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For January - June, 1957

Ames Laboratory Staff

September 11, 1957

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
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U N C L A S S I F I E D

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Semi-Annual Summary Research Report in Chemistry

For the period January - June, 1957

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

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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, G. Hammond, R. S. Hansen, L. D. Jennings,
D. S. Martin, J. E. Powell, K. Ruedenberg, R. E. Rundle,
R. Schaeffer, H. J. Svec and A. F. Voigt.

Physical and Inorganic Chemistry

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

1.1 Production of Heavy Rare Earths on Pilot Plant Scale

N-Hydroxyethylethylenediaminetriacetic acid has proved to be very useful in obtaining good separations of Lu and Yb by ion-exchange elution. When a heavy-rare-earth mixture has been eluted far enough with HEDTA to resolve the Lu and Yb, it has been found that good separations are also obtained between Yb and Tm, Tm and Er, and Er and Ho. The resolution of Ho and Dy is poor with this reagent. Final resolution of Ho and Dy mixtures is obtained using EDTA. Noteworthy quantities of various rare earths have been obtained using EDTA for the preliminary concentration of the heavy rare earths as a group and HEDTA for the isolation of Lu, Yb, Tm and Er.

1.2 Separation of Scandium from the Rare Earths

Considerable progress has been made in the use of a partitioning ion in the separation of scandium from the rare earths. Elution of scandium and rare earths with EDTA down a cupric-state resin bed results in the retention of the rare earths while scandium passes through the cupric bed. When HEDTA is used as the eluant and lead as the retaining ion, similar results are obtained.

*Names indicate group leaders in charge of work.

1.3 Separation of Adjacent Rare Earths

A paper entitled "Basic Principles Involved in the Macro-Separation of Adjacent Rare Earths from Each Other by Means of Ion Exchange" by J. E. Powell and F. H. Spedding will be published in Transactions of the Baltimore Meeting of A.I.Ch.E., September, 1957.

Abstract

The separation of rare-earth mixtures by ion exchange using ammonium ethylenediaminetetraacetate and ammonium N-hydroxyethyl-ethylenediaminetriacetate as eluting agents has been discussed in detail. Simple counter-current separation theory has been used to predict the minimum number of displacements of an adsorbed band that are necessary in order to separate the components of binary mixtures. It has been shown how the theory can be applied to even more complex systems and experimental data have been presented for some of the more difficultly separable groups of rare-earth species. Experimental results agree very well with the theoretical predictions.

2. Extraction of Thorium from Ytterbium (F. H. Spedding and J. E. Powell)

Most of the ytterbium produced by elution with EDTA or HEDTA contains traces of thorium if the source material contains thorium. The method of Levine and Grimaldi¹ for the extraction of thorium

¹ H. Levine and F. S. Grimaldi, U. S. Atomic Energy Commission Report No. AECD - 3186 (1950).

nitrate with mesityl oxide has been adapted to the removal of thorium from ytterbium. Instead of making use of aluminum nitrate as a salting out agent for the thorium, ytterbium nitrate has been used. By utilizing solutions which are nearly saturated with ytterbium nitrate, about 110 pounds of thorium-free Yb_2O_3 have been prepared. Of course, some ytterbium extracts into the organic phase along with the thorium, but this material can be readily recovered and processed further.

3. Properties of Rare Earth Salts (F. H. Spedding)

A paper by F. H. Spedding and Gordon Atkinson entitled "Properties of Rare Earth Salts in Electrolytic Solutions" was presented at the meeting of the Electrochemical Society, Washington, D. C., May, 1957, and is to be included in "The Structure of Solutions," to be published by John Wiley and Sons.

Abstract

The rare earths are an ideal set of elements with which to critically examine any theory of electrolytic solutions. They differ among themselves only by a slight change in ionic radii as the atomic number decreases. In addition they hydrolyze only slightly in dilute aqueous solution and complex very weakly with many common anions. This paper reviews the extensive work done in the Ames Laboratory on the conductances, transference numbers, activity coefficients, heats of solution and dilution, and partial molal volumes and compressibilities of aqueous rare earth solutions. These studies are discussed with respect to present solution theory and other regularities.

4. Preparation of Carbonate-Free Bases (F. H. Spedding and J. E. Powell)

A Communication to the Editor entitled "Preparation of Carbonate-Free Bases" by J. E. Powell and Maynard A. Hiller was published, J. CHEM. EDUC. 34, 330 (1957), and is reproduced here in its entirety.

Preparation of Carbonate-Free Bases

Various methods are known for producing carbonate-free base to be used in titrations. For example, Na_2CO_3 is relatively insoluble in saturated NaOH solutions so it can be filtered off readily. K_2CO_3 , however, is more soluble in KOH and removal of CO_3^{--} by this method is not feasible. A method involving the use of anion-exchange resins has been proposed¹ for the preparation of carbonate-free KOH . However, the exchange constant between Cl^- and OH^- is not very favorable and several liters of KOH must be passed through the anion bed before all Cl^- is gone from the eluate. We wish to propose a new method for producing carbonate-free as well as chloride-free KOH . The concentrated KOH is treated with a sufficient amount of $\text{Ba}(\text{OH})_2$ to precipitate all of the CO_3^{--} . The solution is then filtered, protected from the air by ascarite, diluted with freshly boiled water, and passed through a strong acid cation-exchange bed in the K^+ cycle. Such resins are Dowex-50 or Amberlite IR-120. Ba^{++} is preferentially adsorbed and the effluent KOH is caught in a protected flask from which the air has been displaced by He . Analysis of KOH produced in this way showed no CO_3^{--} as well as no Cl^- . The method is also applicable to the preparation of carbonate-free NaOH , NH_4OH , etc.

¹ C. W. Davies and G. H. Nancollas, Nature, 165, 238 (1950).

5. Preparation of Rare Earth Metals (F. H. Spedding and A. H. Daane)

5.1 Semi-Continuous Reduction

Operation of the furnace for semi-continuous large-scale preparation of rare earth metals resulted in the preparation of a considerable quantity of metal. Essential details of the operation are as follows.

A mixture of calcium metal and rare earth fluoride is heated in a tantalum crucible in an argon atmosphere. The molten reactants are tapped into a water-cooled copper mold and another charge of reactants is added to the furnace to provide a semi-continuous batch process. Ten to twenty pounds of metal per batch (depending on the rare earth being prepared) is the present capacity of the furnace although it is planned to double the capacity as soon as a larger mold can be used. The metal produced represents a yield of 92 to 95%, and it contains 2000 to 5000 ppm calcium and 1000 to 5000 ppm tantalum as the chief impurities. The ingots obtained from this reduction process have been vacuum arc-melted and vacuum induction-melted to reduce the calcium content of the metal.

5.2 Lithium as a Reductant

In reducing the rare earth fluorides with calcium, it is necessary to heat the reactants to a temperature above the melting point of the calcium fluoride slag ($\sim 1400^{\circ}\text{C}$). This temperature is considerably above the melting points of some of the rare earth metals, and much lower temperatures could be used if a lower melting slag were available. Lithium fluoride forms a eutectic with calcium

fluoride at about 80 mole % LiF, melting at 770°C.¹ As lithium is a satisfactory reductant for the rare earth fluorides, a calcium-lithium alloy should also serve this purpose very well, and would have the advantage of giving a low melting slag.

A reduction of lanthanum fluoride by a 2:1 ratio of lithium to calcium was carried out very satisfactorily, yield and purity of the product metal being comparable to that prepared by the conventional calcium reduction process.

6. Properties of Rare Earth Metals (F. H. Spedding and A. H. Daane)

6.1 Europium

The previous progress report (ISC-834) described the preparation and some of the properties of europium metal. Additional physical properties of this metal have been determined, including the vapor pressure, resistivity, compressibility, thermal expansion and corrosion properties.

6.2 Metallography of Yttrium

In examining yttrium metal for impurities, it has been found that a 3/4% solution of nitric acid in absolute alcohol serves as the best metallographic etchant. This solution does not appear to serve equally well as an etchant for the rare earth metals.

6.3 Vapor Pressure of Thulium

A paper entitled "The Vapor Pressure of Thulium Metal" by F. H. Spedding, R. J. Barton and A. H. Daane was accepted for publication in J. AM. CHEM. SOC.

¹ W. E. Roake, U. S. Atomic Energy Commission Report No. HW - 35808 (1955).

Abstract

The vapor pressure of thulium has been measured by two modifications of the Knudsen effusion method, covering the temperature region from 809°K. to 1219°K. The results may be expressed by the equation

$$\text{Log } P_{\text{mm}} = \frac{-1.2552 + 0.0045 \times 10^4}{T} + 9.1761 \pm 0.0457.$$

This represents a heat of sublimation of -57.44 ± 0.20 Kcal. for this temperature region, which is somewhat lower than would be expected for a normal trivalent rare earth element, but appears reasonable for thulium in which the binding may perhaps be weaker due to the nearly filled 4f shell in this metal.

6.4 High Temperature Specific Heat Studies

Calibration of the Bunsen high temperature calorimeter has been completed with the determination of the heat content of synthetic sapphire (α - Al_2O_3) from 100 to 1100°C. The data are given in Table I along with data obtained by the National Bureau of Standards.

7. Heat Capacity Measurements (F. H. Spedding and L. D. Jennings)

7.1 Yttrium

We have measured the heat capacity of yttrium from 15° to 350°K. The form of the heat capacity is very nearly the same as that for lanthanum. The average Debye temperature (which gives the correct result for the entropy at 300°K) is 218° as contrasted with a value of 130° for lanthanum. The value of the entropy at 300° is 44.57 joules/mole-deg and of the enthalpy function, H/T , 20.04.

Table I. Heat Content of α -Al₂O₃ (12.3136-gm sample)

$t^{\circ}\text{C}$	$\Delta H \int_0^{t^{\circ}\text{C}} \text{cal/gm}$	% Reproducible	$\Delta H \int_0^{t^{\circ}\text{C}} \text{N.B.S.}$	% Deviations
100.5	19.70	.21	19.69	-.05
301.5	42.85	.07	42.92	-.16
301.5	68.41	.06	68.40	-.01
402.1	95.29	.11	95.25	-.04
500.9	122.42	.08	122.43	-.01
600.6	150.8	.06	150.80	-.03
698.2	178.94	.03	179.03	-.05
800.0	208.28	.06	208.97	-.10
901.6	239.13	.03	239.23	-.04
1001.5	268.77	.10		
1102.0	298.72	.07		

7.2 Lutetium

The heat capacity of lutetium again shows the same form. Although we have not yet computed the thermodynamic functions for this metal, the average Debye temperature is about 167°. The similarity in the heat capacities of yttrium, lanthanum, and lutetium gives us confidence that we can establish the non-magnetic contributions to the heat capacity of the other rare earths. This, in turn, allows us to determine the details of the magnetic ordering in these other rare earths.

7.3 Samarium

We have measured the heat capacity of samarium from 13° to 350°K. We find that there is an anomaly at some temperature below

the lowest one that we can achieve and there is also an anomaly at 105.2°K. The latter is intermediate in shape between the rounded anomalies characteristic of the light rare earths and the sharp anomalies characteristic of the heavy rare earths. Roberts¹ has found the lower anomaly to be at 13.6°K, but our data show that it must be at least one degree lower than this for the sample we studied. Nevertheless, if we use Roberts' data up to 20°K, we calculate the entropy at 300°K to be 69.8 joules/mol-deg. The average Debye temperature calculated from this value is 140°. This value puts S_m below the smooth curve of Debye temperature vs. atomic number for the rare earths. This fact has previously been found from the sound velocity measurements by J. F. Smith of the Ames Laboratory.

7.4 Terbium

A paper entitled "The Heat Capacity of Terbium from 15 to 350°K" by L. D. Jennings, R. M. Stanton and F. H. Spedding has been submitted to J. CHEM. PHYS.

Abstract

The heat capacity of terbium has been measured in the temperature range 15 to 350°K. A lambda anomaly has been observed with the peak at 227.7°K. There is, in addition, an anomalous region near 220°K. The heat capacity in this region depends on the thermal history of the sample. The value of the entropy at 273.16°K is 17.50 cal/(g atom-deg)

¹ L. M. Roberts, Proc. Phys. Soc. B 70, 434 (1957).

in agreement with the value predicted on the assumption that, at room temperature, the 4f electrons have the same configuration as in the free tripositive ion.

7.5 Holmium

A paper entitled "The Heat Capacity of Holmium from 15 to 300°K" by B. C. Gerstein, Maurice Griffel, L. D. Jennings, R. E. Miller, R. E. Skochdopole and F. H. Spedding was accepted for publication in J. CHEM. PHYS.

Abstract

The heat capacity of holmium has been measured over the range 15 to 300°K. Two maxima have been observed which occur at 19.4 and 131.6°K. The one at the lower temperature exhibits a dependence on the thermal history of the sample and this dependence was investigated. The thermodynamic functions have been tabulated and a correlation made of the contributions to the entropy at room temperature. The value of $S_{298.16}^0$ is $17.97 \text{ cal } (^{\circ}\text{K})^{-1} (\text{g atom})^{-1}$ to which the magnetic contribution is $R \ln (2J + 1)$.

8. Rare Earth Alloys (F. H. Spedding and A. H. Daane)

8.1 The Rare Earth-Carbon Alloy Systems

The lanthanum-carbon alloy system has been determined from 4 wt % carbon to 100% carbon. The carbides La_2C_3 and LaC_2 exist in this region and appear to be the only compounds formed in this system. The region from 0 to 4 wt % carbon is under study.

Other rare earth carbides have been identified, including a new carbide of as yet undetermined composition, but known to exist in the range R_5C_2 to R_4C . The structure of this carbide is face-centered cubic, with rare earth atoms occupying the corners and face centers of the cube. Intensity measurements indicate that the carbon atoms occupy some of the octahedral holes in a random manner. For yttrium, this carbide has a pycnometric density of 4.65 gms/cc compared to an X-ray value of 4.68 gms/cc. Rare earths found to have this carbide are given in Table II.

Table II

<u>Rare Earth Carbide</u>	<u>Lattice Constant A_0 in A</u>
Y_mC	5.1271 ± 0.0007
Sm_mC	5.14 ± 0.01
Tb_mC	5.107 ± 0.002
Ho_mC	5.061 ± 0.002
Er_mC	5.00 ± 0.01

The rare earth sesquicarbides shown in Table III have been observed, some with a range of composition as indicated by different lattice constants, depending on the composition of the alloy from which the sample is taken.

Table III

	<u>A_0 Rare Earth-Rich Side</u>	<u>A_0 Carbon-Rich Side</u>
Ce_2C_3	8.4476 ± 0.0004	(no solid solubility)
Pr_2C_3	8.5731 ± 0.0005	8.6072 ± 0.0006
Sm_2C_3	8.3989 ± 0.0012	8.4257 ± 0.0012
Gd_2C_3	8.3221 ± 0.0005	-----
Tb_2C_3	-----	8.2617 ± 0.0007

The rare earth dicarbides, isomorphous with LaC_2 , which have been examined, and their lattice constants are given in Table IV.

Table IV

	A_0	C_0
CeC_2	3.870 ± 0.001	6.488 ± 0.002
PrC_2	3.855 ± 0.002	6.434 ± 0.004
SmC_2	3.770 ± 0.001	6.331 ± 0.003
GdC_2	3.718 ± 0.001	6.275 ± 0.003
YC_2	3.664 ± 0.001	6.169 ± 0.004
TbC_2	3.71 ± 0.01	6.17 ± 0.01
HoC_2	3.65 ± 0.01	6.07 ± 0.01
ErC_2	3.59 ± 0.01	6.03 ± 0.01
YbC_2	3.65 ± 0.01	6.04 ± 0.01

8.2 Miscellaneous Rare Earth Alloys

The La-Fe system has been investigated by arc-melting alloys whose compositions range across the system, and then examining these alloys by metallographic and X-ray diffraction methods. No intermetallic compounds are found in this system, the metals being miscible in the liquid state and immiscible in the solid state. Lanthanum is somewhat unusual in this respect in that all of the other rare earth metals examined (Pr, Nd, Gd, Lu) form intermetallic compounds with iron.

The yttrium-iron system has been found to contain the compounds YFe , YFe_2 and probably YFe_9 . Eutectics occur between Y and YFe and between YFe and YFe_2 at 67 at. % Y and 40 at. % Y, respectively.

The Y-Cr system appears to be a simple eutectic system, with the eutectic at 78 at. % Y and melting between 1175 and 1200°C.

Results of a study of uranium-rare earth alloys are given in the section of this report entitled "Pyrometallurgy".

9. Rare Earth Compounds (F. H. Spedding and A. H. Daane)

9.1 Rare Earth Fluorides

An examination of the literature on rare earth halides reveals a scarcity of information on the fluorides. As these compounds are among the most important ones in our metallurgical studies, we are studying their preparation and properties. Since many of the rare earths are available in only limited quantities, a preparatory scheme was needed that would work well on a small scale and, if possible, would be operable in a laboratory without entailing HF hazards and disposal problems. The method being used satisfies these requirements rather well, and depends on the following reaction:

Twenty per cent excess ammonium bifluoride is mixed with the rare earth oxide, and the mixture is heated to 300°C in a stream of dry air in an Inconel tube. It is not certain at present whether or not the ammonium fluoride also acts as a fluorinating agent in this reaction. The rare earth fluorides prepared in this manner have been found to have the same oxygen contents as fluorides prepared using anhydrous hydrofluoric acid gas at considerably higher temperatures.

Thermal analyses have been carried out on the rare earth fluorides to determine their melting points. It has been found that some of the rare earth fluorides have high temperature transformations as indicated in Table V.

Table V

	<u>Transition Temp. (°C)</u>	<u>M.P. (°C)</u>
YF ₃	1046	1152
LaF ₃		1493
CeF ₃		1430
PrF ₃		1395
NdF ₃		1374
SmF ₃		1306
GdF ₃	1007	1231
TbF ₃		1173
DyF ₃		1154
HoF ₃		1143
ErF ₃	1096	1140
TmF ₃	1043	1158
YbF ₃	947-956	1157
LuF ₃	927	1182

9.2 Rare Earth Chlorides

In studies on very high purity rare earth metals, we have had occasion to use rare earth chlorides. To avoid the laborious preparation of these chlorides by dehydrating their hydrated salts, a procedure has been devised for preparing the salts directly from

the oxides. In this process, the oxide is heated to 230°C in a stream of HCl and an inert gas such as helium or nitrogen, the temperature being carefully maintained by diluting the HCl in the gas stream as the exothermic reaction takes place. The success of the process is due to the low temperature conversion of the oxide to the chloride and the removal of the water vapor product before it can form the oxychloride. A mixture of LaCl_3 and LaOCl cannot be converted to LaCl_3 by bubbling HCl through the molten mass, which indicates further the extreme stability of this compound.

10. Vapor Pressure of Palladium (A. H. Daane)

A paper entitled "The Vapor Pressure of Palladium" by James F. Haefling and A. H. Daane will be published in J. METALS (TRANSACTIONS).

Abstract

The vapor pressure of palladium has been determined over the pressure range 10^{-2} mm to 10^{-4} mm using the Knudsen effusion method. The vapor pressure equation for palladium is

$$\log P_{\text{mm}} = \frac{-16860 \pm 85}{T^{\circ}\text{K}} + 8.30 \pm .04.$$

The heat of vaporization at 0°K was calculated to be -80 kcal/mole. The unusually weak binding in palladium metal appears to be consistent with other physical properties of this metal.

11. Fused Salts (F. R. Duke and J. D. Corbett)

11.1 Determination of Transport Numbers (F. R. Duke)

Transport numbers were determined for pure KCl and pure NaCl. The t_+ (fraction of current carried by cation) is $.80 \pm .05$ for NaCl and $.75 \pm .05$ for KCl. The transport numbers in pure PbCl_2 were determined by a moving boundary method using ZnCl_2 as the following cation salt and the values agreed with the data from the moving bubble cell ($t_+ = .25 \pm .02$).

The transport numbers of all three ions in a KNO_3 - AgNO_3 system were determined as a function of temperature and composition. It was found that temperature variations had no noticeable effect on transport numbers in this system. The variation in ion mobility with composition is as follows: the nitrate ion mobility is constant; the K^+ ion increases in mobility as KNO_3 is diluted with AgNO_3 ; and the Ag^+ ion decreases in mobility as AgNO_3 is diluted with KNO_3 .

The transport numbers and mobilities were determined in the system KCl - PbCl_2 as a function of composition and temperature. Again, the transport numbers are not affected by the temperature. As the composition varies, the mobility varies as follows: the chloride ion mobility decreases on going from pure PbCl_2 to pure KCl; the mobility of Pb^{++} decreases as KCl is added to PbCl_2 ; and the K^+ mobility decreases sharply as PbCl_2 is added to KCl.

The relative mobilities of the cations in KCl - AgCl mixtures were determined. It was found that relative to chloride ion, the transport numbers of the cations were nearly directly proportional to their concentration.

The complexing constants for Pb^{++} , Cd^{++} , Ba^{++} and Ca^{++} with some or all of the ions Cl^- , Br^- , and CN^- , were determined using NaNO_3 - KNO_3 eutectic as solvent. The same constants were determined in LiClO_4 as solvent, and were found to be 2-3 times as large in LiClO_4 . This is attributed to the lower polarizability of ClO_4^- as compared with NO_3^- . These were all determined by the solubility method.

By using potentiometric methods, some of the above constants were redetermined and found to be the same as by the solubility method.

11.2 Surface Tensions of Fused Salt Systems (F. R. Duke)

A report (ISC-923) entitled "Surface Tensions of Some Binary Fused Salt Systems" by June Lomnes Dahl and F. R. Duke is being distributed.

Abstract

The surface tension of eight pure fused salts-- NaNO_3 , KNO_3 , AgNO_3 , LiCl , NaCl , KCl , PbCl_2 , and ZnCl_2 --and nine binary mixtures-- NaNO_3 - KNO_3 , AgNO_3 - NaNO_3 , AgNO_3 - KNO_3 , NaCl - KCl , PbCl_2 - LiCl , PbCl_2 - NaCl , PbCl_2 - KCl , PbCl_2 - RbCl , and PbCl_2 - CsCl --were measured by the maximum bubble pressure method. Surface tension showed essentially linear variation with temperature in all cases.

As would be expected, large differences were found between the surface tensions of the pure fused salts. The higher surface tension of molten AgNO_3 compared to NaNO_3 was explained

in terms of differences in the polarizability of the metal ions in the melts. The low surface tension of ZnCl_2 was assumed to result from extensive association in this melt.

The surface tension isotherms of the systems NaNO_3 - KNO_3 and NaCl - KCl were found to exhibit small negative deviations from ideality. The greater negative deviations from ideality which were found in the systems AgNO_3 - NaNO_3 and AgNO_3 - KNO_3 were attributed to polarizability differences between the metal ions. The limited data suggested that in binary mixtures of fused salts with a common anion, the deviations of the surface tension isotherms from ideality increase as the differences between the sizes of the replacing cations increase.

Actual minima were observed in the surface tension isotherms of the systems PbCl_2 - KCl , PbCl_2 - RbCl , and PbCl_2 - CsCl ; no minima were observed in the systems PbCl_2 - LiCl and PbCl_2 - NaCl . These minima were attributed to the presence of complex ions or other surface active aggregates in these melts. Other physical measurements strongly support the existence of complex ions, very likely anionic complexes of lead, in the system PbCl_2 - KCl .

The trend in the character of the PbCl_2 -alkali metal chloride surface tension isotherms was shown to be in accord with the fact that any anionic complexes in these melts would be more stable in the presence of large cations with low polarizing power than in the presence of small ions with large polarizing power.

Further evidence for complexing in the PbCl_2 -alkali metal chloride melts was the presence of a yellow color in those melts whose surface tension isotherms exhibited minima; no yellow color was observed in the PbCl_2 -LiCl and PbCl_2 -NaCl systems. This yellow color which persisted in the solid state at high temperatures was found to increase in intensity with increase in the size of the alkali metal ion.

It was pointed out that there is no reason to assume that the complexing in these melts consists only of discrete ions. It is proposed that there are also local aggregations of ions whose structures resemble the structure of the solid state.

11.3 Subhalides in Metal-Metal Halide Systems (J. D. Corbett)

A reinterpretation of the literature data on the Bi- BiCl_3 system has been particularly successful. Reduction of BiCl_3 by excess metal above 330° gives a limiting composition of about $\text{BiCl}_{1.4}$, while separation of solid BiCl therefrom occurs at a syntectic temperature of 328° . Accordingly, reaction of metal with liquid BiCl_3 at lower temperatures has resulted in the preparation of pure BiCl. As the rate of this reaction is quite slow once appreciable amounts of the monochloride have formed, the excess metal is best removed in a dry box and the unreacted trichloride sublimed away at 175° . The resulting black solid is better than 99% BiCl. The salt is quite unreactive and is similar to BiAlCl_4 in being diamagnetic.

Bismuth(I) bromide has also been made by a comparable procedure.

The Ga_2Br_4 -GaBr system is quite similar, with a eutectic temperature near $\text{GaBr}_{1.9}$ at 152° . The limit of reduction of the liquid by metal corresponds to $\text{GaBr}_{1.8}$, from which solid GaBr separates below 163° . Reduction of Ga_2Br_4 by metal at 160° gives a composition $\text{GaBr}_{1.3}$, a considerably better yield of GaBr than can be obtained in the all-liquid system. Separation of pure monobromide from this mixture is currently under investigation.

A paper "The Solubility of the Post-Transition Metals in Their Molten Halides" by John D. Corbett, Samuel von Winbush and Frank C. Albers was published, J. AM. CHEM. SOC. 79, 3020 (1957).

Abstract

The solubilities of the respective metals in molten PbI_2 , SbCl_3 , SbI_3 , ZnCl_2 , ZnI_2 , CdI_2 and GaBr_2 are reported. An interpretation of the solution of the post-transition representative metals in their molten halides is presented in terms of the formation of slightly-stable subhalides. The apparent stabilities of the lower halides increase both with increasing atomic weight of the metal within a group, and with increasing atomic weight of the halide with a given metal, except for cadmium. The halide effect is attributed to a corresponding decrease in the extent to which the higher oxidation state of the metal is stabilized by complex formation with halide. The relative stabilities of the metal-halide complexes observed parallel those reported in aqueous solution for the same ions, including the inversion in order found for cadmium.

The formation of gaseous subhalides of antimony, bismuth and gallium is indicated by transport experiments. A direct correspondence is found between those systems in which gaseous subhalides of appreciable stability are formed and those in which metal dissolves in the molten salt to an appreciable extent. Diamagnetic solutes are formed in the zinc, cadmium, gallium, antimony and bismuth systems.

12. Ferric-Stannous Reaction (F. R. Duke)

A paper entitled "The Role of Chloride Ion in the Ferric-Stannous Reaction" by F. R. Duke and Norman C. Peterson was submitted to the IOWA STATE COLL. J. SCI. for publication.

Abstract

A re-examination of the rate of the chloride-catalyzed reaction between ferric and stannous ion in perchloric acid solution has been made. Total chloride ion concentration was determined by a method of successive approximations, taking into account the various complexes formed by ferric and stannous ions with chloride ion. The dependence of the second order rate constant k_2 upon free chloride ion concentration was found to be in better agreement with the expression $k_2f(C) = 8.7 \times 10^4 C^4 + 26 \times 10^4 C^5$ than with the rate originally found,

$$k_2f(C) = 1.2 \times 10^3 C^3 + 72 \times 10^3 C^4 + 27 \times 10^4 C^6.$$

13. Adsorption from Aqueous Solutions (R. S. Hansen)

A paper entitled "Functional Group Effects in the Adsorption of Organic Compounds from Aqueous Solution by Mercury" by Robert S. Hansen, Robert E. Minturn and Donald A. Hickson was accepted for publication in J. PHYS. CHEM.

Abstract

Isotherms for the adsorption of pentanol-1, pentanone-3, pentanenitrile, 2,4-pentanedione, phenol and octanoic acid from aqueous perchloric acid solution by mercury are inferred from differential double layer capacitance measurements in these systems. Standard free energies of adsorption are calculated using standard states based on unit activity coefficient in solution for infinitely dilute solute and unit activity coefficient in monolayer for infinitely dilute monolayer. The standard free energy of adsorption is approximately proportional to the difference in optical polarizabilities per unit volume between adsorbate and solvent and to the adsorbate molar volume raised to the two-thirds power. The interaction free energy in the monolayer (difference in free energy between adsorbate standard states based on unit activity coefficients in infinitely dilute and complete monolayers) is approximately one half the corresponding difference in bulk solution. In the compounds investigated, functional groups appear to influence adsorption only to the extent that they influence molecular polarizability and character of adsorbate-solvent interactions.

14. Contact Angle Hysteresis (R. S. Hansen)

A Communication to the Editor entitled "Relaxation Phenomena and Contact Angle Hysteresis" by Robert S. Hansen and Mirella Miotto was published; J. AM. CHEM. SOC. 79, 1765 (1957).

15. Isotope Abundance in Nitrogen (H. J. Svec)

Determination of the absolute abundance of the nitrogen isotopes in the atmosphere was completed. Two mass spectrometers were calibrated with mixtures prepared from separated isotopes in the form of $(\text{NH}_4)_2\text{SO}_4$ solutions. The NH_4^+ content of these solutions was determined by Kjeldahl distillations to 1 part in 1000, and the solutions were found to contain 99.983 atoms % N^{14} and 99.793 atoms % N^{15} . Mixtures were made by weight and the resulting preparations oxidized to N_2 by NaOBr . The absolute $\text{N}^{14}/\text{N}^{15}$ ratio for atmospheric nitrogen was found to be 272.0 ± 0.3 which compares favorably with the currently accepted value of 273 ± 1 obtained by Nier.¹ While no significant difference was found, the improved precision of this abundance measurement removes the abundance as the limiting factor in the precise determination of the atomic weight of atmospheric nitrogen. No differences were found in the nitrogen isotope abundances for air obtained from several sites in North America and up to 36,000 feet above sea level. This corroborates the report of Dole et al.² Differences up to 1% were found for the $\text{N}^{14}/\text{N}^{15}$ ratio in commercial sources of gaseous nitrogen and in NH_4^+ salts.

¹ A. O. Nier, Phys. Rev. 77, 789-793 (1950).

² M. Dole et al., Geochim. et Cosmochim. Acta 6, 65-78 (1954).

16. Mass Spectra of Chromyl Chloride (H. J. Svec)

Preparations of CrO_2Cl_2 have classically been prepared by the reaction of HCl with some dichromate or chromate or with chromic acid (CrO_3). The HCl is generally prepared in situ using concentrated H_2SO_4 and NaCl . The solid reactants are usually mixed thoroughly and when the acid is added, considerable heating takes place and CrO_2Cl_2 distills as a dark red vapor along with some Cl_2 which forms due to the strongly oxidizing conditions. The presence of Cl_2 in appreciable amounts interferes with the mass spectrometry of the CrO_2Cl_2 to the extent that considerable peak height uncertainty is introduced because of extensive noise, and the cracking patterns are unstable. In searching for methods to eliminate Cl_2 as an impurity, new preparation methods were sought. One which gives excellent results is the reaction between anhydrous AlCl_3 and CrO_3 which proceeds slowly at room temperature and rapidly at $40\text{--}50^\circ\text{C}$. Little or no Cl_2 is formed in the reaction and only a very small amount of the dimeric compound is formed.

17. Reactions of Water Vapor with Strontium and Barium (H. J. Svec)

A paper entitled "Metal-Water Reactions. VI. Kinetics of the Reactions of Water Vapor with Strontium and Barium" by Harry J. Svec and H. Gene Staley was submitted to J. ELECTROCHEM. SOC.

Abstract

Strontium and barium were reacted with water vapor and the kinetics determined in the temperature range 40 to 66°C for water vapor pressures from 17.5 to 92.5 mm of Hg. The stoichiometry varied according to the reaction conditions.

For the strontium reactions the products were H_2 and $Sr(OH)_2$. For vapor pressures below 44 mm the products of the barium reactions were H_2 and $Ba(OH)_2$ while for pressures above 44 mm they were H_2 and $Ba(OH)_2 \cdot H_2O$.

Manometric and gravimetric methods were employed in the kinetic studies. Both the Sr and lower-vapor pressure Ba reactions followed the parabolic rate law. At higher pressures the Ba reaction followed a linear law. An activation energy of -5.2 ± 0.2 kcal/mole was found for the Sr reactions. The activation energy for the Ba reactions was found to depend upon the reaction conditions.

Higher temperature studies of the reactions between water vapor and Sr, Ba and Ca indicated that in certain temperature ranges above $100^\circ C$ completely protective coatings were formed similar to those observed in the oxidation of Al or Cr.

18. Theory of Pi-Electron in Organic Molecules (K. Ruedenberg)

An investigation concerning the interdependence of radial and circular motion in benzene-like rings of atoms was completed. The lowest ten energy levels E_n and the corresponding wavefunctions (ψ_n) were calculated for electrons in a torus. The width of the torus (W) was varied, while the diameter (R) was held constant. The limiting values of the E_n for $(W/R) = 0$ were found to differ only by a constant ($1/4$) from those obtained from the one-dimensional Schroedinger equation. In the same limit the radial parts of the normalized eigenfunctions (ψ_n) became trigonometric functions, vanishing at the torus boundary. Both results indicate that, for

a very narrow torus, its curvature has a negligible effect on the motion. Of interest was the nature of the deviations from this limiting behavior when the width was increased. To this end the energies E_n were studied as functions of $\Delta = (W/R)$, which varies from 0 to 2. In order to obtain a measure for the deviation of the wavefunctions, the following quantities were calculated:

$$\delta\psi_n(\Delta) = \left[\int dV (\psi_n^\Delta - \mathcal{S}_n^\Delta)^2 \right]^{1/2}$$

where ψ_n^Δ is a normalized eigenfunction for the torus width Δ , and $\mathcal{S}_n^\Delta$ is the normalized wavefunction obtained by replacing the radial part of ψ_n^Δ by the corresponding trigonometric function (having the same number of nodes and vanishing at the torus boundary). These integral-wavefunction-deviations $\delta\psi_n^\Delta$ were again studied as functions of $(W/R) = \Delta$.

For the energies and the wavefunctions, marked deviations from the limiting character were found to set in only when the width of the torus markedly exceeded its diameter, i.e., for (W/R) between 1 and 1.5. These deviations are smaller than expected and provide the first theoretical justification for the use of the practically successful linear free-electron model.

19. Table of Exponential Integral Function (K. Ruedenberg)

In the computation of molecular integrals, values of the exponential integral are frequently needed to an accuracy higher than that given by available tables. For this reason a table of exponential integrals was computed according to a method recently published.¹

¹ K. Ruedenberg, C. C. J. Roothaan, and W. Jaunzemis, J. Chem. Phys. 24, 201 (1956).

For argument values from 5 to 25, in steps of 0.5, the table gives values for the exponential integral and as many of its derivatives as are necessary to interpolate the function accurately to 18 decimal places. The table will be submitted for publication.

20. Spectra of Substituted Hydrocarbons (H. Shull)

A paper entitled "Application of the Molecular Orbital Method to the Spectra of Substituted Aromatic Hydrocarbons" by L. Goodman, Ian Ross and H. Shull was published, J. CHEM. PHYS. 26, 474 (1957).

Abstract

The MO theory of the spectra of substituted hydrocarbons is presented in rather general terms, with careful emphasis on the precautions to be observed in introducing the inevitable approximations. Previous treatments of the problem, notably by Sklar, Herzfeld, and Matsen, are then examined. Satisfactory calculations of energy-level shifts are considered to require closer attention to the definition and dissection of the perturbed Hamiltonian. The most interesting intensity effects concern the enhancement of weak transitions: here earlier treatments do not satisfy the requirements of orthonormality of the perturbed MOs, and unjustifiably neglect interactions with intense transitions. The consequences of neglecting overlap in these calculations are discussed in an appendix.

21. Isotopic Equilibria (R. Schaeffer)

A report (ISC-867) "Isotopic Equilibria of Nitrosyl Chloride" by Riley Schaeffer and Hampton Smith is being distributed.

Abstract

The electrolytic solvent characteristics of liquid nitrosyl chloride and general consideration of the factors affecting suitability of a system for isotope separation suggest that exchange reactions of nitrosyl chloride might provide an interesting and useful means for the separation of the stable isotopes of nitrogen or of chlorine or of both in a simultaneous process. Vibrational frequencies of isotope substituted nitrosyl chloride molecules were calculated and used to estimate equilibrium constants for exchange of nitrosyl chloride with nitric oxide and with chlorine.

Pyrometallurgy

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

1.1 Extraction of Fission Products with Silver

In previous work on the extraction of various fission products from uranium by molten silver, difficulty was experienced in the lack of reproducibility of results. Attempts have been made to discover the reasons for this trouble which seemed to be related to the reactions of the fission products with oxygen, carbon or some other impurity in the metal. Such reactions could be more favored than extraction of particular fission product elements and could give rise to the inconsistent results.

Since there had been some attack by the metals on the tantalum crucibles, several extractions were made in tantalum crucibles, the interiors of which were coated with tantalum carbide. Uranium containing 0.1 % cerium tracer was extracted with silver. Both phases

of the melt were cut into slices and examined by autoradiographic technique. Those slices which showed inhomogeneities were discarded. The homogeneous slices were analyzed, and the results are given in Table VI.

Table VI. Extraction of Cerium by Silver

	<u>Dist. Coeff.</u>	<u>Decont. Factor</u>	<u>% Removed</u>	<u>% Extracted</u>	<u>% Reacted</u>
I	64 $\pm$ 15	94 $\pm$ 19	98.9 $\pm$ 0.2	41 $\pm$ 6	58 $\pm$ 6
II	400 $\pm$ 200	400 $\pm$ 200	99.7 $\pm$ 0.1	59 $\pm$ 14	41 $\pm$ 14

The stated errors were determined by statistical treatment of the analytical data from the various slices.

The removal has been broken down into two processes, (1) removal by extraction and (2) removal by all other processes which remove the tracer from the uranium layer (per cent reacted). It can be seen that the removal was quite complete, roughly half by extraction and half by reaction. The reactions were with the crucible or impurities and the reacted material was probably in the hot spots of the inhomogeneous samples which were discarded.

It was shown satisfactorily that the silver layer from a silver extraction of uranium fuel could be freed of its fission product content by melting it with silver chloride or sodium chloride-silver chloride mixtures containing as little as 5% silver chloride.

1.2 Extraction of Carbon with Zirconium

In order to investigate further the relation between the fission products and light element impurities, a study was made of the vertical distribution of both zirconium and carbon in a sample of U-Zr alloy prepared from uranium metal. It was also felt that the zirconium might act as a "getter" for the carbon and produce a uranium sample with a lower than usual carbon content.

The results of the distribution study are shown in Table VII.

Table VII. Zirconium and Carbon Distribution

<u>Sample</u>	<u>Carbon (ppm)</u>	<u>Zr (wt %)</u>	<u>Mole ratio (Zr/C)</u>
Original U	600		
Top, including slag	4050	2.4	0.8
Top, good metal	1800	2.0	1.4
Center	150	0.15	1.3
Bottom	100	0.18	2.4

Thus a 40-fold difference in carbon content from top to bottom of this slug is accompanied by a much lower difference in the Zr/C ratio. This suggests that a zirconium-carbon compound forms which tends to collect at the top of the melt. These results would explain the difficulty experienced in obtaining a uranium-0.1% zirconium alloy with a uniform distribution of zirconium. However, the carbon content of the best metal was still 100 ppm so this does not seem to be an easy method for the removal of the last traces of carbon from uranium metal.

1.3 Metal Purification in Packed Columns

An investigation is being made of the feasibility of passing molten metal through packed columns as a technique for purifying the metal. The first major problem is to get the recovery of the metal in these experiments up to an acceptable value. Columns were constructed of graphite or tantalum and filled with graphite or oxide particles. Silver and uranium-chromium eutectic were used as the mobile phase. Recovery of these metals at the bottom of the column has varied from 30 to 95% and reasons for the variability are being studied.

One typical experiment will be cited in which a uranium-chromium eutectic containing tracer zirconium and cerium was passed at 1000-1100°C through a one-inch tantalum column packed with graphite particles to a depth of 4 inches. Sixty-eight per cent of the eutectic passed through the column, 30% was held up in it and 2% remained on top as a skull. The portion which passed through the column had 78% of its cerium and 76% of its zirconium removed from it. When the graphite of the column was leached with acid to remove the materials for analysis, the uranium was recovered completely but much of the cerium and zirconium was not removed. This indicates that the fission products reacted with the graphite, while the uranium was merely mechanically trapped in the column.

2. Uranium-Rare Earth Studies (F. H. Spedding and A. H. Daane)

The degree of immiscibility of uranium and the rare earth metals has been determined, and the results are given in Tables VIII and IX.

Table VIII. Wt % Rare Earths in Uranium

	<u>1150°C</u>	<u>1175°C</u>	<u>1200°C</u>	<u>1225°C</u>	<u>1250°C</u>
Y		.09	.12	.14	.11
La	.77	.76	.80	.85	
Ce	1.13	1.19	1.10	.93	
Pr	.22	.27	.30	.32	.39
Nd	.14	.15	.18	.12	.19
Sm	.20	.21	.25	.25	.21
Eu					
Gd	.04		.10		
Tb	.04		.32		
Dy	.08		.19		
Ho			.18		
Er	.01		.18		
Tm				.04	
Yb	.22		.13		.22
Lu					

Table IX. Wt % Uranium in Rare Earths

	<u>1000°C</u>	<u>1050°C</u>	<u>1100°C</u>	<u>1150°C</u>	<u>1175°C</u>	<u>1200°C</u>	<u>1225°C</u>	<u>1250°C</u>
La		.42	.58	.58	.68	.82	.79	1.02
Ce	1.28		2.41	2.48	2.89	3.61	3.0	3.60
Pr	1.06		1.19	1.55	1.50	1.99	1.75	2.03
Nd		1.30	1.00	1.68	1.55	2.00	1.65	1.76
Sm		.76	.76	.76	1.0	1.35	1.35	1.10
Yb		.18		.41		.71		.31
Eu								

Analytical Chemistry1. Analytical Procedures (C. V. Banks and J. S. Fritz)1.1 Analysis of Boron-Lanthanum Alloys (C. V. Banks)

Boron was determined in boron-lanthanum alloys by dissolving the alloy in a minimum of hydrochloric acid, separating the boron from the lanthanum on a cation exchange column, and titrating the boric acid in the eluate by the standard "mannitol" procedure.

1.2 Analysis of Rare Earths in Uranium (C. V. Banks)

A method was developed for the determination of trace amounts of rare earths in uranium. The rare earths are quantitatively separated from the uranium and determined spectrophotometrically.

1.3 Determination of Ruthenium (C. V. Banks)

A paper by C. V. Banks and J. W. O'Laughlin "Spectrophotometric Determination of Ruthenium with 1,10-Phenanthroline" was accepted for publication in ANAL. CHEM.

Abstract

A new spectrophotometric method for the determination of ruthenium is described. This method is based on the reaction of ruthenium(III) or ruthenium(IV) with 1,10-phenanthroline in the presence of a reducing agent to form the very stable and intensely colored tris(1,10-phenanthroline)ruthenium(II) ion. The method is sensitive and accurate. As little as 0.1 part of ruthenium per million parts of solution can be quantitatively determined. A method for the rapid separation of trace amounts of ruthenium from most other metals based on the distillation

of ruthenium tetroxide is described. For the distillation a mixture of sulfuric and perchloric acids is employed as the oxidizing agent and the ruthenium tetroxide evolved is quantitatively absorbed in a dilute hydrochloric acid solution containing hydroxylammonium chloride. A simple and easily constructed distillation apparatus is used.

1.4 Determination of Carbonyl Function in Organic Compounds

(J. S. Fritz)

A new method has been devised for the quantitative determination of the carbonyl function in organic aldehydes and ketones. An excess of hydroxyl ammonium chloride and a measured amount of standard base (N-dimethylaminoethanol) are added to the sample. Isopropanol is used as the solvent. After 20 to 30 minutes at room temperature, the excess base is titrated with standard hydrochloric acid in isopropanol. About 12 representative aldehydes and ketones have been analyzed with very good results. This method is comparable to other methods in speed, but has the advantage that the end point is much sharper than is possible by other methods. For this reason, the new method is capable of better precision and accuracy.

1.5 "Arsenazo" Indicator (J. S. Fritz)

A new indicator called "arsenazo" (chemical name: 3-(2-arsonophenylazo)4,5-dihydroxy-2,7-naphthalenedisulfonic acid, trisodium salt) has been found to be excellent for the EDTA titration of rare earths and yttrium in weakly acid solution.

Thorium can be titrated at a more acidic pH, and magnesium and calcium can be titrated in alkaline solution. In many cases use of masking agents or a simple preliminary separation permits determination of rare earths in samples containing foreign metal ions. Aluminum is masked by sulfosalicylate, and interferences for calcium and magnesium are avoided by proper pH control. Small amounts of uranium, iron, and most divalent metals are masked by diethyldithiocarbamate; larger amounts of these metals are removed by extraction of their diethyldithiocarbamate complexes. Thorium interferes with the titration of rare earths as does zirconium, chromium and tin. At pH 1.8 to 2.6, however, titration of thorium in the presence of uranium is possible.

Arsenazo has been found to be an excellent color-forming reagent for the determination of small amounts of rare earths and yttrium. The method is very sensitive; less than 0.5 ppm of rare earths can be determined with good accuracy. The method does not distinguish between the different rare earths, the molar absorptivity being around 26,000 in each case. Through the use of masking agents and/or quick preliminary separations, the method has good selectivity for rare earths (as a group). Many interfering cations can be removed quite simply by means of a mercury cathode. Chromium, iron, tin, and zinc are among the important interferences eliminated by this treatment. Aluminum is masked by sulfosalicylic acid, and small to moderate amounts of uranium are successfully extracted away from the rare earths as the uranium diethyldithiocarbamate complex.

Arsenazo shows excellent promise as a sensitive, selective reagent for the quantitative determination of uranium. We intend to investigate this possibility further.

A sensitive, selective qualitative test for thorium has been developed. Thorium forms a violet colored complex with arsenazo at pH 6 to 8 even in the presence of a strong complexing agent such as EDTA. EDTA masks most other cations (including moderate amounts of zirconium) under these conditions.

1.6 Titration of Nitro Aromatic Amines (J. S. Fritz)

A paper "Titration of Nitro Aromatic Amines as Acids" by James S. Fritz, Anthony J. Moye and Marlene Johnson Richard has been submitted to ANAL. CHEM.

Abstract

Anilines substituted in the 2,4, or 6 positions with at least two nitro groups, or with one nitro group and one or more chloro groups, can be titrated as acids in pyridine using triethyln-butylammonium hydroxide as the titrant. Diphenylamine derivatives with at least one nitro group in the 4 position can be titrated in a similar manner. Trinitrotoluene and trinitrobenzene can also be titrated as monobasic acids. In several cases a selective determination of the different components in a mixture is possible.

1.7 Service Analyses (C. V. Banks)

A total of 5142 service analyses was made during this period.

2. Study of Chelating Agents (C. A. Goetz)

Picolinaldoxime was synthesized and a study of its chelating properties was begun. This compound forms colored chelates with manganese, iron(II), iron(III), cobalt, and copper. It also forms a colorless complex with nickel.

A detailed study has been made of the picolinaldoxime-cobalt chelate, including the determination of the ligand to metal ratio, the apparent formation constant, the molar extinction coefficient, the obedience of the complex to Beer's Law, and the effect of various foreign ions on the determination of cobalt with this compound.

Spectrochemistry

1. Spectroscopic Research (V. A. Fassel)

1.1 Spectroscopic Determination of Oxygen in Metals

A paper entitled "Emission Spectrometric Determination of Oxygen in Metals. II. Titanium and Titanium Alloys" by V. A. Fassel and W. A. Gordon, was submitted to ANAL. CHEM. for publication.

Abstract

An emission spectrometric method for the determination of oxygen in titanium and titanium alloys is described. The procedure is based on the d.c. carbon arc excitation of a special electrode assembly which provides a molten platinum bath after the arc is initiated. The oxygen content of the titanium sample is rapidly liberated from this bath into an

argon atmosphere which supports the arc discharge. The intensity ratio of the line pair $\frac{O\ 7771\ A}{A\ 7891\ A}$ is related to the oxygen content of the titanium sample. This procedure provides oxygen determinations with a precision comparable to the vacuum-fusion or bromination-reduction techniques, but has the advantage of greatly reduced time requirements.

1.2 Spectrographic Determination of the Oxygen Content of Metal Fluorides

Many metals of interest to the AEC are prepared by reducing fluoride salts to the metal. Any oxyfluoride or unreacted oxide content of the fluoride may be retained by the metal as interstitial oxygen content. Since oxygen in metals generally exerts a deleterious effect on the physical properties of metals, there is great interest in controlling the oxygen content of metals. This requires a knowledge of the oxygen content of the fluoride from which the metal is made. There is no known chemical test for determining the total oxygen content of fluorides. We have observed that the oxygen content of fluorides can be readily detected with our spectroscopic techniques. The fluoride samples are pressed into 100-mg pellets, and are then placed in the cavity of a graphite supporting electrode. The latter is used as the anode of a d.c. arc discharge in pure argon. Although the behavior of the oxygen content of fluoride samples under the excitation conditions has not been definitely established, it has been observed that the empirical intensity ratio of $O\ 7771/A\ 7891$ can be related to the apparent

oxygen content of the sample. For example, if the ratio is <0.5 , yttrium metal of oxygen content less than 2000 ppm can be prepared. Similarly, greater oxygen content of metals is found if the observed ratio for fluoride samples increases above 0.5.

Since the chemical state of occurrence of the oxygen content of fluoride samples probably governs the behavior of the oxygen in the arcing process, it may be necessary to establish the over-all chemical constitution before valid standards can be synthesized. Alternatively, it may be possible to prepare series of standards in which the oxygen is added as Y_2O_3 , YOF, or mixtures of these forms. If these should all produce a single analytical curve, then the problem of establishing valid calibrations would be greatly simplified.

1.3 Determination of Yttrium in Rare Earths

A paper "X-Ray Fluorescent Spectrometric Determination of Yttrium in Rare Earth Mixtures" by Robert H. Heidel and V. A. Fassel has been submitted to ANAL. CHEM.

Abstract

The great similarity in the chemical properties of yttrium and the rare earth group of elements prevents the use of classical chemical methods for the separation and determination of yttrium. In this paper an X-ray fluorescent method for determining yttrium in mixtures of rare earths and thorium is described. For the determination of yttrium in ores, a preliminary rare earth group separation is required. The samples are analyzed in solution form, using added strontium as an internal standard. At 50% yttrium oxide content the coefficient of variation of the intensity ratio is 0.74. An average time of about 10 minutes is required for a single determination.

1.4 Analytical Spectroscopy of the Rare Earth Elements

The various absorption, emission, and fluorescence spectra of the rare earth elements are the most useful properties available to the analytical chemist for the analysis of rare earth mixtures. The rare earth emission spectra in flames have not been extensively investigated as far as their analytical possibilities are concerned. These spectra can be conveniently excited in integral atomizer-burner assemblies which simultaneously atomize a solution and transport the aerosol into the flame. In oxygen-acetylene flames, the thermal energy available is able to excite only those spectral lines which arise from rather low lying excited states. In the rare earth group, only europium and ytterbium emit atomic lines, but since these are sensitive and free of interference they should prove useful for analytical purposes. In certain zones of the flame, conditions are favorable for the formation of diatomic oxide molecules. The momentary presence of these molecules in these zones is signalled by the emission of characteristic diatomic band spectra. Recordings of these spectra in the wavelength region 4000-10,000 Å show that there is considerable overlap among the individual spectra. Portions of the band systems for lanthanum, yttrium, and scandium are well isolated and appear promising for analytical purposes.

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

During this period, 6921 samples were analyzed or examined by emission, absorption and fluorescent spectroscopic techniques.

Radiochemistry1. Radiochemical Studies of Mercury (A. F. Voigt)

A report (ISC-892) entitled "Radiochemical Studies of Mercury and Its Ions in Dilute Solutions" by Herbert C. Moser and A. F. Voigt is being distributed.

Abstract

Equilibrium studies have been performed with the objective of elucidating some of the chemical characteristics of mercury and its ions in dilute solutions. Experiments utilizing radioactive mercury tracer to determine low concentrations have been carried out in a threefold area of investigation.

The behavior of mercurous ions in dilute aqueous solutions has been studied. The principal aim of this endeavor was that of resolving between two alternate mechanisms describing the instability of mercurous ions in dilute solutions: dissociation of the dimers into monomeric mercurous ions and dismutation according to the equation:

The ions were found to be unstable toward dismutation, and values of 5.3×10^{-9} and 5.6×10^{-9} were calculated for the dismutation constant K at 25°C. Measurements of the distribution of dissolved free mercury between n-hexane, cyclohexane and dilute aqueous solutions of mercurous nitrate were used to obtain these estimates for K .

The above values for the dismutation constant are in fair agreement with the values 1.8×10^{-9} to 3.6×10^{-9} which were calculated using a different approach. The latter figures were obtained as products of the measurements of the concentration ratio $[\text{Hg}^{++}] / [\text{Hg}_2^{++}]$ and the solubility of mercury metal. Values of 0.0060 to 0.0120 were found in the literature for $[\text{Hg}^{++}] / [\text{Hg}_2^{++}]$ for systems containing mercurous and mercuric ions and liquid mercury metal. The solubility of mercury in aqueous solutions was determined in this study to be 3.0×10^{-7} g atoms per liter at 25°C.

Although the possibility of dissociation of the mercurous dimers into monomeric mercurous ions cannot be completely excluded, the results of this study can be satisfactorily interpreted without considering this effect. The results indicate that a dissociation constant as large as 1×10^{-7} is highly unlikely.

In addition to the determination of the solubility of mercury in aqueous solutions, the solubility of the metal in several organic solvents was measured. The solubilities which would be expected on the basis of current theory were calculated with Hildebrand's "solubility parameter" equation and are included in the table for comparison with the experimental values.

Solubility of Mercury in Organic Solvents at 25°C

<u>Solvent</u>	Conc. Hg x 10 ⁶ Observed <u>g atoms/liter</u>	Conc. Hg x 10 ⁶ Calculated <u>g atoms/liter</u>
<u>n</u> -Hexane	6.1 - 6.7	6.2
Cyclohexane	11.0 ± 0.2	21
Carbon tetrachloride	7.5 ± 0.3	37
Toluene	12.5 ± 0.5	48
Benzene	12.0 ± 0.6	72
Nitrobenzene	9.3 ± 0.7	157

Distribution constants defined as the concentration of free mercury in the aqueous phase divided by the concentration of the metal in the organic phase were found to be 0.048 for n-hexane and 0.031 for cyclohexane. These compare favorably with the ratios of the solubilities of the metal in water to that in each solvent which are 0.047 for water-n-hexane and 0.028 for water-cyclohexane.

In another area of study, equilibria between mercuric iodide and iodide ions have been investigated. Use was made of the extraction of mercuric iodide into benzene from dilute aqueous solutions of mercuric nitrate containing excess potassium iodide. The results were found to be consistent with the occurrence of the following equilibria:

Values for the equilibrium constants K_1 and K_2 were determined to be $(5.0 \pm 0.1)10^3$ and $(5.1 \pm 0.1)10^5$, respectively.

1.1 Extraction of Mercury(II) Iodide

A paper "The Extraction of Mercury(II) Iodide" by Herbert C. Moser and Adolf F. Voigt was accepted for publication in J. INORG. NUCL. CHEM.

Abstract

The extraction of mercury(II) iodide into benzene at various acid and iodide concentrations was used as a means of determining the formation constants of the HgI_3^- and HgI_4^{2-} species. Radioactive tracer techniques were used to measure the extent of extraction at low mercury concentrations. With reasonable assumptions about activity coefficients the thermodynamic values of the constants for the formation of HgI_3^- and HgI_4^{2-} from HgI_2 and I^- were found to be 5.0×10^3 and 5.1×10^5 , respectively.

2. Photonuclear Reactions (D. S. Martin)

2.1 Cross-Section Measurements

A program for the Schiff formula to give the thin target bremsstrahlung was prepared for the I.B.M. 650 computer. The spectra have now been tabulated by the computer at 0.5-Mev. increments in the photon energy and in the limit energy below 50 Mev. For limit energies between 40 and 100 Mev. the spectra have been tabulated at 1-Mev. increments.

In preparation for a complete cross-section measurement of the $\text{Ga}^{71}(\gamma, \text{pn}) \text{Zn}^{69}$ reaction, yield ratios of the Zn^{69} isomer pair in gallium targets have been measured for a number of bremsstrahlung-limit energies. The activity of the ground state

(52-min. half-life) in the zinc fractions has been counted with a G-M counter. Since the isomeric state has a longer half-life, the yields of both isomers can be inferred from the results. The yield ratios are computed from the over-all decay curve with the utilization of a least squares calculation by the I.B.M. 650 computer. Results have been obtained from about 28 Mev., where a tentative value of 1.95 for the $\text{Zn}^{69}/\text{Zn}^{69m}$ ratio has been observed, to 45 Mev. where the yield ratio has fallen to about 1.5. Final results will require adjustment of the integrator energy control of the synchrotron.

Additional activations have been carried out in the cross-section determinations for the $A^{40}(\gamma, p)\text{Cl}^{39}$, $A^{40}(\gamma, pn)\text{Cl}^{38}$ processes.

A paper "Cross Section for the $\text{Ca}^{40}(\gamma, 3p3n)\text{Cl}^{34}$ Reaction" by Fritz D. Schupp, Clifford B. Colvin and Don S. Martin, Jr., was accepted for publication in PHYS. REV.

Abstract

The cross section of $\text{Ca}^{40}(\gamma, 3p3n)\text{Cl}^{34}$ as a function of photon energy was determined up to 70 Mev. With a threshold for the process below 35 Mev the cross-section function was found to have a resonance shaped peak of 0.3 millibarns at 50 Mev with a width at half-height of 6 Mev. The integrated cross-section was 2.7 Mev-mb. The mode of the process is discussed on the basis of a statistical model.

2.2 Yields from Photonuclear Reactions

A paper "Comparative Yields of (γ , 2n) and (γ , pn) Processes for Fe⁵⁴ by 70 Mev Bremsstrahlung" by Raymond M. Henry and Don S. Martin, Jr., was accepted for publication in PHYS. REV.

Abstract

Relative yields of Fe⁵⁴(γ , 2n)Fe⁵²: Fe⁵⁴(γ , pn)Mn⁵²: Fe⁵⁴(γ , pn)Mn^{52m} were found to be 1:8:19 for irradiations by 70 Mev bremsstrahlung. These yields were compared with yields of the same products by alpha-particle bombardment, and results were discussed in terms of a statistical model for the reactions.

3. Exchange Reactions (D. S. Martin)

Recent experiments have clarified many of the features of the processes by which isotopic exchange of chlorine is effected between $\text{[Pt(NH}_3\text{)Cl}_3\text{]}^-$ and Cl^- . The evidence indicates that in the reaction

the cis-chloride is replaced by water. An additional exchange for $\text{[Pt(NH}_3\text{)Cl}_3\text{]}$ has been demonstrated and all three chlorides of the complex undergo exchange. The alternative exchange may occur by an aquation process such as equation (1) for the trans-chloride in which the reverse reaction is so rapid that the corresponding aquo-species is not detected. In addition, the species, $\text{[Pt(NH}_3\text{)Cl}_2\text{(H}_2\text{O)]}$, was found to exchange chloride. $\text{[Pt(NH}_3\text{)Cl}_2\text{(H}_2\text{O)]}$ solutions have been prepared free of Cl^- and $\text{[Pt(NH}_3\text{)Cl}_3\text{]}^-$ by means of an anion-exchange column. Studies have shown that the neutral

molecule is stable for long periods at a pH of 4. Above pH 5, however, it ionizes appreciably as an acid and substitutes a second hydroxide for chlorine. A measure of the equilibrium constant for the reaction

has been possible by the titration of the increased acid in solutions of the dichloroaquoammineplatinum(II). A tentative value of 4×10^{-5} was obtained for the constant.

The reverse reaction of equation (2) has been followed spectrophotometrically by acidifying solutions following the base hydrolysis of $\left[\text{(H}_3\text{N)PtCl}_2 \text{(OH)} \right]^-$. The results are very inaccurate, and it is believed that equation (2) may account for the exchange observed in $\left[\text{(H}_3\text{N)PtCl}_2 \text{(H}_2\text{O)} \right]$. Some combined exchange-substitution experiments with $\left[\text{(NH}_3\text{)PtCl}_2 \text{(H}_2\text{O)} \right]$ have indicated that the two chlorides are not equivalent and therefore cannot be trans to each other. It is indicated that the chloride trans to the H_2O in the cis-complex must be labile. The kinetics in a $\left[\text{(NH}_3\text{)PtCl}_3 \right]^- \text{Cl}^-$ system therefore involve the solution of a four-variable problem. A good approximate solution can be made easily at high chloride. However, for the more interesting low chloride system the solution to the kinetics has been solved by the analog computer of the Iowa State College Department of Theoretical and Applied Mechanics.

The exchange between $\text{[Pt en Br}_2\text{]}$ and $\text{[Pt en Br}_4\text{]}$ (where en is ethylenediamine), has been studied further with the utilization of $\text{Pt}^{195\text{m}}$. Careful fractional distillation of the dimethylformamide solution for these compounds gave a system in which exchange half-times at 25° were as high as two hours. However, it was not possible to duplicate experiments from one batch of solvent to another. A gas-phase chromatogram indicated traces of an impurity in the solvent. It was shown also that exchange was induced by light. Moreover, changes in the ultraviolet spectrum of (Pt en Br_4) dimethylformamide solutions in light were observed which did not occur in the dark. The exchange was sufficiently slow that it was possible to demonstrate that exchange did not occur rapidly in the exceptionally stable, lustrous, dark green crystals with the formula, Pt en Br_3 , which are formed by combination of the two compounds. Apparently, Pt^{II} and Pt^{IV} retain their identity in these crystals. Crystals of Pt en Br_3 were grown sufficiently large for single crystal X-ray analysis for the first time.

Discs of AgCl have been prepared by pressing the precipitated and dried compound under a vacuum. It has been found that at 300°C . diffusion of the silver occurs rapidly over distances of the order of the beta-particle range of Ag^{110} .

X-Ray Chemistry

1. Structure Determinations (R. E. Rundle and L. S. Bartell)

1.1 The Silver Perchlorate-Benzene Complex (R. E. Rundle)

This structure has been refined by least squares on the I.B.M. 650 computer using full three-dimensional data obtained by copper

radiation. The discrepancy factor, $R = \frac{F_{\text{obsd}} - F_{\text{calcd}}}{F_{\text{obsd}}} = 0.094$, is about as low as can be expected from visual estimates of intensities. Even more important, standard errors for bond distances in the benzene ring were only 0.01 to 0.02 Å, and other important distances had smaller deviations.

As previously reported, the silver ion sits above a C-C bond of the benzene ring in either of two positions. This C-C bond is the shortest in the benzene molecule. The shortest Ag-C distances to the benzene ring are 2.496 and 2.634 Å.

This structure has considerable significance for the theory of charge-transfer complexes.

1.2 The Carbides of Lanthanum, LaC_2 and La_2C_3 (R. E. Rundle and F. H. Spedding)

These carbides have been studied by neutron diffraction to obtain the carbon positions accurately. Though these structures are of common types and are important in uranium and transuranic chemistry, the carbon positions have not previously been determined for any compounds of these types.

Both compounds contain C_2 groups or C_2^- ions. The C-C distance in LaC_2 is 1.29 Å, while the C-C distance in La_2C_3 is 1.34 Å. Evidence can be cited supporting the idea that in LaC_2 there are essentially La^{+++} ions, C_2^- ions and an electron in the conduction band which also serves partly as an antibonding electron in C_2^- , lengthening the C-C bond above that of a triple bond. There is an even greater concentration of extra electrons in La_2C_3 , lengthening the C-C distance even more.

Preparation of CaC_2 and solid solutions of LaC_2 and CaC_2 is underway to test the above proposal further. The C-C distance in CaC_2 should be shorter than any of those reported, and should increase with the La concentration in solid solutions.

Data have been collected at Argonne National Laboratory using Dr. S. Sidhu's equipment.

1.3 Trimethylindium (R. E. Rundle)

Three-dimensional data for this compound have been refined on the I.B.M. 650, and with very pleasing results. The R value is ~ 0.10 , and standard deviations for In-C bonds are about $0.04\text{--}0.05 \text{ \AA}$, which seems very satisfactory considering the low relative scattering power of carbon in this compound. Since the rough structure reported in the previous semi-annual (ISC-834) is substantially correct, a further report of the structure will not be made.

1.4 Magnus Salts (R. E. Rundle)

A paper "On the Crystal Structures of the Magnus Salts, $\text{Pt}(\text{NH}_3)_4\text{PtCl}_4$ " by Masao Atoji, James W. Richardson and R. E. Rundle was published, J. AM. CHEM. SOC. 79, 3017 (1957).

Abstract

The crystal structure of the Magnus green salt, $\text{Pt}(\text{NH}_3)_4\text{PtCl}_4$, is tetragonal, $a = 9.03 \text{ \AA}$ and $c = 6.49 \text{ \AA}$, with space group $D_{4h}^{66} - P4/mnc$, and two formula units per unit cell, showing that the structure previously reported is incorrect. The planar $\text{Pt}(\text{NH}_3)_4^{++}$ and PtCl_4^{--} ions are stacked over one another along the c -axis with Pt-Pt distance,

$c/2 = 3.25 \text{ \AA}$. The bond distances of $\text{Pt-Cl} = 2.34 \text{ \AA}$ and $\text{Pt-N} = 2.06 \text{ \AA}$ are obtained with high accuracy by means of the generalized Fourier synthesis. The interatomic distances and the infra-red spectrum indicate no significant $\text{NH}\cdots\text{Cl}$ hydrogen bonding in this compound. The comparison between the radial distribution functions of this salt and its isomeric pink salt reveals that there is no direct Pt-Pt contact in the Magnus pink salt, but other distances are comparable.

1.5 Structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (R. E. Rundle)

A paper "Antiferromagnetic Ordering and Electron Structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as Determined from Nuclear Magnetic Resonance" by R. E. Rundle was accepted for publication in J. AM. CHEM. SOC.

Abstract

The nuclear magnetic resonance study of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ by Poullis and Hardeman is coupled with neutron diffraction data on proton positions to obtain the type of antiferromagnetic ordering in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and the distribution of the odd-electron in the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ "molecule". It is found that the odd-electron must be about 25% on each chlorine, 50% on copper. This distribution is consistent with a molecular orbital treatment of the complex, but not with crystal field theory or with Pauling's theory of directed valence in square copper complexes. The use of nuclear magnetic resonance in crystals as a probe for determining the distribution of magnetic electrons appears to be sensitive and deserving of further use.

1.6 Polynuclear Metal Carbonyls (R. E. Rundle)

Two papers "Polynuclear Metal Carbonyls. I. Structures of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ " by L. F. Dahl, Etsuro Ishishi and R. E. Rundle, and "Polynuclear Metal Carbonyls. II. Structures of Iron Tetracarbonyl by X-Ray Diffraction" by L. F. Dahl and R. E. Rundle were published as Communications to the Editor, J. CHEM. PHYS. 26, 1750 (1957), and J. CHEM. PHYS. 26 1751 (1957). A third paper in this series, "Polynuclear Metal Carbonyls. III. Infrared Analysis of Iron Tetracarbonyl" by L. F. Dahl and R. E. Rundle was accepted for publication as a Note in J. CHEM. PHYS.

1.7 Alkyl Phosphines (L. S. Bartell)

Preliminary structural results have been obtained for the alkyl phosphines, the diffraction patterns of which were obtained using the facilities of the University of Michigan. The carbon-phosphorus bond distances were found to be approximately:

<u>Compound</u>	<u>C-P Distance</u>
$\text{P}(\text{CH}_3)_3$	1.843Å
$\text{HP}(\text{CH}_3)_2$	1.849Å
H_2PCH_3	1.855Å

The trend of the bond distance with increasing methyl substitution is just opposite to that found for the analogous isoelectronic series of alkyl silanes. The bond angles, complete structures, and correlations with dipole moments have yet to be determined.

2. Electron Density in X-Ray Methods (R. E. Rundle)

A paper "On the Electron Density in X-Ray Methods" by Masao Atoji has been submitted to ACTA CRYST.

Abstract

A simple but useful relation between the curvature in an X-ray Fourier map and the temperature factor coefficient B is given. The approximate formulae for the peak shapes in the generalized Fourier map are discussed. The effect of the outer electrons on the atomic scattering factor is evaluated using the Thomas-Fermi method.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-687 John Gibson and J. M. Keller. Multi-Band Electrical Conduction.
- ISC 700 D. A. McCutchan and Glenn Murphy. The Stress-Strain Characteristics of Uranium.
- ISC-726 R. M. Henry and D. S. Martin. Comparative Yields of $\text{Fe}^{54}(\gamma, \text{pn})\text{Mn}^{52}$ and $\text{Fe}^{54}(\gamma, 2n)\text{Fe}^{52}$.
- ISC-729 Thomas Hendrickson and J. M. Keller. Ferromagnetic-Antiferromagnetic Phase Transitions.
- ISC-746 Joseph I. Genco, M. Griffel, F. R. Duke and L. D. Jennings. The (C-H) Bond Dissociation Energy in the Methyl Group of Toluene.
- ISC-757 Ames Laboratory Staff. Chemistry. Semi-Annual Summary Research Report. January-June, 1956.
- ISC-758 Ames Laboratory Staff. Physics. Semi-Annual Summary Research Report. January-June, 1956.
- ISC-759 Ames Laboratory Staff. Metallurgy. Semi-Annual Summary Research Report. January-June, 1956.
- ISC-777 Charles Apel and H. J. Svec. Kinetics of the Reaction Between Calcium and Water Vapor.
- ISC-779 Dale Gibbs and H. J. Svec. Kinetics of the Reaction Between Magnesium and Water Vapor.
- ISC-802 Ernest L. Koerner, Jr., Morton Smutz and H. A. Wilhelm. Separation of Niobium and Tantalum by Liquid Extraction.
- ISC-804 G. W. Eakins, B. J. Loupee, W. A. Rhinehart, G. Schupp and E. N. Jensen. A Method for Reducing Time-Jitter in the Output of a Single Channel Analyzer.
- ISC-812 K. A. Gschneidner, D. J. Beerntsen, R. W. Vest, J. A. Kingston and J. F. Smith. Tabulation, Bibliography, and Structure of Binary Intermetallic Compounds. II. Compounds of Beryllium, Magnesium and Calcium.
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APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
Dr. Gilbert Eggert Sandia Corp. Albuquerque, New Mexico	650 gm zinc-zirconium alloy
University of Minnesota Minneapolis, Minnesota	1 gm hafnium metal
University of Kansas Lawrence, Kansas	25 gm cerium metal
State University of Iowa Iowa City, Iowa	5 gm terbium oxide 2 gm special N ¹⁵ sample
Union Carbide Nuclear Company Oak Ridge, Tennessee	100 gm yttrium oxide 10 gm lanthanum oxide 10 gm neodymium oxide 10 gm samarium oxide 10 gm gadolinium oxide 10 gm dysprosium oxide 5 gm praseodymium oxide 1 gm ytterbium oxide 500 mg holmium oxide 500 mg erbium oxide 250 mg terbium oxide 250 mg thulium oxide 100 mg lutetium oxide 2 kgm dysprosium oxide 1 kgm ytterbium oxide 20 gm samarium metal 20 gm gadolinium metal
General Electric Research Laboratory Schenectady, New York	5 gm holmium metal
Brookhaven National Laboratory Upton, Long Island, New York	1 gm holmium oxide 1 gm thulium oxide 1 gm terbium oxide 1 gm lutetium oxide 4 pieces erbium metal 100 mg thulium metal
Princeton University Palmer Physical Laboratory Princeton, New Jersey	3 gm hafnium oxide
Lansen-Naeve Corp. New York 4, New York	10 gm ytterbium metal

<u>Destination</u>	<u>Item</u>
Oak Ridge Institute of Nuclear Studies Oak Ridge, Tennessee	1 gm holmium oxide 1 gm lutetium oxide
University of Kentucky Lexington, Kentucky	2 gm samarium oxide 2 gm neodymium oxide
Dr. John Owen The Clarendon Laboratory Oxford, England	2 specimens of gadolinium- yttrium alloy
Heavy Minerals Company Chattanooga, Tennessee	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm yttrium oxide 1 gm gadolinium 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
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	20 gm yttrium oxide 20 gm lanthanum oxide 20 gm praseodymium oxide 20 gm neodymium oxide 20 gm samarium oxide 20 gm gadolinium oxide 5 gm erbium oxide 5 gm ytterbium oxide 3 gm terbium oxide 3 gm dysprosium oxide 3 gm holmium oxide 3 gm thulium oxide 3 gm lutetium oxide
Institut für Physikalische Chemie an der Technischen Hochschule Vienna, Austria	10 gm hafnium metal
Dr. Frank Benner National Research Corp. Cambridge, Massachusetts	5 samples yttrium metal

<u>Destination</u>	<u>Item</u>
Purdue University Lafayette, Indiana	10 gm cerium oxide
Massachusetts Institute of Technology Cambridge, Massachusetts	2 gm yttrium oxide 2 gm lanthanum oxide 2 gm erbium oxide 3 gm dysprosium metal 1 gm gadolinium metal
Columbia-Southern Chemical Corp. Barberton, Ohio	50 gm xenotime sand
Physikalisches Institut der Technischen Hochschule Munich, Germany	1 gm terbium metal 1 gm holmium metal 1 gm thulium metal
National Bureau of Standards Washington 25, D. C.	2/10 gm each of the following oxides: cerium dysprosium holmium thulium ytterbium thorium
Universitetet Institute for Teoretisk Fysik Copenhagen, Denmark	1 gm dysprosium oxide 1 gm erbium oxide
Dr. Joseph Graca Iowa State College Ames, Iowa	9.7 gm yttrium oxide 13.45 gm erbium oxide 11.17 gm dysprosium oxide 200 ml each of the following 5% solutions: holmium ethylenediamine- tetraacetate yttrium chloride thulium chloride ytterbium chloride terbium chloride holmium chloride cerium chloride dysprosium chloride samarium chloride gadolinium chloride erbium chloride