complexes with quinone or pyrazine, but that paraphthalic acid does.

6. The Lower Oxidation States of Antimony (J. D. Corbett)

The first indication of the lower iodide formed by solution of antimony metal in the liquid triiodide has been obtained. Carbon has been found to act as a reversible oxidation-reduction electrode in such a melt, so that the nature of the metal-metal halide reaction can be deduced from concentration cell measurements. With a reference anode of the Sb-SbI<sub>3</sub> solution in equilibrium with excess metal, the EMF is found to vary linearly with the logarithm of the concentration of metal "dissolved" in the catholyte. The slope of this plot indicates the oxidation-reduction process is  $2\text{SbI}_3 + 2\text{C} = \text{Sb}_2\text{I}_4 + 2\text{I}^-$ . The only other species satisfying the data is the SbI monomer, which is eliminated by its presumed paramagnetism. Such a method will be applied to other fused salt systems.

7. The Gold Chlorides (J. D. Corbett)

A paper (ISC-1093), "The Gold(I) Chloride-Gold(III) Chloride System; The Nonexistence of the Intermediate Au(AuCl<sub>4</sub>)" by John D. Corbett and Leonard F. Druding, was submitted for publication in J. INORG. NUCL. CHEM.

Abstract--The possibility of the formation of  $\text{Au}(\text{AuCl}_4)$  by a simple acid-base interaction between  $\text{AuCl}$  and  $\text{AuCl}_3$  has been investigated since published thermodynamic data do not appear adequate to eliminate such an intermediate. However, a partial phase diagram and powder pattern data for the system show no evidence for its formation. Gold(I) chloride disproportionates in the presence of liquid  $\text{AlCl}_3$  or  $\text{GaCl}_3$ . The absence of compound formation between  $\text{AuCl}$  and the halide acids is considered in terms of the apparent covalency and borderline stability of the monochloride.

## 8. Adsorption Studies (R. S. Hansen)

### 8.1 Adsorption Kinetics

A paper (ISC-1078), "The Kinetics of Adsorption of Organic Acids at the Water-Air Interface" by Robert S. Hansen and Terry C. Wallace, was submitted to J. PHYS. CHEM. for publication.

Abstract--The vibrating jet method with theory modified for non-uniform velocity profile is applied to the determination of dependence of surface tensions of aqueous solutions of pentanoic acid, heptanoic acid, octanoic acid, and heptanol-1 on concentration and time. Results are independent of orifice and flow rate for orifices designed to permit the necessary theoretical treatment, and extrapolate uniformly to results obtained by Addison for decanoic acid, and Dervichian for

hendecanoic acid, by conventional surface tension methods.

Where  $\pi$  is the spreading pressure at time  $t$ , and  $\pi_{\infty}$  the equilibrium spreading pressure, the empirical equation

$$\frac{\pi}{\pi_{\infty} - \pi} e^{-b\pi/\pi_{\infty}} = k\pi_{\infty}^2 \tau$$

was found to represent well the data obtained in the present work as well as the data of Addison and Dervichian. No mechanism of adsorption could be devised leading explicitly to this relation.

Observed rates of surface tension depression in the systems studied were too slow to correspond to diffusion controlled mechanisms, but could be well represented by a second order kinetic mechanism implying a dimeric transition state located substantially in the surface film.

Equations based on this model are derived and shown to agree well with experimental results.

Work on the study of time-dependent surface tensions has continued. At present a study of the dependence of surface tension on concentration and time in aqueous solutions of normal 6, 7, and 8 carbon nitriles is in progress, aimed at establishing whether the ability to form hydrogen bonds is necessary for a dimeric transition state in the adsorption process. Adaptation of the vibrating jet technique to the study of liquid metals is under study using mercury as proto-type liquid metal.

Theoretical work on single component and mixed gas adsorption isotherms has continued. Effects of non-uniform density distribution functions (i. e., short range order) in the neighborhood of the surface and of van der Waals repulsive potentials have been investigated; these appear to have negligible effect on isotherm character beyond the first adsorbed layer. Representation of helium adsorption on non-porous adsorbents appears very good beyond the second adsorbed layer; representation of  $N_2$  and  $O_2$  adsorption appears very good only beyond the third layer. The treatment of adsorption in the first two layers has not been satisfactorily resolved.

## 8.2 Relaxation Phenomena in Electrical Double Layer

The study of relaxation phenomena in the electrical double layer has continued. A tentative analysis of frequency dependence of double layer impedance at the mercury aqueous 0.1N  $HClO_4$  interface indicated two relaxation times of approximately  $5 \times 10^{-4}$  and  $5 \times 10^{-5}$  seconds, moderately polarization dependent. At high frequencies the double layer equivalent series resistance is small compared to total resistance, and is therefore subject to appreciable error as a small difference between large numbers. To improve precision, these experiments have been in part repeated with 1N  $HClO_4$  solution, reducing solution resistance, and in this repetition, techniques have been modified to minimize parasitic

inductances. Two relaxation times were again obtained, less in both cases by a factor of approximately two, and nearly independent of polarization. Temperature dependence of these relaxation times will be established.

### 8.3 Adsorption at Carbon Surfaces

A study of the chemical properties of carbon surfaces has continued. Work in other laboratories has indicated a maximum electron spin resonance in carbons prepared by charring sugar at 600°C, with unpaired electron concentration of the order of magnitude 1 meg. per gram. One meq. per gram of triphenylmethyl was found to be adsorbed from benzene solutions by charcoal at immeasurably small equilibrium concentrations with little change in amount adsorbed as concentration increased. It is tentatively concluded that the unpaired electrons in the sugar charcoal are located on surface free radicals, and that these chemisorb the triphenylmethyl radicals stoichiometrically. It has also been found possible to obtain potentiometric titration curves for reaction of base with carbon blacks; curve forms strongly indicate that the curves correspond to titration of surface carboxyl groups. Base uptake corresponds approximately to hydrogen liberation on treatment of the same carbon blacks with lithium aluminum hydride which would be expected if surface carboxyl groups were responsible for both phenomena.

#### 8.4 Adsorption from Solution (L. S. Bartell)

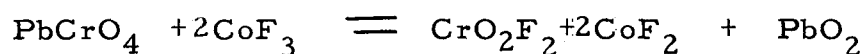
The optical polarimetric study of adsorption from solution onto flat metal slides of small area has yielded useful and novel adsorption isotherms. Studies of the surface tension of the solution and of contact angles of the solution against the adsorbed film were run concurrently with the isotherms. This work represents the first successful research to date in which adsorption and wetting were measured simultaneously on the same surface. It has clarified materially the basic principles involved in the wetting of high energy surfaces, where adsorption always takes place. A unified theory of wetting of low energy and high energy surfaces in air-liquid-solid and liquid-liquid-solid systems is being devised.

### 9. Isotope Abundance Measurements

#### 9.1 Isotopic Abundance of the Cr Isotopes (H. J. Svec)

Samples of eighteen chromite ores have been obtained from well characterized locations in New Caledonia, Transvaal, Rhodesia, Phillipine Islands, Turkey, Russia, Cuba, Quebec, Pennsylvania, Maryland, Montana, and Texas. One sample of the mineral crocoite, a lead chromate, was obtained from Tasmania. These were all treated chemically to quantitatively extract the chromium which was then converted to  $\text{CrO}_2\text{F}_2$ , in which form the element was introduced into the mass spectrometer. Chromyl

fluoride was produced according to the solid-solid reaction:



In the abundance studies, the parent molecular positive ions were used to obtain the data. The results of these studies are presented in Table II in three different ways.

Table II

Isotope Abundance Data for Chromium from Chromite Ores\*

Isotope	% Abundance $\pm \sigma$	% Abundance $\pm \sigma$	% Abundance $\pm 3\sigma$
50	4.351 $\pm$ 0.006	4.351 $\pm$ 0.008	4.351 $\pm$ 0.024
52	83.778 $\pm$ 0.009	83.778 $\pm$ 0.012	83.778 $\pm$ 0.036
53	9.501 $\pm$ 0.007	9.501 $\pm$ 0.009	9.501 $\pm$ 0.027
54	2.370 $\pm$ 0.005	2.370 $\pm$ 0.006	2.370 $\pm$ 0.024

\* Corrected for oxygen isotopes. The maximum observed variation in these does not affect the numbers given in this table.

The results shown in column two represent the average for the eighteen ores, giving the observed values for each the same statistical weight. In column three, the 180 items of data collected during the work are considered in the treatment of data. Observe that the only change in the results is one involving the increased value for the standard deviation. Column four represents the same treatment of data as column three with

the limit of  $3\sigma$  applied to the data. It is significant that, of the 180 items of data considered, only two fall outside the limit of  $3\sigma$  and none outside  $4\sigma$ . A careful check of the mass spectrometer by means of mixtures of separated isotopes indicates that these results may be considered as absolute values within the limits given in Table II.

In comparing the results obtained for the individual ores with these values, one must conclude that when the 99.7 per cent confidence criteria is applied there is no natural fractionation of the Cr isotopes in chromite ores despite their world-wide distribution. M. Ingrahm and H. Brown report that a comparison of meteoritic Cr with laboratory reagent Cr shows no difference. Since all commercial Cr chemicals are produced from chromite, it is probable that isotope abundance values of meteoritic Cr are identical with those obtained here. It is therefore appropriate to speculate that our solar system had a common primordial source of the element Cr.

## 9.2 Nitrogen

A report (ISC-1138), "Nitrogen Isotope Abundance Measurements" by Gregor Junk and H. J. Svec, is being distributed.

Abstract--The absolute abundance of the isotopes in atmospheric and commercial compressed  $N_2$  from various sources has been determined. Nitrogen gas standards, prepared by mixing separated

nitrogen isotopes in the form of  $(\text{NH}_4)_2\text{SO}_4$  solutions, were employed to calibrate two  $60^\circ$  sector mass spectrometers. As a result, the absolute ratio of  $\text{N}^{14}/\text{N}^{15}$  in atmospheric nitrogen was found to be  $272.0 \pm 0.3$ . Small variations from this value were found for commercial compressed gas.

The mass spectrometric procedure used in determining the  $\text{N}_2^{29+}/\text{N}_2^{28+}$  ratio allowed for detection of differences to 1 part in 3500. However, the absolute accuracy of the abundance measurements was limited to 1 part in 1000 because of the semi-micro Kjeldahl distillation employed to determine the amount of  $(\text{NH}_4)_2\text{SO}_4$  present in the solutions of the separated isotopes.

In these measurements, instrumental background played a very significant role. A reliable method of correcting the observed  $\text{N}_2^{29+}/\text{N}_2^{28+}$  ratio for the contribution of the background at these mass positions was developed.

#### 10. Metal-Water Vapor Reactions (H. J. Svec)

The study of the kinetics of the reaction between Y and  $\text{H}_2\text{O}$  vapor is nearly complete. The fate of hydrogen in the reaction has been determined. As a result of X-ray diffraction studies on the products, the reacted metal and the pure materials, we have concluded that  $\text{YH}_2$  is formed as

a distinct second phase within all yttrium metal which has come in contact with water vapor in the temperature range 600-800°C.

Yttrium dihydride has been prepared from the elements at 750°C. Analysis of X-ray powder photographs show that the material is f. c. c. with a lattice constant of 5.194<sup>o</sup>Å. Analysis of similar photographs of material obtained<sup>1</sup> from the General Electric Co. gave identical results within the experimental uncertainty. A f. c. c. phase with a lattice constant of 5.285<sup>o</sup>Å was found in Y metal which had reacted with water vapor. X-ray powder photographs of this phase are identical with those of the pure YH<sub>2</sub> in every respect except the expansion of the lattice constant. No other possible identity of the f. c. c. phase is feasible; therefore, one concludes that this second phase is YH<sub>2</sub> and the expanded lattice is due to the solution of oxide which is present in the hydride.

Our measurements of the lattice constants for Y metal are  $a = 3.652\overset{\circ}{\text{Å}}$  and  $c = 5.746\overset{\circ}{\text{Å}}$ , compared to values of 3.6474<sup>o</sup>Å and 5.7306<sup>o</sup>Å previously reported by Spedding, Daane and Herrmann [Acta Crystal. 9, 559-63 (1956)]<sup>7</sup>. Some extra lines due to impurities in the metal we used were indexed as a b. c. c. phase with a lattice constant of 10.645<sup>o</sup>Å. This appears to be Y<sub>2</sub>O<sub>3</sub> whose value has been given previously as 10.60<sup>o</sup>Å.

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<sup>1</sup> By A. H. Daane of this Laboratory

In a similar case, some faint extra lines in X-ray powder photographs of the outer portion of our  $\text{YH}_2$  preparation were identified as the f.c.c. YN with a lattice constant of  $4.95\overset{\circ}{\text{A}}$ , which compares favorably with the unpublished data of Daane<sup>2</sup> of  $4.905\overset{\circ}{\text{A}}$ . The definitely expanded yttrium nitride lattice is probably due to the presence of interstitial H in the crystals.

#### 11. Mass Spectrometry of Stannane (H. J. Svec)

$\text{SnH}_4$  has been prepared by the reaction of  $\text{NaBH}_4$  with  $\text{Sn}^{++}$  in HCl, and has been examined mass spectrometrically with one unusual result. No parent positive ion was observed when normal tin was employed in the experiments. The computed monoisotopic fragmentation pattern for 70 volt electrons was found to be

$\text{SnH}_4^+$	< 0.1
$\text{SnH}_3^+$	100.0
$\text{SnH}_2^+$	53.6
$\text{SnH}^+$	21.6
$\text{Sn}^+$	71.8

Additional work is planned using separated isotopes to examine further the question of the absence of  $\text{SnH}_4^+$  and to also determine the appearance potential of the various fragments.

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<sup>2</sup> This Laboratory

12. Paramagnetic Susceptibilities of Chromium III Halides

A paper (ISC-1067), "The Paramagnetic Susceptibilities of the Chromium(III) Halides" by Wilford N. Hansen and Maurice Griffel, was submitted for publication in J. CHEM PHYS.

Abstract--The paramagnetic susceptibilities of  $\text{CrF}_3$ ,  $\text{CrCl}_3$ ,  $\text{CrBr}_3$ , and  $\text{CrI}_3$  have been measured by the Gouy method from room temperature down to a temperature at which the susceptibility is field-dependent. Above approximately  $100^\circ\text{K}$  these susceptibilities all obey the Curie-Weiss law with respective constants as follows:  $\theta(^{\circ}\text{K}) = -124, 31, 51$  and  $70$ ;  $P_{\text{eff}}$ (Bohr magnetons) = 3.85, 3.69, 3.94 and 4.03.  $\text{CrF}_3$  evidently becomes ferrimagnetic below  $70^\circ\text{K}$ .

13. Bondorders in Homonuclear Conjugated Systems (K. Ruedenberg)

A paper (ISC-1033), "The Topological Matrix as Generatrix of Bondorders in Homonuclear Conjugated Systems" by Klaus Ruedenberg, was submitted for publication in J. CHEM. PHYS.

Abstract--It is shown that in homonuclear conjugated systems the various bondorders and similar quantities can be written as matrix functions of the topological incidence matrix. This entails the existence of a number of useful general relations between these various quantities. The relations include as special cases: Coulson

and Rushbrooke's theorem on chargeorders in alternants; G. G. Hall's theorem on bondorders in alternants; McWeeny's theorem on the formal charges; Ham and Ruedenberg's correlation between Coulson and Mulliken bondorders for neighbors in alternants. A number of new relations between bondorders are derived and discussed. The generalization from alternants to non-alternants is given particular attention.

### Pyrometallurgy

#### 1. Liquid Metal Extraction of Plutonium from Uranium (A. F. Voigt)

##### 1.1 Extraction with Silver

Research on the distribution of plutonium between uranium and an immiscible metal phase has continued. Emphasis has been placed on completing the systems previously studied and performing a few preliminary experiments on some other systems.

In completing the work on the uranium-silver system, two pieces of information were desired: (1) Does the observed extraction coefficient represent an equilibrium value? (2) Can the extracted plutonium be removed from the silver by a simple fused salt extraction? In order to do these experiments it was necessary to prepare a silver-

plutonium alloy. With the material available, the best method of preparation appeared to be to extract larger quantities of the U-Pu alloy with silver, a process which has been found to result in the transfer of up to 90 per cent of the plutonium.

These preparative extractions were run very similarly to the previous experiments and the results were much the same as before. Less statistical accuracy was available since most of the silver layer was not used for analysis but was saved for re-extraction. The results, however, agreed adequately with the earlier ones showing that the extraction process is reproducible.

In testing the approach to equilibrium by a reverse extraction, several experiments were planned but only one could be carried through because of crucible failure and other technical difficulties. In this experiment, 20 g of uranium was equilibrated with 12 g of silver for 20 minutes at 1225°C with stirring. The original plutonium analysis of the final uranium was 0.05 mg/g.

These figures give a distribution coefficient of  $28 \pm 2$  which can be compared to  $32 \pm 3$  for seven extractions in the normal direction at this temperature. Thus, it appears that the experiments on this system essentially represent equilibrium conditions for the extraction.

Two extractions of plutonium from silver by fused salts were made. In each case, the fused salt phase contained NaCl with 5 mole per cent AgCl. Total recovery was poor because of crucible attack, and the results probably do not represent equilibrium. In these two experiments, 93 to 99 per cent of the plutonium was removed from the silver phase, but only 33 to 64 per cent was recovered from the salt phase. However, the feasibility of this method of removing the extracted plutonium from silver was demonstrated, and better recovery should result from choice of proper crucible material and refinement of technique.

Four additional extractions with lanthanum metal were made at temperatures from 1230 to 1375°C. In these, three or four samples were taken from each phase and quite good agreement was obtained, as shown in Table III. Agreement with previous experiments at 1225°C was also very good. It is apparent that there is no demonstrable temperature coefficient.

Table III

## Distribution of Plutonium Between Uranium and Lanthanum

Run No.	157	160	163	164
Temperature	1230	1375	1300	1300°C
Kd	0.68 ± .02	0.68 ± .02	0.67 ± .01	0.67 ± .01
D.F.	1.33 ± .03	1.24 ± .07	1.20 ± .02	1.32 ± .04
% Extd	15.2 ± .7	17.4 ± 1	18 ± 1	18 ± .5
% Removed	25 ± 2	19 ± 4	17 ± 1	24 ± 3

## 1.2 Extraction with Magnesium-Silver Alloy

Since both silver and magnesium are immiscible with uranium and both have been suggested as extractants for plutonium, it was considered a possibility that a magnesium-silver alloy might combine the good properties of both and be more effective than either. To test this possibility a quantity of the Mg-48 weight per cent Ag eutectic was prepared. Samples of this material were equilibrated with the U-0.1 per cent Pu alloy, with this alloy mixed with U-Cr to produce the U-5 percent Cr eutectic and with U-Cr eutectic containing cerium and zirconium. The plutonium extractions were at  $1175^{\circ}\text{C}$ , those with the fission products at  $1000^{\circ}$ . The high vapor pressure of magnesium made it necessary to use a static system and, at the higher temperature, most of the Mg-Ag phase was lost in two experiments. Thus, the data obtained from the experiments are somewhat meager but sufficient to show some very interesting behavior. The extraction of plutonium was much smaller than in the case of either magnesium or silver alone. A distribution coefficient of 0.3 to 0.6 was observed, compared to 2 to 3 for magnesium and about 30 for silver. As a result of this low extraction coefficient, only about 10 per cent of the plutonium was removed.

The fission product experiments showed essentially the same behavior for zirconium as for plutonium, but cerium was removed with exceptionally

high efficiency. Distribution coefficients of the order to 1000 - 3000 were observed, resulting in the removal of 99.5 to 99.9 per cent of the cerium. This selective extraction behavior is interesting, and it would seem of value to find if it is restricted to cerium or observable for other rare-earth fission products.

### Analytical Chemistry

#### 1. Analytical Procedures (C. V. Banks and J. S. Fritz)

##### 1.1 Oxygen

##### 1.1.1 High Temperature Fluorination Method

Work was continued on the determination of oxygen in inorganic materials by the high temperature fluorination,  $\text{KBrF}_4$ , technique. The basis of the method is the reaction of an inorganic compound with  $\text{KBrF}_4$  to give molecular oxygen. The apparatus and procedure were greatly simplified during this period. Several reaction chambers can now be used and the necessary reaction time was found to be two hours or less for many compounds. A second two-hour heating cycle is necessary for yttrium fluoride, however, and massive yttrium metal fails to react completely. Materials analyzed for oxygen by this method include bromine insolubles, molybdenum silicide, titanium carbide, uranium dioxide, vanadium metal, yttrium fluoride, yttrium-magnesium

alloy, and yttrium sponge. The results obtained are regarded as tentative, pending establishment of the accuracy and reliability of the method. An extensive correlation of results obtained on standardized yttrium fluoride samples by this method with results obtained by spectrographic, vacuum fusion, and inert gas fusion is planned. Results obtained to date are shown in Table IV.

Table IV  
Comparison of Oxygen Values of  $YF_3$

<u>Sample</u>	<u>Spectro- graphic</u>	<u>Oxygen in ppm</u>	
		<u>KBrF<sub>4</sub></u>	<u>Inert gas fusion</u>
A	500 <sup>1</sup>	440 - 480	440, 440, 570, 450
B	1500 <sup>1</sup>	800 - 1800	1560, 1450, 1500, 1460
<u>56-S-7-M(b)</u>	---	800 - 850	640, 720, 610, 760

<sup>1</sup> Estimated from Intensity Ratio.

#### 1.1.2 Inert Gas Fusion Method

Analysis of yttrium metal samples by the inert gas fusion method gave results in good agreement with results obtained by spectrographic or vacuum fusion methods. It was also found that the method could be extended to the analysis of yttrium fluoride samples with some modification of the apparatus. In the case of yttrium fluoride samples it was necessary to

include an absorbent for silicon tetrafluoride. A specially prepared magnesium oxide-asbestos reagent was found to be satisfactory for this purpose. Table IV shows the results obtained.

### 1.2 Niobium

Work has been started on the development of a general method for separating and determining niobium from complex mixtures in which tantalum may also be present. Preliminary work on the extraction of niobium from strong hydrochloric acid solutions with tribenzylamine seems promising. The niobium can be back-extracted with a reagent containing 4,5-dihydroxy-1,3-benzenedisulfonic acid (Tiron) and determined spectrophotometrically.

### 1.3 Rare Earths

#### 1.3.1 Ion Exchange

An ion exchange separation and spectrophotometric method has been developed which permits the determination of rare earths in thorium with a maximum error of 5 per cent provided the thorium to rare earth ratio does not exceed 200. If the separation step is repeated, samples in which the ratio is much larger can be analyzed.

#### 1.3.2 Differential Spectrophotometric Analysis

Work was continued in an effort to establish the optimum conditions for maximum precision and accuracy with this method. A number of erbium-thulium mixtures were analyzed with fairly good results.

## 1.4 Uranium

### 1.4.1 Separation by Solvent Extraction

An investigation of various organophosphorus compounds as extractants for uranium and the subsequent determination of uranium in the organic phase has been undertaken. It was found possible to completely extract uranium with a number of organophosphorus compounds but not always possible to subsequently determine uranium in the organic phase with the commonly used reagents such as 2-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)-benzenearsonic acid (Arsenazo) or 1-(2-pyridylazo)-2-naphthol (PAN). The better extractants, such as tri-n-octylphosphine oxide (TOPO), apparently bind the uranium so tightly that it does not react with the chromogenic reagent. It has been found that the addition of alcohol to the organic phase permits complex formation between uranium and PAN, as well as other chromogenic reagents, to go to completion even in the presence of TOPO. This phenomenon has permitted the development of a tentative method for uranium based on the reaction of uranium with PAN directly in the organic phase (TOPO) after extraction.

The synthesis of methylenetetraalkyldiphosphine oxide has been started. It is expected that this reagent might have very interesting properties as an extractant.

#### 1.4.2 Separation by Mercury Cathode (C. V. Banks)

Magnetic mercury cathode electrolysis has been used satisfactorily to separate molybdenum from uranium prior to the spectrophotometric determination of uranium by the thiocyanate method.

#### 1.4.3 Direct Titration with EDTA (J. S. Fritz)

Uranium (VI) can be determined by direct titration with EDTA in 60 per cent acetone. The end point of the titration is determined potentiometrically using mercury indicator electrode or visually using pyridylazonaphthol (PAN) indicator. This is unique among EDTA titration methods in that a 2 to 1 uranyl--EDTA complex is formed. Thorium interferes with the method; zinc is titrated quantitatively with the uranium. The effect of other metal ions will be investigated.

#### 1.5 Thorium (J. S. Fritz)

Work is proceeding successfully on a photometric titration of thorium with EDTA using copper(II) as the indicator. This method is highly selective for thorium, although zirconium and a few other metals that form very stable EDTA complexes interfere. Accurate results for thorium have been obtained in the presence of up to 60 to 1 mole ratio of uranium, aluminum, praseodymium, samarium and calcium. Other potential interferences will be studied.

### 1.6 Scandium (J. S. Fritz)

A paper (ISC-1034),<sup>†</sup> "Photometric Titration of Scandium" by James S. Fritz and Donald J. Pietrzyk, was submitted for publication in ANAL. CHEM.

Abstract--A scandium solution containing copper(II) can be titrated photometrically in acid solution with EDTA, (ethylene-dinitrilo) tetraacetic acid. The absorbance of copper(II)-EDTA at 745 m $\mu$  is used to follow the course of the titration. By this method scandium can be successfully titrated in the presence of up to 60 times as much rare earth (on a molar basis). Large amounts of aluminum(III) calcium(II), magnesium(II) and uranium(VI) and significant amounts of iron(II) and other metal ions do not interfere. Bismuth(III), hafnium(IV), zirconium(IV), fluoride and sulfate are the most important interferences. The sum of scandium(III) and thorium(IV) can be determined by this method.

### 1.7 Alcohols and Phenols (J. S. Fritz)

We have found that the standard method of determining alcohols and phenols by quantitative acetylation is much faster and more convenient if the acetylation is catalyzed by an acid. Of several acids tested, perchloric was found to be the most efficient. Acid catalyzed acetylation proceeds at a faster rate in ethyl acetate than in other solvents tested.

Acids also catalyze acetylation in pyridine solvent, and this medium may be useful in determining unhindered alcohols and phenols in the presence of compounds that are not sterically hindered. Quantitative results have been obtained for a number of primary and secondary alcohols.

### 1.8 Aliphatic Thiols (J. S. Fritz)

Aliphatic thiols have been determined by titration in acetone with a standard solution of mercury(II). The end point is detected potentiometrically with a mercury indicator electrode or visually with Thiomichler's ketone indicator. Advantages of this method are that precipitation is avoided and that a good visual indicator is available.

### 1.9 Ion Exchange Separations (J. S. Fritz)

#### 1.9.1 Chromatographic Separations Based on Ion Charge

A paper (ISC-1066), "Ion Exchange Separations. I. Chromatographic Separations Based on Ion Charge" by James S. Fritz and Shirley K. Karraker, has been accepted for publication in ANAL. CHEM.

Abstract--The greater affinity of a cation exchange resin for a trivalent than for a divalent metal ion is used as the basis of a rapid chromatographic separation. A solution of ethylenediammonium chloride serves as the eluting agent. Conditions are worked out for separation of zinc and lanthanum, and the effect of variables is

studied. This type of separation should be applicable to a wide variety of analytical problems.

Batchwise distribution coefficients have been determined for uranyl, cupric, lanthanum and thorium ions as a function of ethylenediammonium concentration and starting metal ion concentration. This information should be valuable in many types of ion exchange work. It will also be helpful in predicting proper elution conditions for practical analytical separations.

#### 1.9.2 Behavior of Metal Ions in Aqueous-Organic Mixtures

We have started work on a project to determine the anionexchange behavior of metal ions in aqueous hydrochloric acid--alcohol solvent mixtures. Preliminary experiments show that most metals are taken up by the resin at significantly lower acid concentrations in 80 per cent isopropyl alcohol than in water. Distribution coefficients of copper(II) have been determined as a function of solvent composition and of hydrochloric acid concentration.

## 2. Service Analyses

A total of 5101 service analyses was made during the period of this report.

## Spectrochemistry

### 1. Spectroscopic Research (V. A. Fassel)

#### 1.1 Emission Spectroscopic Methods of Analysis

##### 1.1.1 Determination of Rare Earth Impurities Commonly

##### Associated with Purified Samarium, Gadolinium, Terbium and Europium

The specific determinations covered by these calibrations are:

neodymium and gadolinium in samarium; neodymium, samarium, terbium, europium, yttrium, and dysprosium in terbium; and samarium, gadolinium, and ytterbium in europium. These procedures provide quantitative determinations in the concentration range from the detection limit up to 1 weight per cent. Direct current arc excitation of rare-earth oxide-graphite mixtures is employed. The coefficient of variation is less than  $\pm 5$  per cent of the amount present for all determinations.

##### 1.1.2 Determination of Rare-Earth Impurities in Th, Y, Lu and Sc

A paper (ISC-1035), "Quantitative Spectrographic Analysis of the Rare-Earth Elements. X. Determination of Rare-Earth Impurities Commonly Associated with Purified Thulium, Ytterbium, Lutetium and Scandium" by Richard N. Kniseley, Velmer A. Fassel, Raymond W. Tabeling, B. George Hurd and Beverly B. Quinney, was submitted for publication in SPECTROCHIM. ACTA.

Abstract--Emission spectrometric methods are described for the following quantitative determinations: yttrium, holmium, erbium, ytterbium and lutetium in thulium; samarium, yttrium, erbium, thulium, lutetium and scandium in ytterbium; yttrium, thulium, ytterbium and lutetium in scandium. The basic method involves the direct-current carbon arc excitation of rare-earth oxide - graphite mixtures, utilizing the unique similarity in excitation behavior of many of the rare earths to provide a high degree of internal standardization. In all cases the per cent deviation from the mean is less than + 5 per cent.

### 1.1.3 Determination of Gadolinium in Yttrium Matrices at High Sensitivity

The most sensitive emission lines of gadolinium (3646.196A and 3422.466A) can be detected down to about 200 ppm under conventional d.c. carbon arc excitation conditions. This sensitivity is far above the 0.1 to 1 ppm sensitivities required for evaluating the purity of reactor grade yttrium metal. Since the sensitive lines occur in the CN band region, the exclusion of nitrogen from the arc column reduces the background radiation to the degree that 10 ppm gadolinium can be detected by just sweeping the analytical gap with CO<sub>2</sub>. A further

reduction in detection sensitivity down to 1 ppm can be achieved by arcing the samples in a chamber containing a supporting atmosphere, blended from He at 10 lbs. pressure and oxygen at 2 to 4 lbs. pressure. In order to attain sensitivities in the 0.01 to 1.0 ppm ranges, a preliminary chemical concentration of the gadolinium with respect to the yttrium is necessary. A concentration factor of 20 is readily obtained by 3 extractions with the tributylphosphate-nitric acid system.

#### 1. 1. 4 Determination of Common Impurities in Yttrium Metal

Five per cent solutions of the sample in HCl are excited directly by the rotating graphite disk technique. The spectra are excited with high voltage AC spark discharges. Pertinent analytical data are summarized in Table V.

### 1. 2 Oxygen Content of Metals and Metal Fluorides (V. A. Fassel)

#### 1. 2. 1 Oxygen in Vanadium Metal

The emission spectrometric technique has been extended to the determination of oxygen in vanadium in the concentration range 0.006 to 0.5 per cent. The oxygen content of the vanadium is liberated as CO into an argon atmosphere by the high temperatures attained in d-c arc discharges between a graphite counter electrode and the sample supported in a graphite electrode. The rate and degree of oxygen evolution from the sample is critically dependent on the geometry of the supporting electrode.

Table V.

Analytical Data for the Determination of Common  
Impurities in Yttrium Metal and Sponge

Line Pair (Å)	Useful Conc. Range (ppm)	Estimated Det. Limit (ppm)	Conc. Index (ppm)	Remarks
<u>Ca 3933.67</u> Y 3945.9	10-200	5	55	Fe 3933.605 A interferes at Fe conc. > 0.3%
<u>Ca 3933.67</u> Y 3931.5	100-1000	5	610	
<u>Ni 3524.54</u> Y 3521.53	200-1500	100	1000	Zr 3524.538 A does not interfere at Zr conc. < 10%
<u>Mg 2852.13</u> Y 2850.05	30-1000	10	80	Fe 1852.13 A does not interfere at Fe conc. < 0.2%
<u>Zr 3020.47</u> Y 3018.5	1000-20,000	300	6600	Fe 3020.489 A interferes at Fe conc. > 0.1%
<u>Zr 3019.84</u> Y 3018.5	2500-20,000	1000	4000	
<u>Si 2881.58</u> Y 2882.3	125-250	100	350	
<u>Cu 3273.96</u> Y 3252.29	10-500	5	190	
<u>B 2497.73</u> Y 2492.66	10-500	10	40	
<u>B 2496.78</u> Y 2492.66	20-500	20	70	

### 1.2.2 Oxygen in Yttrium Fluoride

A new approach to the quantitative determination of the oxygen content of metal fluorides has yielded promising results when applied to  $YF_3$  samples. When  $YF_3$  is distilled in vacuo from a carbon crucible and condensed in the cooler part of a specially designed crucible, appreciable quantities of carbon monoxide are liberated. This suggests that the  $Y_2O_3$  and/or YOF impurity in the  $YF_3$  matrix tends to be retained in the crucible, where the reducing action of carbon causes decomposition of the oxygen containing compounds. The liberated CO is transferred to a gas analysis apparatus for quantitative measurements. The degree of evolution of the oxygen content (as CO) is enhanced by the presence of platinum metal in the crucible, even though the molten platinum is immiscible with the fluoride. In the presence of platinum, quantitative recovery of the oxygen was obtained when  $Y_2O_3$  or YOF were added to  $YF_3$  matrices in amounts corresponding to 0.3 to 0.6 per cent oxygen. The function of the platinum has not been established, although it has been shown that a gas burst which occurs at  $1800^\circ C$  - the melting point of platinum - accounts for the evolution of approximately 80 to 85 per cent of the total gases evolved. In the absence of platinum, the gas burst is not observed. Instead, continuous evolution occurs over a much longer

period of time, and only about 50 per cent of the total oxygen content is recovered. The oxygen content of the purest  $YF_3$  prepared in the Ames Laboratory was found to be in the 150-300 ppm range.

## 2. Spectroscopic Service Analyses (V. A. Fassel)

During the period covered by this report, 5663 samples were analyzed or examined by optical emission, X-ray fluorescent, and infrared absorption spectrometric techniques, and by vacuum-fusion manometric method.

## Radiochemistry

### 1. Extraction of Inorganic Species (A. F. Voigt)

The extraction of cadmium iodide into iso-amyl alcohol is being used to study the formation constants for the various cadmium-iodide complexes. This extraction increases with increasing iodide concentration up to a point and then quite sharply decreases. This indicates that a species, which is considered to be  $CdI_2$ , extracts and that higher species, such as  $CdI_3^-$ , do not. The shape of the curve of extraction coefficient vs. iodide concentration can be used to determine the formation constants of the various species. The dependence of the extraction on hydrogen ion concentration and other variables is now being studied.

## 2. Activation Analysis

### 2.1 For N and C in Metals (A. F. Voigt)

The use of the synchrotron to produce 10-minute  $N^{13}$  from  $N^{14}$  and 20-minute  $C^{11}$  from  $C^{12}$  by ( $\gamma, n$ ) reactions is being applied to the analysis of metals for nitrogen and carbon. The metal vanadium appears to be one for which such a method would be of value. Thus far nitrogen has been found to be detectable down to lower limits than carbon, but both can be observed in the range of 100 ppm. Establishment of the sensitivity and accuracy of the method is proceeding.

### 2.2 For Iridium in Platinum (D. S. Martin)

Additional neutron activation analyses for iridium in a sample of very pure platinum have been performed. The method has a very high sensitivity. However, the reproducibility of the method for samples of the same batch of platinum has been disappointing. It will be necessary to monitor each step in the radiochemical analysis to determine that  $Ir^{192}$  activity is not lost. The dependence of the assay upon the energy spectrum of the neutrons also suggests that possibly the flux spectrum has not been satisfactorily thermal in some of the irradiations. The possibility of self absorption of resonance neutrons in the standard must also be investigated.

## 3. Radiation and Hot-Atom Chemistry (A. F. Voigt)

Research in this area is proceeding in two related directions, the hot-atom behavior of  $C^{11}$  as produced in organic compounds by the

synchrotron induced reaction  $C^{12}(\gamma, n)C^{11}$ , and the behavior of  $C^{14}$  in labelled compounds during  $Co^{60}$  gamma irradiation. In both cases, separation of products is made by gas chromatography using counting chambers to detect the radioactive products.

The irradiation of  $C^{14}$ -labelled hydrocarbons by  $Co^{60}$  gamma rays is done using a 1500 curie cobalt source with the target compound in the gas phase. In the irradiation of ethane, observed products have included compounds with one, three and four carbons. The specific compounds are being identified. Work with higher hydrocarbons and at various temperatures is planned.

#### 4. Photonuclear Reactions (D. S. Martin)

A paper (ISC-1044), "Photonuclear Reactions of Gallium and Arsenic with 70 Mev Bremsstrahlung" by F. D. Schupp, C. B. Colvin and D. S. Martin, Jr., was submitted for publication in PHYS. REV.

Abstract--Radiochemical techniques were utilized in the measurement of yields of photonuclear reactions induced by 70 Mev bremsstrahlung in gallium and arsenic targets. For As targets the yields of  $As^{74}$ ,  $Ga^{73}$ ,  $Ga^{72}$ ,  $Ga^{68}$ ,  $Zn^{69}$ , and  $Zn^{69m}$  were determined. In the gallium targets the yields of  $Zn^{69}$ ,  $Zn^{69m}$ ,  $Ni^{65}$ , and  $Co^{61}$  were measured. The integrated cross sections for

the indicated photonuclear reactions were estimated from the yields. The integrated cross sections of five ( $\gamma$ , 3p3n) processes were compared. The relative yields of the  $Zn^{69}$  isomeric pair depended upon the process of formation.

#### 5. Isotopic Exchange Reactions (D. S. Martin)

Procedures for the synthesis of  $cis-\overline{Pt}(NH_3)_2Cl_2\overline{}$  have been improved, and the ultraviolet absorption spectrum of the preparations has served as a very sensitive criterion of their purity. Several experiments to evaluate exchange between chloride ions and the chloride ligands have been carried out. It has been found that when  $Ag^+$  is added to precipitate chloride, a separation-induced exchange has occurred. Consequently, an alternative separation has been sought. The use of an anion exchange column to remove chloride and anion complexes has given satisfactory results. The effluent contains neutral and cationic complexes, and the chloride ligands from these species have been removed with no separation induced exchange. The use of a cation exchange column, following the anion exchanger, is being tested for the possible separation of cationic from neutral species. Several exchange experiments have been carried out in the system, but not enough results are at hand to characterize the exchange.

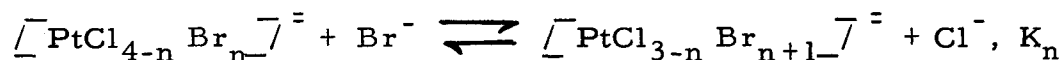
Procedures for the synthesis of  $\text{trans-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]^-$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$  have been investigated so that isotopic exchange reactions may be undertaken with these compounds also.

Preliminary experiments with the compound  $\text{K} [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$  have been performed. The anion apparently is stable only in solutions of high acidity so the use of a sulfuric acid-bisulfate buffer has been utilized. The ultraviolet absorption spectrum has been followed over a period of time. However, changes in the spectrum have not been sufficient to characterize a slow acid hydrolysis which might be expected to occur.

The isotopic exchange of  $\text{Pt}^{195}$  between the complexes  $[\text{Pt}(\text{en})_2]^{++}$  and  $\text{trans-}[\text{Pt}(\text{en})_2\text{Cl}_2]^{++}$  (where en = ethylenediamine) has been observed. The separation of the complexes was effected by the precipitation of the tetraphenylboron salt of the  $\text{Pt}^{\text{II}}$  complex. However, at least one reprecipitation has been necessary to give a satisfactory radiochemical purity. There appear to have been no separation induced exchange and the correlation of this platinum exchange with the isotopic exchange between chloride and the ligands of the  $\text{Pt}^{\text{IV}}$  complex has been indicated by the present incomplete data.

6. Inorganic Chemical Equilibria and Kinetics (D. S. Martin)

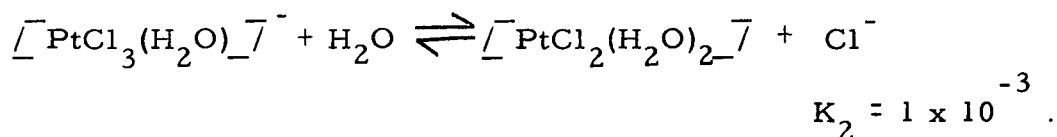
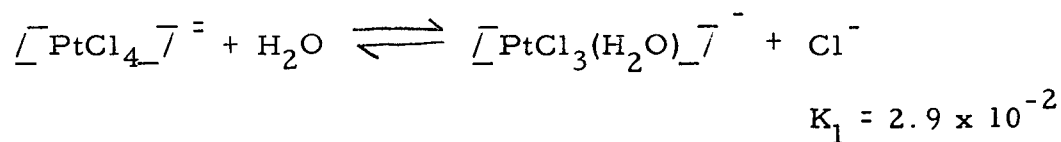
The program has been improved for the computation of the four equilibrium constants for the successive replacement of chloride ligands in  $[\text{PtCl}_4]^{2-}$  by bromide, i. e.



where  $n = 0, 1, 2, 3$ . The computation has been based upon radiochemical data; the replacement of  $\text{Cl}^{36}$  from the complexes as  $\text{Br}^-$  was added to the system. The results have indicated that the  $\Delta H^\circ$  for the indicated successive reactions are the same, within an uncertainty of 0.3 kcal. However, the successive equilibrium constants do decrease because of a statistical factor. It has been concluded from the results that any  $\pi$ -bonding contribution to the stability of bromide ligand-platinum bond is rather small. The results indicate that Grinberg and Nikolskaya (Zhur. Priklad. Khim 24, 893 (1951)) have made a much better estimate of  $\Sigma \Delta F^\circ$  than has Latimer ("Oxidation Potentials" 2nd Edition, p. 206).

Dilute solutions of  $[\text{PtCl}_4]^{2-}$  have been allowed to age and the resulting acid content of the solutions has been determined after steady states have been obtained. From the results it appears that, in addition to the previously known first acid-hydrolysis, a measurable reversible

second acid-hydrolysis occurs also. Equilibrium constants (in terms of molar activities) for the system are:



This indicated value of  $K_2$  is surprisingly large.

#### 7. Diffusion in the Solid States (D. S. Martin)

Attention has been given to the deposition of very thin layers of AgCl bearing either  $\text{Ag}^{109}$  or  $\text{Cl}^{36}$  on the surface of simple crystals of AgCl. The absorption curves of the deposits by AgCl absorbers have been measured, and they serve as a rather good criteria for the thickness of the deposits. Crystals bearing such deposits have been heated in the temperature range of  $150^\circ$  up to about  $400^\circ\text{C}$ .

The decrease of the counting rate from the surface of the deposit is a measure of the diffusion into the crystal which has occurred. Significant decreases in the counting rates have been observed. It remains to be tested whether the method will yield diffusion coefficients which agree with the conventional slicing techniques.

#### 8. Decay of $\text{Sb}^{127}$ (A. F. Voigt)

The decay of the 90-hour activity assigned to  $\text{Sb}^{127}$  is of interest

because it seems to be more complex than it had been previously considered to be. Some of the gamma transitions appear to have half-lives different from others and considerably longer than the 90-hours observed for the beta radiation. This isotope is a fission product, but it can also be produced from  $\text{Te}^{128}$  by the  $(\gamma, p)$  reaction. We have now observed the same decay characteristics in synchrotron-produced antimony that had been reported in the fission product material. However, in both of these production methods, the product may contain more than one isotope, since other tellurium isotopes may undergo the  $(\gamma, p)$  reaction, and in fission all antimony isotopes between masses 125 and 134 could be present.

The irradiation of a separated isotope greatly reduces the number of possible antimony isotopes that could be produced. Highly enriched  $\text{Te}^{128}$  has been obtained from Oak Ridge for this study and chemical methods have been worked out for the separation of  $\text{Sb}^{127}$  from the irradiated tellurium. In this way it can be determined whether the complex decay is due to a single isotope of antimony in several isomeric states or to a mixture of several isotopes.

#### 9. Exchange Reactions (A. F. Voigt)

A report (ISC-1096), "Exchange and Chemical Reactions of Cyclopentadienyl Cobalt Compounds" by Seymour Katz and A. F. Voigt, is being distributed.

Abstract--Chemical and exchange properties of the compounds bis-cyclopentadienyl cobalt II, or cobalticene, and the salts of bis-cyclopentadienyl cobalt III, or cobalticinium, ions have been studied. These interesting complexes are known as sandwich structures since the two cyclopentadienyl rings are in parallel planes with the cobalt between them. Cobalticinium perchlorate and cobaltous ions in aqueous solutions were found not to exchange, indicating great stability of the bonds between cobalt and the cyclopentadienyl rings. Electron exchange between the cobalticene and cobalticinium ion was found to be very rapid. The study was complicated by the rapid oxidation of cobalticene by traces of oxygen in the system. The oxidation product underwent a slow exchange reaction with the other forms of cobalt present in the system. The nature of the oxidation product was studied, and it is believed to be an oxide in some form.

A product of reaction between cobalticene and carbon tetrachloride was studied in some detail. The formula of the compound was found to be  $(C_2H_5)_2CoCCl_3$ , but there is some uncertainty regarding its structure and bonding. Elucidation of the structure will provide a better understanding of the nature of these very interesting complexes.

A paper (ISC-1072), "Reaction of Bis-Cyclopentadienylcobalt(II) with Organic Halides" by Seymour Katz, James F. Weiher and Adolf F. Voigt, was published in J. AM. CHEM. SOC.

Abstract--The exchange reactions between the compounds of cyclopentadiene and cobalt in its different valence states are being studied. These complexes, examples of an interesting type of chemical bonding known as  $\pi$ -bonding, are structurally considered to be sandwich-like, with the metal atom between two parallel planar organic groups.

As a part of this study the oxidation products of bis- $\pi$  cyclopentadienyl cobalt (II),  $(C_5H_5)_2Co(II)$ , in various media have been investigated. A new type of reaction and compound was observed when this compound reacted with carbon tetrachloride. Two products result from this reaction, a well-known ionic complex involving Co(III),  $[\bar{C}_5H_5)_2Co\bar{]}^+$ , and an addition product with the formula,  $(C_5H_5)_2CoCCl_3$ . Examination of the latter indicates that the two cyclopentadienyl rings are probably not both  $\pi$ -bonded, but one is attached to the cobalt in the more usual or  $\sigma$ -bonded manner. However, on slow hydrolysis, the new compound reacts to produce the other product of the reaction in which this compound was found, that is, the  $[\bar{C}_5H_5)_2Co\bar{]}^+$  ion. In the latter both

cyclopentadienyl rings are  $\pi$ -bonded. This reversible alternation from  $\pi$  to  $\sigma$ -bonding has not been observed previously.

### X-Ray Chemistry

#### 1. Hydrogen Bonding (D. R. Fitzwater)

The structure of MM'-dibromobenzoyl methane was recalculated using rejudged intensities with the results being significantly improved parameters for the structure. The new o-o distance is 2.45 $\overset{\circ}{\text{A}}$  but with a standard deviation of 0.03 $\overset{\circ}{\text{A}}$ . In view of the difficulties of obtaining more accurate results using the bromo compound, the chloro compound was prepared and a structural study initiated.

A report (ISC-1074), "Crystal Structure and Magnetic Properties of  $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ " by Peter H. Vossos and R. E. Rundle, is being distributed.

Abstract--Interest in the study of the effect of cation size upon the configuration assumed by a complex anion led to the determination of the crystal structure of  $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ . A unique  $(\text{Cu}_2\text{Cl}_6)^-$  dimer ion was discovered in the structure that was determined by conventional X-ray diffraction techniques. These dimer ions are linked together into a zigzag chain by means of long Cu-Cl bonds between the dimers. The chains in any given unit cell of the crystal are related to each

other by a two-fold screw axis. Each dimer has two water molecules associated with it through long Cu-O interactions, giving a distorted octahedral array about each copper ion. There are two additional water molecules per dimer ion which are "lattice waters" and which, along with one of the other oxygens and a chlorine ion, form a tetrahedral hole in which the lithium ion is probably located.

Magnetic susceptibility measurements were taken on  $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$  down to temperatures approaching  $1^\circ\text{K}$ . The paramagnetic susceptibility increased as the temperature was lowered and at  $5.9^\circ\text{K}$  the substance became antiferromagnetic. It was found, from the slope of  $1/\chi_M$  versus temperature, that the spins of the magnetic electrons of the copper ions were coupled in parallel fashion (a triplet state) in each dimer. It is suspected that the antiferromagnetism arises from the fact that the net dimer spin directions alternate in regular manner throughout a given chain.

## 2. Nickel and Palladium Dimethylglyoximes (R. E. Rundle)

A paper (ISC-1104), "Crystal Structures of Nickel and Palladium Dimethylglyoximes" by Donald E. Williams, Gabriele Wohlauser and R. E. Rundle, was submitted to J. AM. CHEM. SOC.

Abstract--Palladium and nickel dimethylglyoximes (PdDMG and NiDMG) crystallize in the same space group and are of the same structure type. The PdDMG structure, however, has a much longer hydrogen bonded O-O distance and unequal Pd-N distances, in contrast to the very short hydrogen bonded O-O distance and equal Ni-N distances in the NiDMG structure. These observations are consistent with an unsymmetrical hydrogen bonded structure for PdDMG and a symmetrical hydrogen bonded structure for NiDMG.

## APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-867 Riley Schaeffer and Hampton Smith. Isotopic Equilibria of Nitrosyl Chloride.
- ISC-907 R. D. Redin. Thermomagnetic and Galvanomagnetic Effects.
- ISC-941 Robert E. Eberts and F. H. Spedding. Relative Apparent Molal Heat Contents of Some Rare-Earth Chlorides and Nitrates in Aqueous Solutions.
- ISC-943 Marlowe Iverson and F. R. Duke. Complex Metal Halides in Fused Alkali Nitrates.
- ISC-944 Richard Fleming and F. R. Duke. Transport Numbers and Ion Mobilities in the Fused Salt KCl-PbCl<sub>2</sub>.
- ISC-945 William J. Lane and J. S. Fritz. Metal-Indicator Systems in (Ethylenedinitrilo)tetraacetic Acid Titrations.
- ISC-946 Wilfred G. Borduin and G. S. Hammond. Substituent Effects of the Stability of Metal Chelates.
- ISC-947 John J. Barghusen and M. Smutz. Processing of Monazite Sands.
- ISC-975 Ames Laboratory Staff. Physics. Semi-Annual Summary Research Report. July-December, 1957.
- ISC-976 Ames Laboratory Staff. Chemistry. Semi-Annual Summary Research Report. July-December, 1957.
- ISC-977 Ames Laboratory Staff. Metallurgy. Semi-Annual Summary Research Report. July-December, 1957.
- ISC-978 Ames Laboratory Staff. Engineering. Semi-Annual Summary Research Report. July-December, 1957.
- ISC-979 P. Chiotti. Metallurgical Development for Hanford Program. Semi-Annual Report. July-December, 1957.
- ISC-1030 R. G. Barnes. Bibliography of Titles of Articles in the Field of Nuclear Quadrupole Resonance Spectroscopy of Solids.
- ISC-1037 Benny A. Loomis and O. N. Carlson. Brittle-Ductile Transition in Vanadium.

- ISC-1045 Wilfred G. Borduin and G. S. Hammond. Further Relationships in the Grunwald Treatment of Acid-Base Equilibria in Hydroxylic Solutions.
- ISC-1047 R. M. Stanton, P. F. Woerner, C. L. Vold, J. A. Kingston, and J. F. Smith. Tabulation, Bibliography, and Structure of Binary Intermetallic Compounds. IV. Compounds of Zinc, Cadmium and Mercury.
- ISC-1048 Ames Laboratory Staff. Physics. Semi-Annual Summary Research Report. January-June, 1958.
- ISC-1051 Ames Laboratory Staff. Engineering. Semi-Annual Summary Research Report. January-June, 1959.
- ISC-1056 Richard T. Oliver and James S. Fritz. Ion-Exchange Separation of Metals by a Single Pass Method.
- ISC-1059 Robert L. Skaggs and D. T. Peterson. Entrainment of Non-Volatile Solids in Sublimation at Reduced Pressure.
- ISC-1074 Peter H. Vossos and R. E. Rundle. Crystal Structure and Magnetic Properties of  $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ .

## 2. Publications

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Electron Deficient Compounds. VIII. The Crystal and  
Molecular Structure of Trimethylindium. *J. Am. Chem. Soc.*  
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## APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	6 thulium pellets
	20 gm thulium metal
	100 gm thulium oxide
	20 gm lutetium metal
	100 gm lutetium oxide
State University of Iowa Iowa City, Iowa	10 gm lanthanum metal
	10 gm cerium metal
	10 gm praseodymium metal
	10 gm neodymium metal
	10 gm samarium metal
	10 gm gadolinium metal
	50 gm lanthanum oxide
	50 gm cerium oxide
	50 gm praseodymium oxide
	50 gm neodymium oxide
	50 gm samarium oxide
	50 gm gadolinium oxide
	50 gm ytterbium oxide
	20 gm terbium oxide
10 gm thulium oxide	
10 gm lutetium oxide	
U. S. Bureau of Mines Albany, Oregon	150 gm dysprosium metal
Ohio State University Columbus, Ohio	100 mg erbium oxide
	100 mg cerium oxide
	100 mg praseodymium oxide
	100 mg neodymium oxide
	100 mg samarium oxide
	100 mg europium oxide
	100 mg gadolinium oxide
	100 mg terbium oxide
	100 mg dysprosium oxide
	100 mg holmium oxide
	100 mg erbium oxide
	100 mg thulium oxide
	100 mg ytterbium oxide
100 mg lutetium oxide	
Midwest Microlab, Inc. Indianapolis, Indiana	1 pkg. organo metallic compound
Brown University Providence, Rhode Island	1 lanthanum cylinder

Dr. Joseph Graca  
Iowa State College  
Ames, Iowa

5-200 mg pellets each of  
yttrium metal  
lanthanum metal  
cerium metal  
neodymium metal  
gadolinium metal  
ytterbium metal  
dysprosium metal

150 pellets, 100 mg each of  
yttrium metal  
cerium metal  
neodymium metal  
gadolinium metal  
dysprosium metal  
ytterbium metal

Duke University  
Durham, North Carolina

cylinders of neodymium  
metal as follows:  
6 1" x 2" diam.  
6 1/2" x 2" diam.  
6 1/4" x 2" diam.  
6 1/8" x 2" diam.

Battelle Memorial Institute  
Columbus, Ohio

50 gm dysprosium metal

Carnegie Institute of Technology  
Pittsburgh, Pennsylvania

5 gm lanthanum metal

General Electric Research Laboratory  
Schenectady, New York

200 gm yttrium metal

University of Arizona  
Tucson, Arizona

20 gm neodymium oxide

Syracuse University  
Syracuse, New York

491 gm calcium