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Semi-annual summary research report in chemistry

Ames Laboratory Staff

Iowa State College

F. H. Spedding

Iowa State College

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ISC-976

Semi-Annual Summary Research Report in Chemistry

For the period July - December, 1957

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

Previous research reports in this series are:

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ISC-69
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ISC-530
ISC-574
ISC-606
ISC-643
ISC-706
ISC-757
ISC-834
ISC-902
1. Separation of Rare Earths by Ion-Exchange (F. H. Spedding and J. E. Powell)*

1.1 Pilot Plant Separations

Research and development was continued on the six-inch and four-inch series of ion-exchange columns and nearly ideal conditions were determined for use in resolving Lu, Yb, Tm, Er and Ho mixtures with HEDTA after a preliminary separation from Y and the light rare earths with EDTA. Since this work was begun, the overall recovery of Lu₂O₃ per thousand pounds of xenotime R₂O₃ increased from 1300 grams to 3600 grams. This notable boost in yield was due to the discovery that hydrogen ion in the copper retaining bed aided in the retention of Lu during the preliminary short elution with EDTA. Subsequent elution with HEDTA or hydrogen-form resin allows recovery of better than 95% of the available Lu in a purity greater than 99.9%. The remainder of the Lu is contained in binary Lu-Yb mixtures. Most of the resolution of Lu is carried out on six-inch columns at 200 ml per minute using 5 grams of HEDTA per liter at a pH of 7.5, then the Lu and the Lu-Yb overlap is shunted onto four-inch columns at 50 ml per minute and final recovery is performed at 25 ml per minute.

* Names indicate group leaders in charge of work.
The first several Lu samples generally contain Pb, but this is removed prior to recovery of the Lu by bubbling \( H_2S \) through the solution and filtering off the PbS which forms.

Table I is a compilation of noteworthy rare earth fractions produced from xenotime concentrate during the period of this report. The 9,227 grams of \( \text{Tb}_4\text{O}_7 \) is the largest amount of this scarce element that we have produced to date.

Table I.

<table>
<thead>
<tr>
<th>Material</th>
<th>Wt. in grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.9% ( \text{Lu}_2\text{O}_3 )</td>
<td>5,549</td>
</tr>
<tr>
<td>99.9% ( \text{Yb}_2\text{O}_3 )</td>
<td>50,687</td>
</tr>
<tr>
<td>99.9% ( \text{Tm}_2\text{O}_3 )</td>
<td>7,103</td>
</tr>
<tr>
<td>99.9% ( \text{Er}_2\text{O}_3 )</td>
<td>53,182</td>
</tr>
<tr>
<td>99.9% ( \text{Ho}_2\text{O}_3 )</td>
<td>26,493</td>
</tr>
<tr>
<td>99.9% ( \text{Dy}_2\text{O}_3 )</td>
<td>89,363</td>
</tr>
<tr>
<td>99.9% ( \text{Y}_2\text{O}_3 )</td>
<td>14,348</td>
</tr>
<tr>
<td>99.9% ( \text{Tb}_4\text{O}_7 )</td>
<td>9,227</td>
</tr>
<tr>
<td>99.9% ( \text{Gd}_2\text{O}_3 )</td>
<td>4,429</td>
</tr>
</tbody>
</table>

1.2 Determination of Rare Earth Chelate Solubilities

Chelate compounds of rare earths formed with both EDTA and HEDTA have been isolated in pure form and the solubilities of the individual species are being determined at various temperatures in order to establish the working range for both EDTA and HEDTA eluants. Complete data are not yet available but it is apparent that the compound
HR(EDTA) is much less soluble than NH₄R(EDTA) and that the solubility of HR(EDTA) increases somewhat from HLa(EDTA) to HLu(EDTA). This explains the precipitation of the light rare earth mixtures at 10 grams per liter concentrations of EDTA, whereas the heavy rare earths can be separated with an eluant of this composition. Lanthanum forms a precipitate on the resin bed even at a concentration of only 4.5 grams per liter at pH 8.4.

In the case of HEDTA, the solubility of R(HEDTA) is fairly high for the middle rare earth chelates Nd(HEDTA) and Sm(HEDTA). Lu(HEDTA) and the other heavy rare earth chelates are not nearly as soluble. Whereas a maximum of 5 grams of HEDTA per liter can be used to elute Lu, Yb and Tm at pH 7.5, it is possible to use concentrations up to 30 or 40 grams with Pr, Nd and Sm. An economical separation of monazite components appears to be possible at concentrations of HEDTA around 10-15 grams per liter, but actual runs will be necessary in order to judge the feasibility of using such conditions and recovering the reagent in good form for reuse. There is evidence that La(HEDTA) and Ce(HEDTA) are much less soluble than Pr(HEDTA), Nd(HEDTA) and Sm(HEDTA).

1.3 Order of Elution of Rare Earths and Common Elements with EDTA, HEDTA, DTPA and Citric Acid

The elution sequence of rare earths and common elements with various chelating agents is being investigated. It is possible that certain separations can be achieved more economically by using several reagents one after the other instead of a single reagent during a given elution of crude material.
A report (ISC-1014) by Lyle K. Matson and F. H. Spedding entitled "Elution of Copper and Neodymium from a Cation-Exchange Resin with Ammonia-Ethylenediaminetetraacetic Acid Solutions" is being distributed.

Abstract

Several experiments were performed eluting neodymium bands behind copper bands with dilute ammonia-ethylenediaminetetraacetic acid (EDTA) solutions. When there was a certain amount of ammonium and hydrogen mixed homogeneously with the copper in the resin, very flat elution curves were obtained. Thus, the concentrations of the ions in solution were constant throughout the band, and the composition of the resin changed very little during the elution.

The charge balance equations, several equilibria, and the material balance equations in solution were indicated for both the copper band and the neodymium band. Equations were derived for the material balance at the boundary between the mixed copper band and the ammonium band formed behind the copper band. For these equations to be obeyed, one must have flat elution curves. Two experiments were found to deviate only slightly from this ideal system.

Equations were also derived for the material balance at the boundary between the ammonium band and the mixed neodymium band which forms between the mixed copper band and the ammonium band.

Since essentially all of the complexing agent forms one-to-one complexes with the copper band eluate, the concentration
of the total copper in solution is equal to the total EDTA concentration plus the cupric ion concentration. The hydrogen ion concentration can be calculated from the equilibria set up between the copper-EDTA complexes and hydrogen.

Since part of the EDTA is not complexed with the neodymium, the mass-action stability constant of the neodymium-EDTA complex was estimated from the column data, the ion-exchange constant for neodymium and ammonium, and the stability constants of the hydrogen complexes of EDTA.

The experiments described in this report establish the groundwork which is necessary to design an ideal elution system. If conditions can be established so that the retaining bed is completely compatible with the eluant and flat-top elution curves can be obtained by the choice of suitable boundary conditions, then a powerful tool is available for determining the equilibrium constants of complex ions in solution. Having established this system, one has \( n \) equations and \( n \) unknowns and can calculate a constant for each variable determined experimentally. By determining the mass action constants at various ionic strengths and equivalent fractions on the resin, the activity coefficient ratios for various pairs of ions can be determined as a function of these variables.

1.4 Separation of Yttrium, Magnesium and Calcium

An ion-exchange process for separating yttrium, magnesium and calcium is being investigated. The mixture is obtained as waste in the Laboratory's yttrium production program, in which magnesium is
used to lower the melting point of the metal phase. The line of attack which has been rather successful is to selectively elute yttrium with HEDTA leaving calcium and magnesium behind. Since the HEDTA can be recovered for reuse, the reagent cost is relatively low.

2. **Properties of Rare Earth Salts** (F. H. Spedding)

   A report (ISC-941) "Relative Apparent Molal Heat Contents of Some Rare Earth Chlorides and Nitrates in Aqueous Solutions" by Robert E. Eberts and F. H. Spedding is being distributed.

   **Abstract**

   An adiabatically jacketed differential calorimeter, with a sensitivity of $5 \times 10^{-4}$ calories per millimeter pen displacement of a recording potentiometer, was used to measure the heats of dilution of solutions of lanthanum chloride, ytterbium chloride, lanthanum nitrate and ytterbium nitrate. The concentrations of the solutions ranged from about 0.10 molal to about 0.25 molal. The heats of dilution, which ranged from about 0.05 to 2.0 calories, were measured to within a few thousandths of a calorie.

   The "short-chord" method of treating the heat of dilution data was used for the very dilute concentration range. This treatment yielded limiting equations for the concentration dependence of $\Phi_1$, which is the slope of a $\phi_1$ versus $m^{1/2}$ plot. Lanthanum chloride and nitrate gave limiting slopes of 6630 and 6230, respectively, compared to the theoretical limiting slope of 6925 as predicted by the Debye-Hückel interionic attraction theory. However, the ytterbium salts showed anomalous behavior in that the plot of $\Phi_1$ versus $m^{1/2}$ exhibited a maximum at about
\( m^{1/2} = 0.045 \), dipping away from the theoretical limiting value below this concentration. The limiting slope was 247 for ytterbiunm chloride and -1393 for ytterbium nitrate. The anomalous behavior has been tentatively explained by the presence of some polymeric type species which form when the sample solution is diluted.

Empirical expressions were derived for the relative apparent molal heat content of solute, \( \mathcal{Q}_L \); the relative partial molal heat content of solvent, \( \mathcal{L}_1 \); and the relative partial molal heat content of solute, \( \mathcal{L}_2 \). Comparing the data to the predictions of the Debye-Hückel theory, it was found that the \( \mathcal{Q}_L \) values for the lanthanum salts began deviating from the theoretical curves at a concentration of about 0.001 molal. The data for the ytterbium salts did not agree with the theory due to their anomalous behavior in the very dilute concentration range.

An isothermally-jacketed calorimeter, utilizing a transposed bridge type thermometer with a sensitivity of about 3.5 \( \times \) 10\(^{-4} \) degrees per microvolt, was used to measure the heat of solution of neodymium chloride hexahydrate. From the values of the integral heats of solution at various molalities, the relative apparent molal heat content was calculated for the neodymium chloride in the solutions. The \( \mathcal{Q}_L \) values thus obtained were in agreement with those previously reported from heats of dilution, but not with those derived from heats of solution of anhydrous neodymium chloride. Two possible explanations have been offered for the discrepancy in the previous heat of solution data. The first is based on a slow type reaction which might
accompany the dissolution of the anhydrous salt; the second depends upon the hydrolysis of the rare earth ion when the salt is dissolved.

A paper "Heats of Dilution and Related Thermodynamic Properties of Aqueous Rare Earth Salt Solutions at 25°C; Integral Heats of Solution of NdCl₃" by F. H. Spedding, A. W. Naumann and R. E. Eberts, and based in part on report ISC-941, has been submitted for publication in J. AM. CHEM. SOC.

3. The Separation of N₁⁴ and N₁⁵ by Ion-Exchange (F. H. Spedding and J. E. Powell)

A small pilot plant for separating N₁⁴ and N₁⁵ has continued in operation.

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

4.1 Low-Oxygen Metal

Our study on the preparation of the rare earth metals has centered on methods of lowering the oxygen content of the product metals, and as calcium and the rare earth fluoride are the only raw materials entering into the reaction, we are studying methods of lowering the oxygen content of these reactants. The use of ammonium bifluoride as the fluorinating agent to convert the rare earth oxides to the trifluorides appears to give a good quality salt, but since the preparation is carried out at a relatively low temperature (275-350°C), the salt has an open, porous structure on which a considerable quantity of oxygen-containing gases (O₂, CO₂, H₂O) adsorbs. A vacuum sintering of this salt at 800°C removes much of this gas and results in the lowest oxygen content of any fluoride we have prepared.
To eliminate oxygen from the calcium, we have taken pure, redistilled calcium prepared by Metallurgy Group V and redistilled this into a tantalum reaction crucible, where it was melted down in situ. To prepare yttrium using this calcium, the vacuum sintered yttrium fluoride was added to the reaction crucible, and the reduction was effected in the usual manner. The yttrium metal resulting from this reaction was found to have an oxygen content of 780 ppm, which is about 700 ppm lower than our best previous effort.

Several attempts were made to lower the oxygen content of our yttrium by vacuum arc melting the metal after adding carbon to it. Some evolution of CO was evident during the melting, but the overall effect was a higher carbon content with only a small lowering of the oxygen content.

4.2 Europium

A paper "The Preparation and Properties of Europium" by F. H. Spedding, J. J. Hanak and A. H. Daane was submitted for publication in J. METALS.

Abstract

A quantity of 70.4 grams of europium metal of high purity was prepared by heating Eu$_2$O$_3$ with lanthanum metal in vacuo at 1200°C. The following properties were determined:

- Melting point: $826 \pm 10^\circ$C
- Boiling point (calculated): $1489^\circ$C
- Lattice constant at 298°K (bcc lattice): $4.5820 \pm 0.0004\,\text{Å}$
Density at 298°C (calculated) .......... 5.245 g/cm³
Heat of sublimation at 298°K .......... 42,066 ± 75 cal.
Compressibility at 300°K .......... 6.99 x 10⁻⁶ cm²/kg
Electrical resistivity at 298°K .......... 81.3 x 10⁻⁶ ohm-cm
Temperature coefficient of electrical resistance at 298°K .......... 0.00480 (°C)⁻¹
Coefficient of thermal linear expansion
293 to 1053°K ................. 26 x 10⁻⁶ (°C)⁻¹
Change of volume on melting .......... +4.8 pct
The vapor pressure was determined as a function of temperature. The resulting data were fitted to a straight line, yielding the expression

$$\log P_{nm} = \frac{-8.982 + 16}{T} + 8.160 \pm 0.027,$$

Europium reacts rapidly in moist air, following a linear law, Eu(OH)₂ • H₂O resulting.

5. Properties of Rare Earth Metals

5.1 High Temperature Transformation in Cerium (F. H. Spedding and A. H. Daane)

The high temperature allotropic modification of the light rare earth metals, which was first detected in this Laboratory, has been studied by various methods in an effort to determine the nature of this form and these metals. Previous X-ray diffraction studies did not give patterns that permitted identification of the crystal structure of this allotrope, but recent work with cerium in a high temperature powder camera has shown the metal to be body-centered
cubic at 750°C with a lattice constant of 4.09 Å. This represents a 2% increase in density in transforming from the room temperature face-centered cubic form to the body-centered cubic structure.

5.2 Crystal Structures of Some Rare Earth Carbides (F. H. Spedding, A. H. Daane and R. E. Rundle)

A paper "The Crystal Structure of Some of the Rare Earth Carbides" by F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane was submitted for publication in J. AM. CHEM. SOC.

Abstract

A study of the rare earth-carbon systems has been made. The existence of the reported LaC₂, CeC₂, PrC₂, NdC₂ and SmC₂, and the Ce₂C₃ has been confirmed. The existence of the tetragonal CaC₂ type structure for the other rare earth dicarbides has been shown. The lattice constants of these compounds decrease in a regular fashion, except for the YbC₂, whose lattice parameters lie between those of HoC₂ and ErC₂. The body-centered cubic Pu₂C₃ type structure has been found to exist in all of the rare earths from La to Ho. The lattice constants decrease in a normal manner, except for Ce₂C₃, whose lattice parameter is smaller than would be expected. A new rare earth carbide has been found, R₃C, which is similar to the face-centered cubic NaCl type structure, except that it is deficient in carbon. This compound appears to exist over a range of composition, i.e., in the case of yttrium it was found to vary from YC₀.25 to YC₀.40. This compound has been found to exist in the rare earth-carbon systems of Sm to Lu, and the lattice parameters decrease in a regular manner. No X-ray evidence was found for
the existence of this lower carbide in the La-, Ce-, Pr- and Nd-C systems.

A paper "The Structures of Lanthanum Dicarbide and Sesquicarbide by X-Ray and Neutron Diffraction" by Masao Atoji, Karl Gschneidner, Jr., A. H. Daane, R. E. Rundle and F. H. Spedding was submitted for publication in J. AM. CHEM. SOC.

Abstract

Lanthanum dicarbide, with a structure of the calcium carbide type, is body-centered tetragonal, \( a = 3.934 \pm 0.002 \text{ Å} \), \( c = 6.572 \pm 0.003 \text{ Å} \). The C-C distance of the \( C_2 \) group is \( 1.28 \pm 0.02 \text{ Å} \), intermediate between double and triple bond.

C-C distances.

Lanthanum sesquicarbide is body-centered cubic with the plutonium sesquicarbide (\( D_{5c} \)-type) structure, and a lattice constant between 8.803 and 8.819 Å. It also contains \( C_2 \) groups but with a C-C distance (\( 1.32 \pm 0.03 \text{ Å} \)) about that of a double bond. A possible relation between electron density and C-C distance is noted.

Carbon positions in both structures were determined by neutron powder data, and were refined by a statistical method based on the least squares method.

5.3 Thermal Properties of Lutetium (L. D. Jennings and F. H. Spedding)

The work on the heat capacity of lutetium has been completed. We find that, at 300°K, the enthalpy function, \( H/T \), has the value 21.51 joules/mole-deg, and that the entropy has the value 51.23. This value of entropy corresponds to an average Debye temperature of 166.4.
5.4 Magnetic Properties (L. D. Jennings and F. H. Spedding)

We have completed the magnetic moment studies of erbium metal and have interpreted the data according to the theory of Pratt. This theory attributes the ordering in the rare earth metals to the interaction between the 4f electrons and the conduction electrons. Our results show that the conduction electron susceptibility is increased 17-fold at room temperature because of this interaction.

Using the mutual inductance method, we have measured the initial susceptibility of terbium metal and of CrF$_3$ in an alternating field of about one gauss. These experiments were motivated by the fact that these two substances had previously been found to have anomalies in their heat capacities which were unobserved in the available magnetic data.

For terbium, the heat capacity showed a lambda-type anomaly near 228°K, with a small shoulder near 220°K. Thermal hysteresis was displayed within a 10° interval centered on 220°K. In addition, there was a lambda anomaly near 2.4° which has been tentatively attributed to an impurity. We have observed effects in each of these anomalous regions with the mutual inductance method. At 2.5°K, there is a decrease in the slope of the curve of $M'$ (the real part of the mutual inductance) versus temperature. $M''$ (the imaginary part) has a very sharp increase. These results lead one to believe that the electrical conductivity undergoes an anomaly near 2.5°K. Above this temperature, $M'$ rises smoothly to a maximum near 218°K.

---

falls to a minimum near 225°K and rises to a maximum again near 228°K. Above 234°K, $M'$ follows a Curie-Weiss law with a Curie temperature of 228°. $M''$ has the same behavior as does $M'$ in this temperature region. Thermal hysteresis was found in the same region as in the heat capacity measurements. However, a time effect was also observed in the temperature region 100° to 200°K. The time taken for the sample to attain a constant susceptibility after the temperature was changed became appreciable in this region of temperature. At 150°K this time was much longer than one hour and measurements were not taken in this temperature region. No such time effects were observed when the heat capacity measurements were being taken.

The experiment on the CrF$_3$ revealed no discontinuity in the susceptibility near 45°K, the temperature of the lower heat capacity anomaly. A sharp drop in the susceptibility was observed at 69°K, however.

The measurements on both terbium and CrF$_3$ were made on a cylindrical sample 1 inch long and 1/4 inch in diameter. The frequency was 34 cycles per second.

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

Results of alloy studies of yttrium with some common metals may be summarized as follows:

(a) Yttrium - Nickel

A eutectic occurs at 18-20 wt % Ni, between Y and a compound, probably Y$_2$Ni. This eutectic melts at about 950°C.

(b) Yttrium - Manganese

A eutectic, melting at 925°C, was found at
20 to 25 wt % Mn. There is at least one intermetallic compound in this system.

(c) Yttrium - Copper

The compounds YCu, YCu$_2$, YCu$_4$ and YCu$_6$ appear to exist in this system, with YCu and YCu$_4$ decomposing by a peritectic reaction. Eutectics have been observed at 30, 75 and 92 at % Cu, the latter melting at 850°C.

The lanthanum - boron system appears to contain only two compounds, LaB$_4$ and LaB$_6$, and evidences little or no solid solubility of boron in lanthanum.

7. Rare Earth Halides (A. H. Daane and F. H. Spedding)

The melting points of some rare earth chlorides have been determined:

- YCl$_3$ - 709°C
- CeCl$_3$ - 817
- LaCl$_3$ - 862
- NdCl$_3$ - 758
- DyCl$_3$ - 647
- TmCl$_3$ - 824
- LuCl$_3$ - 905

A study was made to determine the feasibility of preparing yttrium metal by thermally decomposing yttrium iodide. The study revealed the following:

Melting point of YI$_3$ = 965-972°C
Vapor Pressure of YI₃

$$\log P_{\text{mm}} = -11.706 \pm 330 + 9.540 \pm 0.0378$$

$$\Delta H \text{ Sublimation} = -53.6 \pm 1.5 \text{ Kcal}$$

No detectable decomposition of YI₃ at 1650°C.

8. **Scandium Ore Treatment** (A. H. Daane and F. H. Spedding)

To obtain scandium for a metallurgical study of this element, 700 grams of thortveitite ore were obtained from Norway. While this ore is rich in Sc₂O₃ (~33%) its high silica content (46%) makes it particularly difficult to break down so that the scandium may be extracted. The following procedure was devised and was found to be very successful:

1. Mix powdered ore with ammonium bifluoride and heat:
   $$(\text{Sc}_2\text{O}_3) (\text{Si}_2\text{O}_3) + \text{NH}_4\text{HF}_2 \rightarrow \text{ScF}_3 + \text{H}_2\text{O} + \text{SiF}_4.$$ 

2. Reduce ScF₃ with calcium:
   $$\text{ScF}_3 + \text{Ca} \rightarrow \text{Sc} + \text{CaF}_2.$$ 

3. Dissolve impure scandium (~70% Sc, with aluminum, iron and the other rare earths as the major impurities) for further purification.¹

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

9.1 **Transport Studies in Fused Salts** (F. R. Duke)

9.1.1 **Potassium Chloride - Lead Chloride System**

A paper "Transport Numbers and Ionic Mobilities in the System KCl-PbCl₂" by Frederick R. Duke and Richard A. Fleming has been submitted for publication in J. ELECTROCHEM. SOC.

¹J. P. Marble and J. J. Glass, American Mineralogist 27, 696 (1942).
Abstract

Values of ionic transport numbers and ionic mobilities were determined for the fused system KCl-PbCl₂. Cation transport numbers of 0.24 (525°C) and 0.78 (850°C) were found for PbCl₂ and KCl, respectively. In each mixture studied, t₋ deviated positively and both t₊ and t₊₊ deviated negatively from linearity when plotted against equivalent fraction. The initial very rapid depression of total equivalent conductance from that of pure KCl, caused by addition of small amounts of PbCl₂, was found to be due to the depression of the ionic conductance of K⁺ rather than complexing between Pb⁺⁺ and Cl⁻ as had been previously supposed. The relative mobilities of K⁺ and Pb⁺⁺ were compared with those of Li⁺ and Pb⁺⁺ in the system LiCl-PbCl₂, calculated from available literature data.

A report (ISC-944) on this work is being distributed.

9.1.2 Nitrate Systems

A paper "Transport Numbers of the Pure Fused Salts, LiNO₃, NaNO₃ and AgNO₃" by Frederick R. Duke and Boone Owens was submitted for publication in J. ELECTROCHEM. SOC.

Abstract

The mobilities of the ions in some molten alkali nitrates and silver nitrate are determined. It is shown that the transport numbers for these uniunivalent salts follow a radius ratio equation, \[ t₊ = \frac{r₊}{r₊ + r₋} \], to a good first approximation.

A report (ISC-992) on this work is being distributed.

9.2 Complex Ions in Fused Salts (F. R. Duke)

A paper "Complex Ions in Fused Salts" by F. R. Duke and M. L. Iverson was submitted for publication in J. PHYS. CHEM.
Abstract

The complex formation constants for a series of bivalent metal halides were determined using fused KNO$_3$ - NaNO$_3$ eutectic as solvent. The method involved measuring the increase in solubility of the slightly soluble metal chromate as halide ion was added.

A report (ISC-943) on this work is being distributed.

9.3 Solubility of Water in Fused Salts

9.3.1 Solubility of Water Vapor in Fused Alkali Nitrates

(F. R. Duke)

A paper "The Solubility of Water Vapor in Fused Alkali Nitrate Mixtures and in Lithium Perchlorate" by Frederick R. Duke and Arthur S. Doan has been accepted for publication in IOWA STATE COLLEGE J. SCI.

Abstract

In the temperature range 240 to 290°C water vapor is insoluble in NaNO$_3$-KNO$_3$ mixtures. When LiNO$_3$ is added, however, the solubility is readily measurable. The heat of solution was found to be $-13 \pm 4$ kcal/mole of H$_2$O. Solubility of the water vapor varied approximately as the square of the mole fraction of Li$^+$. The solubility was also determined in pure LiClO$_4$.

9.3.2 Solubility of Water in Molten Alkali Chlorides (J. D. Corbett)

A paper "The Solubility of Water in Molten Mixtures of LiCl and KCl" by William J. Burkhard and John D. Corbett was published in J. AM. CHEM. SOC. 79, 6361 (1957).

Abstract

The solubility of water in molten mixtures of 50.0, 53.0,
60.0 and 68.6 mole % LiCl in KCl has been determined at 480°, and 50.0 and 60.0% at 390°, over the pressure range 3 to 26 mm. The solubility follows Henry's law to 18 mm. at 480° and 14 mm. at 390°. The reciprocal Henry's law constants are, respectively, 14, 11.8, 11.3 and 10.8 micromoles water per mole LiCl per mm. at 480° and 30.0 and 30.5 at 390°. Heats of solution of -8 and -11.0 kcal. mole⁻¹ are calculated for the 50 and 60% compositions, respectively. The solubility at 480° exhibits a sharp upward break beyond 18 mm. due to hydrolysis of the LiCl at the higher water pressures. At 390° no such behavior is observed, but only a slight upward deviation above about 14 mm. The uniqueness of the lithium ion in this process, and the unusual tenacity with which water is retained by the melt are discussed.

A report (ISC-929) on this work has been distributed.

10. The Gallium(I) Oxidation State (J. D. Corbett)

A paper "The Lower Oxidation Sates of Gallium. II. The Ga₂Br₄-GaBr System" by John D. Corbett and Alex Hershaft has been accepted for publication in J. AM. CHEM. SOC.

Abstract

The compound Ga₂Br₄ is dimorphic, with melting points of 153 and 164.5° for the α-(metastable) and the β-forms, respectively. Reduction of this compound with gallium metal at 170° gives a liquid containing 31.4 mole % GaBr in Ga₂Br₄; the monobromide is stable in the solid state below the syntectic temperature of 164°. Complete reduction to GaBr(s) below this temperature is limited by kinetic effects to about 75% GaBr. Addition of AlBr₃
to the liquid Ga-Ga$_2$Br$_4$ system allows complete reduction of Ga(III) to Ga(AlBr$_4$). Isomorphism between each of the two crystalline forms of Ga(AlBr$_4$) and Ga$_2$Br$_4$ shows the latter compound to be Ga(GaBr$_4$).

11. **The Bismuth(I) Oxidation State (J. D. Corbett)**

Considerable effort has been devoted to the preparation of pure bismuth(I) chloride. Reaction of metal and trichloride liquid phases below the syntectic temperature of 325°C (see ISC-902) gives a maximum of about 80-85 mole % BiCl$_1$, compared to 66% directly from the all-liquid system at 340°C. Subsequent volatilization of BiCl$_3$ therefrom gives ca. 98% BiCl, although the process is very tedious. Extraction of the finely-ground BiCl-BiCl$_3$ mixture batchwise in the dry box with anhydrous benzene or ether is about equivalent in results. A Soxhlet extraction with ether appears much more satisfactory. Liquid water, acetonitrile and dimethylformamide all disproportionate the compound to bismuth and the trichloride at room temperature.

Needlelike single crystals of BiCl can be readily grown in a sealed tube at 300° to 320°C. These have been examined by X-ray diffraction, and have been found to be of orthorhombic symmetry, with unit cell dimensions of 22.9 x 15.0 x 8 Å, space group P$_{21}$ or P$_{2}$, with Z ≈ 50. Some sort of polymerization may be expected for BiCl from its diamagnetism. The crystals are stable in air.

12. **The Niobium Iodides (J. D. Corbett)**

The following is the abstract of the paper "Preparation of the Niobium(IV) and Niobium(III) Iodides" by John D. Corbett and
Pyrtle X. Seabaugh. This paper has been accepted for publication in J. INORG. NUCL. CHEM.

Abstract

Conditions are reported for (1) the preparation of niobium(V) iodide, (2) the preparation and sublimation of niobium(IV) iodide by thermal decomposition of the pentaiodide and (3) the subsequent disproportionation to niobium(III) iodide. Properties and powder patterns are given for the three iodides.

13. Heat Capacity of CrF$_3$ and CrCl$_3$ (L. D. Jennings)

A paper, "The Heat Capacity of CrF$_3$ and CrCl$_3$ from 15° to 300°K" by Wilford N. Hansen and Maurice Griffel has been accepted for publication in J. CHEM. PHYS.

Abstract

The heat capacities of CrF$_3$ and CrCl$_3$ have been measured over the temperature range from 15 to 300°K. CrF$_3$ has two peaks; the upper peak has its maximum at 69.8°K, and is associated with a known magnetic transition. The lower peak has its maximum at 45.6°K, and has not been correlated with magnetic phenomena. The total magnetic entropy is divided almost equally between the two. CrCl$_3$ has a single peak at 16.8°K which is associated with a ferromagnetic transition.

For CrF$_3$, S$_{298.15}$ = 22.44 eu; for CrCl$_3$, S$_{298.15}$ = 29.38 eu. Other thermodynamic functions are tabulated.

14. Surface Tension Measurement (R. S. Hansen)

A paper, "Extension of the Vibrating Jet Method for Surface Tension Measurement to Jets of Non-Uniform Velocity Profiles" by
Robert S. Hansen, Mary E. Purchase, Terry C. Wallace and Robert C. Woody has been accepted by J. PHYS. CHEM.

Abstract

The approximate treatment of Schiller for flow through pipes has been applied to furnish an initial velocity profile for liquids flowing from a cylindrical orifice, and the subsequent velocity profiles and dependence of surface age on axial distance from the orifice have been established. The principle of similitude has been applied to the problem of calculation of surface tensions from measurements on vibrating jets of non-uniform velocity profiles, and an empirical correction factor has been established experimentally.

15. Isotope Fractionation in the Nitric Oxide-Nitrosyl Chloride System (R. Schaeffer)

Studies of the equilibrium

\[ ^{15}\text{NO} + ^{14}\text{NOCl} \rightleftharpoons ^{14}\text{NO} + ^{15}\text{NOCl} \]  

were completed. Precise values for the equilibrium constant of (1) were obtained by measuring the \( ^{15}N/^{14}N \) ratio in both the NO and NOCl after isotopic equilibration. The average measured value of 1.005 was substantially smaller than the theoretical value of 1.015 previously calculated from spectroscopic data. The experimental value obtained from room temperature is in good agreement with the value \( K = 1.013 \) at -50°C measured by workers at Oak Ridge.

One of the most attractive features of the system that led to its investigation was the prediction that essentially no decomposition voltage would be necessary to release NO from the NOCl at
the bottom of an isotope fractionation column. This prediction was subjected to experimental test and found to be correct within the error of the determination. Although the system retains its attractiveness for the separation of nitrogen isotopes insofar as the chemical cost of the process is concerned, the low value for the separation factor probably means that it cannot be made to compete with the Nitrox process. Further study of this system will be left to the group at Oak Ridge.


The number of secondary reactions that can occur in assaying nitrogen in the mass spectrometer has been extended. In addition to forming N₂H⁺ when mixtures of N₂ and hydrogen-containing gases are introduced into our instruments, N₂H₂⁺ is also formed. This molecular species arises by a secondary reaction in the electron gun of the ion source. In "wet" N₂, its presence accounts for our inability to observe a distribution among the 28⁺, 29⁺ and 30⁺ ion currents which corresponds to that expected for equilibrium mixtures of N₂²⁸, N₂²⁹ and N₂³⁰. There is now some evidence, although not completely conclusive, that N₂²⁸H₂ is not easily pumped out of the ion source, being more tightly adsorbed on the elements of the source than is molecular N₂. Reasons for this are obscure at present.

When N₂ is introduced into the mass spectrometer at high pressures, N₃⁺ and N₄⁺ are definitely formed with the latter being more abundant. The number of N₄⁺ ions observed is linearly dependent upon p² so this ion must arise by a secondary process. This was unexpected on the basis of a currently held hypothesis which explains the presence of such "dimeric" ions in mass spectra on the
basis of charge exchange on \( \text{N}_2^{++} \) in the space between the ion source and magnetic field. Formation of \( \text{N}_4^+ \) is endothermic and one would ordinarily not expect to observe its presence in the mass spectrometer. However a small number of \( \text{N}_2^+ \) ions formed in the source may be sufficiently excited to afford enough energy to form \( \text{N}_4^+ \) when collision occurs between \( *\text{N}_2^+ \) and \( \text{N}_2^0 \).

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

A paper, "The Absolute Abundance of the Nitrogen Isotopes in the Atmosphere and Compressed Gas from Various Sources" by Gregor Junk and Harry J. Svec was submitted for publication in GEOCHIM. ET COSMOCHIM. ACTA.

**Abstract**

The absolute abundance of the isotopes in atmospheric and commercial compressed \( \text{N}_2 \) 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° 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
$(NH_4)_2SO_4$ 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 $N_2^{29+}/N_2^{28+}$ ratio for the contribution of the background at these mass positions was developed.


The mass spectral data on chromyl chloride and chromyl fluoride and on the mixed halide, $CrO_2ClF$, have been completed. Some interesting observations have been made on the mixed halide. The appearance potential of the parent molecule ion, $CrO_2ClF$, has been determined. The fragmentation of this molecule has also been measured for various electron energies. Dimeric species have been observed. The equilibrium constant for the reaction

$$CrO_2Cl_2 + CrO_2F_2 \rightleftharpoons 2CrO_2ClF$$

at room temperature has been found to be $1.8 \pm 0.2$. The infra-red spectrum of $CrO_2ClF$ shows a characteristic absorption band at $750$ cm$^{-1}$.

19. Metal-Water Vapor Reactions (H. J. Svec)

The reaction between yttrium and water vapor follows a logarithmic law and appears to be pressure independent at water vapor pressures below 72 mm Hg. The reaction rate at $720^\circ$C and 55 mm H$_2$O pressure is just a little faster than the comparable Ca reaction at $50^\circ$C.

20. LCAO MO Theory of Pi-Electron in Organic Molecules (K. Ruedenberg)

A theoretical investigation of the benzene molecule resulted in a unique determination of the best possible atomic orbitals for a LCAO MO treatment including all neighbor atom interactions. It
proved possible to give a consistent account for the ultra-violet spectra of benzene, the ionization potential and the electron affinity of carbon in its valence state. Interesting simplifications of the bond orders of pi-electrons were also discovered.

It is further possible to formulate the theory generally for any hydrocarbon. Coding for the ISC electronic computer (IBM-650) is in progress; this code should deal with any hydrocarbon containing up to 40 atoms.

Pyrometallurgy

1. Separation of Fuel and Fission Products in a Packed Column
(A. F. Voigt)

During this period considerable effort has been given to the study of the separation of fission products from uranium by the process of pouring the molten fuel through a packed column of graphite or refractory oxide. Solid-molten metal reactions have been shown to be effective in removing fission products from uranium. In view of this it was felt that an attempt should be made to find out if a brief contact with an extensive surface would be sufficient to bring about removal. Such a contact could be achieved by passing the molten metal through a packed column in a refractory tube. One advantage would be that the column packing could be a mixture of several solids which might be able to remove all of the components of the fission product mixture better than a single solid.

Before doing extensive experiments with tracers it seemed necessary to find out if the molten metal would be recovered in
adequate yield. The columns were made of graphite or alumina tubes 3/4" in diameter and packed with 1/8 - 1/4" pieces of the same material to a depth of 8 - 10". The molten metal used was in the form of the U-Cr eutectic. Columns and alloys were prepared in this Laboratory.

The columns were out-gassed in a vacuum at 1000°C before admitting the sample. The pouring operation was done under vacuum, 5 x 10^{-4} to 5 x 10^{-2} mm Hg pressure of air or helium. Samples of 100 to 300 grams of the alloy were poured through the columns at temperatures from 900-1100°C which were maintained for times varying from 0.5 to 2.5 hours.

In experiments which can be considered typical, the yield of metal through the column varied from 65 to 85%. In nine such runs the average yield was 74% with a standard deviation of 7%. Of the rest of the metal in these runs 18 ± 7% was found in the column and the remaining 8% in a skull at the top of the column. There did not seem to be any good correlation between the observed yields and the obvious variables such as temperature, time or even the nature of the column. Alumina seemed to give somewhat higher yields than graphite, but the results were not definitive.

2. Plutonium Handling Facility (A. F. Voigt)

It was desired to follow the behavior of plutonium through extraction and other types of pyrometallurgical processing at a concentration in uranium similar to that expected in actual fuel processing, of the order of 0.2% Pu. Such an alloy was obtained from the Los Alamos Scientific Laboratory and a gloved box facility has been built to house the experiments. During the current period
this facility has undergone its testing and shakedown period and it appears to be in satisfactory condition for use as intended. Included inside the gloved boxes are a resistance furnace with associated vacuum pumps, a saw for sampling the metal, an analytical balance, an area for dissolving the metal samples and one for concreting the wastes. Wet chemical manipulations on the dissolved samples are done in another gloved box array.

Samples of the U-Pu alloy have been put into the proper form, and extraction experiments are underway.

Analytical Chemistry

1. **Analytical Procedures** (C. V. Banks, J. F. Fritz, R. Schaeffer and G. S. Hammond)

1.1 **Hydrogen Fluoride** (C. V. Banks)

An investigation was started for a suitable analytical method for the determination of hydrogen fluoride in the atmosphere. The use of large quantities of this reagent and its extreme toxicity make such a method very desirable. A considerable amount of work has been directed toward adapting to the present problem a conductimetric method for the determination of traces of hydrogen fluoride in gas streams. The method is extremely sensitive but a number of calibration and sampling problems have developed. It is believed the method will be useful for the determination of hydrogen fluoride in the atmosphere and can probably also be used, if coupled with the pyrohydrolysis technique, for the determination of trace amounts of fluoride in metals.
1.2 Oxygen in Metals and Metal Fluorides (R. Schaeffer)

In connection with the interest in the Ames Laboratory in preparing oxygen-free metals, this group has undertaken to apply the high temperature fluorine conversion of oxide to oxygen to the determination of trace oxygen in group III metals and their salts. Vacuum apparatus constructed of copper, nickel and Kel-F has been built and the initial stages of the procedure studied. Solid $\text{KBrF}_4$ has been adopted as the fluorinating agent to permit high temperature operation.

The procedure used at the present time consists of the following steps:

1. A nickel reaction tube is dried and loaded with 0.5 to 2.0 grams of $\text{KBrF}_4$ separately prepared.

2. The tube is attached to the copper vacuum apparatus, evacuated, heated to the selected operating temperature to prefluorinate the container, and cooled.

3. The oxygen released by step 2 is collected and measured in a micro gas measuring system. Step 2 is then repeated until no further oxygen is formed.

4. The reaction tube is filled with a dry, inert atmosphere, quickly loaded with the analytical sample, returned to the copper system and immediately evacuated.

5. Steps 2 and 3 are repeated to release oxygen from the sample. The results of five determinations of the oxygen content of $\text{YF}_3$ are shown in Table II.
Table II
Oxygen Content of YF$_3$

<table>
<thead>
<tr>
<th>Reaction Temperature</th>
<th>Reaction Time (hours)</th>
<th>Oxygen Found (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350°C</td>
<td>24</td>
<td>4165</td>
</tr>
<tr>
<td>450°</td>
<td>35</td>
<td>2510</td>
</tr>
<tr>
<td>500°</td>
<td>15</td>
<td>850</td>
</tr>
<tr>
<td>500°</td>
<td>31</td>
<td>530</td>
</tr>
<tr>
<td>500°</td>
<td>23</td>
<td>230</td>
</tr>
</tbody>
</table>

High values for the oxygen content of the salt in the first two runs are probably associated with incomplete prefluorination of the reaction tube at lower temperatures. A number of factors may contribute to the variation of values for the three samples run at 500°C. In the last sample an accident interfered with the repetition of steps 2 and 3 and the value recorded is for the first heating period only. Although in most other cases only small additional amounts of oxygen were liberated in furtherheatings, this need not necessarily be true. Secondly, as much as a ten percent error may arise from the measurement of the oxygen collected. Sample size has been increased to one gram to reduce this error.

It is anticipated that this work will result in a satisfactory method for the analysis of salts for trace oxygen content.

1.3 Rare Earth Mixtures (C. V. Banks)

A paper, "Differential Spectrophotometric Determination of Rare Earths" by C. V. Banks, J. L. Spooner, and J. W. O'Laughlin, was accepted for publication in ANAL. CHEM.
Abstract

Differential spectrophotometric methods are applied to the determination of neodymium-erbium, praseodymium-erbium, and praseodymium-neodymium-samarium mixtures with a standard deviation of 0.17% for analyses made by the "general" method and a standard deviation of 1.25% for analyses made by the "trace analysis" method. An accurate method of measuring small molar absorptivities is discussed. A statistical breakdown of the data obtained indicates optimum conditions may have to be determined experimentally rather than theoretically.

1.4 Rare Earths in Uranium (C. V. Banks)

A paper, "The Separation and Determination of Small Amounts of Rare Earths in Uranium" by C. V. Banks, J. A. Thompson, and J. W. O'Laughlin, was submitted for publication in ANAL. CHEM.

Abstract

A spectrophotometric method for the determination of rare earths in the range 100 to 200 μg of rare earth is based on the absorbancy of the rare earth complex with 2-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)-benzenearsonic acid (arsenazo). The absorbancy of the rare earth-arsenazo complex is measured at 570 μm and at a pH of 7.0.

The main objective of this investigation was to develop a method of determining rare earths in the presence of large amounts of uranium and small amounts of iron. As both of these metals interfere in the proposed spectrophotometric method for rare earths, an ion exchange method of separation is
presented based on the adsorption of uranium(VI) sulfate and Fe(III) thiocyanate on a quaternary ammonium anion exchange resin.

1.5 Determination of Zinc (C. V. Banks)

A report (ISC-781), "Spectrophotometric Determination of Zinc and Other Metals with \( \alpha, \beta, \gamma, \delta \)-Tetraphenylporphine," by R. E. Bisque and C. V. Banks is being distributed.

**Abstract**

Analytical procedures for the determination of trace amounts of zinc in various metals were developed utilizing the spectrophotometric properties of the zinc complex of \( \alpha, \beta, \gamma, \delta \)-tetraphenylporphine in glacial acetic acid.

The metals to which these determinations are applied are those soluble in acetic or formic acid or those whose oxides are soluble in these acids. One application deserving of particular mention is the spectrophotometric determination of trace amounts of zinc in cadmium metal.

A procedure for an indirect determination of other metals is presented.

1.6 Analytical Ion Exchange Separations (J. S. Fritz)

A report (ISC-1021) "I. Analytical Ion Exchange Separations. II. An Automatic Recording Titrator" by Gerald Umbreit and J. S. Fritz is being distributed.

**Abstract**

Part I

A method is proposed for the separation of metal cations through the use of cation exchange resins and the selective
effect of controlled pH on certain complexes of the metal cations. The method has been applied with good results to several binary mixtures of metal ions. In the method proposed an excess of EDTA [(ethylenedinitrilo)-tetraacetic acid] is added to the metal ion solution. The pH is controlled by buffering at a point where the EDTA complex of one metal ion is quantitatively formed, while the complex of the other metal ion is largely dissociated. The solution is then passed through a previously buffered column containing a controlled amount of Dowex 50-X4 cation exchange resin. The uncomplexed metal ion is quantitatively removed from solution by the resin while the complexed ion passes through the column.

Part II

An automatic recording titrator is described which is applicable to all types of potentiometric titrations. Particular attention has been paid to the maintenance of accurate potential recording of the entire titration curve as well as accurate recording of the volume of titrant used. As a result the instrument is well-suited for analytical research where the complete curve, rather than just the equivalence point of the titration, is of interest.

Simplicity of the instrument is maintained by use of commercially available components for the major functions of amplifying and recording. Each of the major components retains its separate identity, and thus may be used for other applications without alterations. Acceptable substitutes for each of the
major components are suggested, and the relative merits of each are discussed. Suggestions for improving the instrument are also discussed.

A paper describing the automatic recording titrator was submitted for publication in ANAL. CHEM.

Research is being carried out on a single ion exchange separation of metal ions of different charge. The method is based on the fact that a sulfonic acid type cation exchange resin has a much higher affinity for $+3$ ions than for $+2$ ions, and a still higher affinity for $+4$ ions. Using a column in the ethylene-diammonium form and eluting with a solution containing ethylene-diammonium ions, a divalent ion such as zinc can be quantitatively separated from a trivalent ion such as lanthanum or a tetravalent ion such as thorium in 15 to 20 minutes. The zinc can be determined directly in the effluent by an EDTA titration. This method should be of general applicability in the separation of metal ions of different charge.

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

1.7.1 For Rare Earths and Yttrium

A paper "Chelometric Titrations Using Arsenazo Indicator" by James S. Fritz, R. T. Oliver and D. J. Pietrzyk was accepted for publication in ANAL. CHEM.

Abstract

Arsenazo (3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid, trisodium salt) is an excellent indicator for the EDTA titration of rare earths and yttrium in weakly acid 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 interference from calcium and magnesium is 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, but thorium can be titrated at a more acidic pH. Titration of thorium in the presence of uranium is possible.

1.7.2 For Thorium and Uranium

A simple, selective qualitative test for thorium and uranium has been devised and submitted for publication. Thorium can be detected in the presence of zirconium and most other metal cations except uranyl. Likewise the uranyl ion can be detected in the presence of most metal cations except thorium. Thorium and uranium can be detected in the presence of each other after a single solvent extraction of uranyl diethyldithiocarbamate.

A paper, "Detection of Thorium and Uranium with Arsenazo" by James S. Fritz and Evelin Carlston Bradford was accepted for publication in ANAL. CHEM.

1.8 Analysis for Thorium in the Presence of Rare Earths (J. S. Fritz)

A method for determining thorium in the presence of rare earths has been devised. This consists of a photometric titration with EDTA using a relatively large amount of copper(II) as the indicator. Good results were obtained for thorium even in the presence of the highest
members of the rare earth series. We hope to extend the method to the determination of scandium in the presence of rare earths.

1.9 Titrations with EDTA (J. S. Fritz)

Several additional masking agents have been investigated for use in potentiometric titrations with EDTA using a mercury indicator electrode. A paper, "Potentiometric Titrations with Ethylenediaminetetraacetate. Use of Masking Agents to Improve Selectivity" by James S. Fritz, Marlene J. Richard and Carly K. Karraker was submitted for publication in ANAL. CHEM.

Abstract

Potentiometric titration of metal ions with EDTA using a mercury metal indicator electrode is a useful but rather non-selective method. It is shown that the use of complexing agents to mask certain interfering metal ions makes possible a number of interesting and selective analytial determinations. With citrate as a masking agent, Cd$^{+2}$, Cu$^{+2}$, Hg$^{+2}$, Pb$^{+2}$ or Zn$^{+2}$ can be titrated in the presence of any of the following: Be$^{+2}$, Cr$^{+3}$, Fe$^{+3}$, Mo$^{VI}$, Nb$^{V}$, Sb$^{III}$, Sn$^{IV}$, Ta$^{V}$, Th$^{+4}$, Ti$^{IV}$, UO$_{2}^{+2}$, W$^{VI}$ and Zr$^{+4}$: In some cases tartrate can be substituted successfully for citrate. Rare earths and some divalent metal ions can be titrated in the presence of aluminum or uranium using 2,4-pentanedione or sulfosalicylate as a masking agent.

1.10 Metal-Indicator Systems (J. S. Fritz)

A report (ISC-945) "Metal-Indicator Systems in (Ethylenedinitrilo)-tetraacetic Acid Titrations" by William J. Lane and J. S. Fritz is being distributed.
Abstract

Three organic reagents have been studied and applied to titrations with (ethylenedinitrilo)tetraacetic acid. The techniques of photometric titrations and precision spectrophotometry have been applied to titrations of rare earths as dilute as $10^{-6}$ M.

These reagents are 7-(1-naphthylazo)-5-sulfo-8-hydroxyquinoline or Naphthyl Azoxine, 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid or Thorin and 2-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)-benzenearsonic acid or Arsenazo.

Naphthyl Azoxine was used as the indicator for direct EDTA titrations of some transition metals, rare earths and thorium. The interference of uranium was masked by tartrate ion in the titration of the transition metals but not rare earths and thorium. The copper-Naphthyl Azoxine complex was characterized as a 1:2 complex with a formation constant of $1.9 \times 10^{15}$ at pH 6.

Thorin was used as the indicator for indirect titrations of rare earths, several metals and fluoride ion. Lanthanum was used as the titrant of the excess EDTA.

Arsenazo was used as the indicator for the direct EDTA photometric titration of the rare earths. Titrations of as little as 10 micrograms of rare earth were performed with an error of only 2%. A tenfold excess of uranium was successfully masked in these titrations. The lanthanum-Arsenazo complex was characterized as a 1:1 complex with a formation constant of $2.7 \times 10^8$ at pH 7.
1.11 Service Analyses (C. V. Banks)
A total of 6473 service analyses was made during this period.

2. Chelates of $\beta$-Diketones (G. S. Hammond)

2.1 Enolization, Ionization and Spectra
A paper, "Chelates of $\beta$-Diketones. I. Enolization, Ionization and Spectra" by George S. Hammond, Wilfred G. Borduin and Gerald A. Guter, was submitted for publication in J. AM. CHEM. SOC.

Abstract
Observations have been made concerning the indicated properties of two series of $\beta$-diketones, one in which electronic factors are varied by the introduction of substituents in the meta and para positions of dibenzoylmethane, and a second in which the steric requirements of the R-groups in RCOCH$_2$COR are varied by progressive branching.

The aromatic compounds are completely enolized both in the solid forms and in solution. The acidity constants of the symmetrically disubstituted series in "75%" dioxan-water fit the Hammett equation with a rho value of 2.63 as compared to the value of 1.28 for benzoic acids in the same medium.

Increasing the steric requirements of the R-groups in the aliphatic series increases the degree of enolization to such an extent that dipivaloylmethane has no detectable diketo form in the pure liquid. As the degree of enolization increases, the acidity of the enol decreases.

Both visible and ultraviolet spectra of the compounds have been studied. Features previously noted in the spectra of such
compounds are found repeatedly. All indications point to the conclusion that the character of the "carbonyl" group is severely modified by enolization. While the data do not compel the conclusion that the compounds are symmetrical, they are consistent with that view.

2.2 Steric Effects

A paper, "Chelates of $\beta$-Diketones. III. Steric Effects in the Formation Constants of Metal Chelates" by Gerald A. Guter and George S. Hammond, was submitted for publication in J. AM. CHEM. SOC.

Abstract

The formation constants for several metal chelates of acetylacetone, diisobutyrylmethane and dipivaloylmethane were determined experimentally with a view to examining the steric effects of the ligands on their chelating ability. A correlation of the constants indicated that the values for the second formation constants of the copper chelates of diisobutyrylmethane and dipivaloylmethane were low and the separation factors between the first and second constants were unusually large. Relatively small separation factors were found for metals which do not form square planar complexes.

2.3 Substituent Effects

Abstract

Part I

The stability constants of the chelate compounds of a series of substituted diaroylmethanes with several divalent metals in 75 per cent by volume dioxan-water were measured. The data were treated with the Hammett relationship.

\[ \log \frac{k}{k_0} = \rho \delta \]

The expected correlation of rho values with metal-chelate bond type was not observed. This lack of correlation is attributed to the free energy of solution of the metal chelate. If the measured rho values are to reflect the ionic-covalent character of the metal-chelate bond, it must be assumed that the free energy of solution of the metal chelates are independent of the metal. In general this assumption is not valid. In this case it appears that this free energy term completely swamps out effects relating to the bond type.

Part II

It was observed by Grunwald that acid-base equilibria in several pure and mixed hydroxylic solvents could be treated by the relation

\[ \log \frac{f_A}{f_{AH}} = m_A Y \]

wherein \( f_A \) and \( f_{AH} \) are degenerate activity coefficients of a base and its conjugate acid, respectively, \( m_A \) is a parameter depending only upon the base, and \( Y \) is a parameter depending only on the solvent and charge type of the base.
It is shown in this work that the proton donating ability of a solvent can be related to a suitable function of appropriate \( m_A \) values. Utilizing Grunwald's data for mixtures of water and ethanol, values of \( m_A \) are derived for the solvent components.

In addition, a relationship is derived between the proton donating ability of a solvent and the Hammett acidity function. This relationship is shown to correlate data already available in the literature on the Hammett acidity function in water-ethanol mixtures.

**Spectrochemistry**

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

   1.1 **Emission Spectrometric Determination of Oxygen in Metals**

   The emission spectrometric techniques for the determination of oxygen in metals has been extended to the determination of oxygen in zirconium and yttrium metal. The analytical curve previously established for the determination of oxygen in titanium and titanium alloys can be used directly for the determination of oxygen in zirconium. This fact was established by comparing a series of analytical results with those obtained by vacuum-fusion methods.

   Information obtained during our experiments on the determination of oxygen in yttrium metal showed that the analytical curve applicable to titanium and zirconium metals could not be employed for analogous determinations in yttrium metal. The nature of this curve shift has not been established. The availability of standard samples is
therefore a primary requisite in extending the technique to other metals. For the determination of oxygen in yttrium metal, synthetic standards were prepared by quantitatively reacting yttrium oxide with yttrium metal under arc melting conditions. Conventional residual correction techniques were employed to evaluate the oxygen content of the base material from which the standards are prepared. The comparison of analytical results shown in Table III indicates that reliable standards can be synthesized in this manner.

Table III

<table>
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<tr>
<th>Sample No.</th>
<th>Spectrometric</th>
<th>Vacuum Fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.58</td>
<td>0.56</td>
</tr>
<tr>
<td>2</td>
<td>0.36</td>
<td>0.43</td>
</tr>
<tr>
<td>3</td>
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</tr>
<tr>
<td>8</td>
<td>0.27</td>
<td>0.26</td>
</tr>
</tbody>
</table>

A tentative analytical curve has also been established for the determination of oxygen in niobium. Synthetic standards were prepared by reacting molecular oxygen or niobium oxide with niobium metal.

A paper "Emission Spectrometric Determination of Oxygen in Metals" by Velmer A. Fassel, William Gordon and Ray W. Tabeling was submitted for publication by the American Society for Testing Materials.
1.2 Emission Spectrometric Determination of Hydrogen in Metals

The simultaneous determination of oxygen and hydrogen in metals is a desirable extension of the spectrographic method. We have now established that hydrogen can be determined by fusing metal specimens in high current d.c. carbon arc discharges operated under argon pressures of about 1/3 of an atmosphere. The evolution of hydrogen under these conditions is very rapid and appears to be completed in about 10 seconds. The $H_\alpha$ line at 6562Å can be detected at hydrogen concentrations of 3 ppm for 1-gram samples. A calibration curve for the determination of hydrogen in titanium has been established.

1.3 Flame Spectrometric Determination of Lanthanum in Rare Earth Mixtures

A flame spectrometric method for the determination of lanthanum in all combinations of rare earth mixtures has been developed. An aerosol of a solution of the sample is formed in an oxy-hydrogen flame. In these flames, the momentary formation of LaO molecules is signaled by the emission of the LaO electronic-vibrational band systems. The intensity of the band head at 7901.5Å is related to the lanthanum content of the sample. Lanthanum concentrations in the range 2.5-100% can be determined with an experimental error of about ± 1.5% of the actual amount present.

1.4 Analysis of the Rare Earth Elements

A paper "Quantitative Spectrographic Analysis of the Rare Earth Elements. IX. Determination of Neodymium and Gadolinium in Samarium. X. Determination of Holmium, Dysprosium, Neodymium, Samarium,
Terbium and Europium in Gadolinium. XI. Determination of Erbium, Holmium, Dysprosium, Terbium, Gadolinium and Samarium in Yttrium. XII. Determination of Dysprosium, Yttrium, Gadolinium and Samarium in Terbium" by Richard N. Kniseley, Velmer A. Fassel, Beverly B. Quinney, Carl Tremmel, William A. Gordon and William J. Hayles was submitted for publication in SPECTROCHIM. ACTA.

Abstract

Emission spectrometric methods are described for the quantitative determination of rare earth impurities commonly associated with purified samarium, gadolinium, terbium, and yttrium over a concentration range from the detection limits up to 1%. 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. The coefficient of variation is less than ± 5% in most instances.

2. Spectroscopic Service Analyses

During the period covered by this report, 8315 samples were analyzed or their spectral properties determined.

Radiochemistry

1. Radioactivity of Antimony-127 (A. P. Voigt)

The isotope Sb$^{127}$ is produced in fission and has been studied as one of the fission products of uranium. It can also be made by the gamma-irradiation of tellurium in the Iowa State College Synchrotron. As produced by the latter reaction its radiations have been studied in this Laboratory and various gamma rays have been identified.
Recently it has been suggested that the fission product antimony is not a single activity but several species of different half-lives. We have begun an investigation to check this hypothesis by comparing the decay of the Sb\textsuperscript{127} produced by the two different processes on a gamma-ray spectrometer.

2. **Recoil Chemistry of Carbon in Organic Compounds** (A. F. Voigt)

   Study of the recoil chemistry of carbon in organic compounds as initiated by the C\textsuperscript{12} (γ,n) C\textsuperscript{11} reaction, followed by separation of the compounds by gas chromatography, is being continued. Several irradiations of methanol have given similar results; the amount of activity produced has been small and only one product has been found active.

   By the use of several different chromatographic columns, the active compound has been tentatively identified as carbon monoxide. The amount of activity in any other compound was too small to observe. Since the total activity was not large, other active compounds present in small to medium amounts would escape detection.

3. **Exchange Studies on Cyclopentadienyl Compounds** (A. F. Voigt)

   The complex compounds of the transition metals and the cyclopentadienyl ion are interesting from the point of view of their structure and reactions. Cyclopentadiene behaves as a weak acid and forms complexes in which two cyclopentadienyl ions complex with a single metal ion. Of particular interest is the process of electron exchange between similar complexes of an element in two different valence states. The case of the cobalt(II) complex, Co(C\textsubscript{5}H\textsubscript{5})\textsubscript{2} and the cobalt(III) complex, Co(C\textsubscript{5}H\textsubscript{5})\textsubscript{2}\textsuperscript{+}, is under study.
It was first established that exchange between the central cobalt atom and free cobalt ions did not occur. Similar results have been published for cyclopentadiene complexes of other metals.

Exchange experiments have been made which at first appear to indicate the electron exchange between \( \text{Co}(\text{C}_5\text{H}_5)_2 \) and \( \text{Co}(\text{C}_5\text{H}_5)_2^+ \). However, later experiments indicate that the observed exchange is probably not this reaction but that the Co(II) species, \( \text{Co}(\text{C}_5\text{H}_5)_2 \), is rapidly oxidized to some form involving Co(III) which then undergoes relatively slow exchange with the \( \text{Co}(\text{C}_5\text{H}_5)_2^+ \) ion. Investigation of the nature of the compounds found is under way.

4. **Photonuclear Reactions**

4.1 **Propyl Bromides** (A. F. Voigt)

A paper "Chemical Effects of Photonuclear Reactions in the Propyl Bromides" by A. E. Richardson and A. F. Voigt was submitted for publication in *J. Chem. Phys.*

**Abstract**

Two new photo-nuclear reactions are reported: \( \text{Br}^{79}(\gamma,2n)\text{Br}^{77} \) and \( \text{Br}^{79}(\gamma,3n)\text{Br}^{76} \).

The organic retention following the \( \text{Br}^{81}(\gamma,n)\text{Br}^{80m} \) reaction in liquid n- and isopropyl bromides was found to be 47 and 36%, respectively, appreciably higher than reported values following the \( \text{Br}^{79}(n,\gamma)\text{Br}^{80m} \) reaction. Higher retentions were also noted for irradiations of the solid bromides. The relative yields of individual organic products were determined for irradiations of both liquid and solid and were in many respects in striking agreement with data from \((n,\gamma)\) and I. T. activation. In solid n-propyl bromide the \((\gamma,n)\) and \((\gamma,3n)\) reactions gave
the same ratio of parent compound to total organic yield.

Data on the scavenger effect shows that thermal recombination reactions occur in both liquid and solid. Marked increases are shown in the thermal organic yield with only slight increases in the non-thermal retention for both bromides for $(\gamma,n)$ compared to $(n,\gamma)$ activation. The reasons for these increases are discussed.

In general, the data indicate that elastic collision mechanisms are unimportant compared to random fragmentation as an explanation of the results.

4.2 Gallium (D. S. Martin)

Samples of gallium have been irradiated with bremsstrahlung of varying energy limits from the Iowa State College Synchrotron. The relative yield of the Zn$^{69}$ isomer pair has been determined as a function of the irradiation energy by analysis of the decay curves. For this analysis a least squares method, employing the IBM-650 computer, was utilized. The yield ratio Zn$^{69}(52\text{ min})$/Zn$^{69m}(14\text{ hr})$ approaches a limiting value of 1.5 at high bremsstrahlung energies (above 40 Mev). The experiments have been carried down to about 23-24 Mev, as far as practicable with the intensities available, where the yield ratio is approximately 3.5. The cross-section for the formation of the isomer pair will be determined. Also procedures have been worked out to provide the cross-section of the Ga$(\gamma,n)$ reactions in these experiments.
5. Isotopic Exchange Reactions (D. S. Martin)

5.1 Aquation of the Trichloroammineplatinate(II) Ion

A paper "The Acid Hydrolysis (Aquatation) of the Trichloroammineplatinate(II) Ion" by Thomas S. Elleman, John W. Reishus and Don S. Martin, Jr., was submitted for publication in J. AM. CHEM. Soc.

Abstract

The acid hydrolysis of \([\text{Pt(NH}_3\text{Cl}_3]^-\) in aqueous solution has been studied by spectrophotometric and potentiometric titration techniques in the temperature range of 0 to 35°. For the first hydrolysis: \([\text{Pt(NH}_3\text{Cl}_3]^- + \text{H}_2\text{O} \xrightarrow{k_{-1}} [\text{Pt(NH}_3\text{Cl}_2(\text{H}_2\text{O})] + \text{Cl}^-}\),

\(k_1 = 3.6 \times 10^{-5} \text{ sec}^{-1}\) and \(k_{-1} = 2.5 \times 10^{-3} \text{ moles}^{-1} \text{ sec}^{-1}\) at 25°.

\(\Delta H_1^\ddagger = 18.9 \text{ kcal. and } \Delta H_{-1}^\ddagger = 16.8 \text{ kcal.}\) The existence of a second acid hydrolysis has been demonstrated: \([\text{Pt(NH}_3\text{Cl}_2(\text{H}_2\text{O})] + \text{H}_2\text{O} \xrightarrow{k_{-2}} [\text{Pt(NH}_3\text{Cl}(\text{H}_2\text{O})_2]_\ddagger + \text{Cl}^-}\). Approximate values, \(K_2 = k_2/k_{-2} = 4 \times 10^{-5} \text{ mole/l. and } k_{-2} = 0.2 \text{ l. mole}^{-1} \text{ sec}^{-1}\) at 24° were indicated.

5.2 Exchange of Platinum between \(\text{Pt(en)}\text{Br}_4^-\) and \(\text{Pt(en)}\text{Br}_2^-\).

A paper, "Solid State and Solution Exchange of Platinum between \(\text{Pt(en)}\text{Br}_4^-\) and \(\text{Pt(en)}\text{Br}_2^-\)" by Robert E. McCarley, Don S. Martin, Jr., and Lee T. Cox, was submitted for publication in J. INORG. NUCL. CHEM.

Abstract

Isotopic exchange of platinum between its two states in \(\text{Pt(en)}\text{Br}_2^- \cdot \text{Pt(en)}\text{Br}_4^-\) was not detected in 24 hours at 25°C. The exchange between the corresponding states in N,N'-dimethylformamide solutions was found to be strongly catalyzed.
by Br⁻. A rapid exchange in solution, induced by light, was strongly inhibited by IrCl₆⁻. In the absence of Br⁻, an uncontrolled impurity induced an exchange in the dark which prevented reproducible results for solutions made from different solvent batches.

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

Samples of PtCl₄²⁻ tagged with Cl³⁶ have been equilibrated with Br⁻ in aqueous solutions. The specific activity of the complex which is separated from the solution provides the Br/Cl ratio in the complex and in the free halide ion. Equilibrium values of Br/Pt from 0 to 3.4 have been obtained. Various computer methods are being investigated to obtain the equilibrium constants for the four substitution reactions.

7. Activation Analysis (D. S. Martin)

The iridium content of platinum has been measured by a procedure in which the sample and a standard iridium sample are irradiated together in the Argonne CP5 pile. The present sample of platinum was found to contain 1.0 ppm iridium. The accuracy is believed to be within 10%. Another sample analyzed 20 ppm. It is hoped that the platinum X-ray that is induced in the sample will serve to calibrate the irradiation flux. Also the effect of a fast flux is being investigated.

X-Ray Chemistry

1. Rare-Earth Ethyl Sulfates·9H₂O (R. E. Rundle)

Because of the wide interest in the magnetic properties and spectra of the compounds R(C₂H₅SO₃)₃·9H₂O, a careful study of the structure of these compounds was begun. Study of the erbium compound
has been completed with a full-three dimensional refinement using about 1600 X-ray reflections. The structure has been determined with good accuracy, even as to the carbon positions. Er-0 and S-0 bonds have been determined to about +0.01 and 0.02Å, and standard deviations for C-C and C-0 bonds will not be greater than + 0.04Å.

\[
R = \frac{\sum |F_{\text{obsd}}| - |F_{\text{calc}}|}{\sum |F_{\text{obsd}}|} = 10.6\%
\]

for all reflections.

To see if unfilled f-shells perturb the structure, comparison will be made with the yttrium compound (no f-electrons present; nearly the same size as Er) and with praseodymium and lanthanum compounds. Pr\(^{3+}\) has 2 f-electrons and may be subject to Jahn-Teller distortion. Er\(^{3+}\) has an odd number of f-electrons. Er and Y are characteristic of heavy rare earths, Pr and La are characteristic of light rare earths.

This work is possible in this detail only because of the Iowa State College IBM-650 computing facilities.

2. Transition Metal Compounds

The influence of the crystal versus the local field in determining the structure of complex ions of transition metals has been studied. By using very large cations, e.g., \(\mathcal{O}_4\)As\(^+\), the negative transition metal ion MX\(_n\)\(^{-m}\) is relatively isolated and may have a structure determined by repulsion of X\(^-\) ions, irrespective of other factors. By using small cations, e.g., Li\(^+\), the field of X\(^-\) ions on each other
can presumably be neutralized.

$\text{CuCl}_4^-$ ion should be square-planar by "local" field and directed valence arguments, but is known only as a tetrahedral ion. We have tried to make the square-planar ion as $\text{Li}_2\text{CuCl}_4$, but have not yet succeeded. However, the ion, $\text{Cu}_2\text{Cl}_6^-$, which is planar,

![Diagram of $\text{Cu}_2\text{Cl}_6^-$](image)

has been made (in $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$). Cu-Cl distance are $\sim 2.3\text{ Å}$, both bridge and terminal.

Since from other information the odd electron on each Cu is partially distributed on the chlorines, the bridge chlorines are seen to have a contribution of the magnetic electron from 2-centers, and this may be most important in determining the low temperature susceptibility. In $\text{CuCl}_3$ (anhydrous) where chains

![Diagram of $\text{CuCl}_3$](image)

are formed, a simple argument can be given for a ferromagnetic chain. This point is being examined further.

An attempt to prepare $\phi\text{As}^+\text{AuCl}_4^-$ has been successful but the $\text{AuCl}_4^-$ ion is planar as previously noted. Hence for this singly charged ion the repulsion among $\text{Cl}^-$ ions does not lead to a tetrahedral $\text{AuCl}_4^-$. 
In PtBr$_3$En, the X-ray analysis of the structure confirms

\[ \text{PtBr}_2\text{En and PtBr}_4\text{En ions (En = ethylenediamine), with Pt IV and Pt II.} \]

Chains,

\[
\begin{array}{c}
\text{Br-Pt-Br} \\
\text{IV} \\
\text{. . . Pt . . . Br-Pt-Br} \\
\text{II}
\end{array}
\]

run along the needle axis, and lead to a very high dichroism.

New nuclear magnetic resonance data by Poulis on CuCl$_2$·2H$_2$O in the antiferromagnetic state leads to an odd electron distribution of

\[
\begin{array}{c}
\sim 2\% \\
\sim 5\% \\
\sim 5\% \\
\sim 2\%
\end{array}
\]

This is more reasonable than the previously reported distribution.

3. **Cubic Spherical Harmonics (M. Atoji)**

A paper "On the Cubic Spherical Harmonics" by Masao Atoji was submitted for publication in PHYS. REV.

**Abstract**

All of the previous results have less generality in view of obtaining the higher terms in the cubic spherical harmonics. A general expression for the coefficients in the cubic harmonics is derived by the inductive method.

4. **Neutron Diffraction Studies (M. Atoji)**

The neutron diffraction data from a study of a single crystal of sodium tungsten bronze indicate that the cubic cell dimension should be at least twice as large as the one obtained from the X-ray method.
and the average structure may be described as a super-lattice of distorted perovskites.

The neutron diffraction study of gypsum, CaSO₄·2H₂O, has been completed and will be submitted for publication.

The structures of lanthanum dicarbide and sesquicarbide by neutron diffraction have been reported (see page 18 of this report).
APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories


ISC-781 R. E. Bisque and C. V. Banks. Spectrophotometric Determination of Zinc and Other Metals with $\alpha, \beta, \gamma, \delta$-Tetraphenylporphine.


2. Publications

Atoji, Masao

Banks, C. V., K. E. Burke, J. W. O'Laughlin and J. O. Thompson

Banks, C. V. and J. W. O'Laughlin

Barlett, R. H., M. H. Rice and R. H. Good, Jr.

Burkhard, W. J. and J. D. Corbett

Dahl, F. and R. E. Rundle

Duke, F. R. and J. P. Cook

Duke, F. R. and N. C. Peterson

Fritz, J. S., A. J. Moye and Marlene Johnson Richard

Fritz, J. S. and S. S. Yamamura

Gerstein, B. C., M. Griffel, L. D. Jennings, R. E. Miller, R. E. Skodkopole and F. H. Spedding

Good, R. H., Jr.
Griffel, M., R. W. Vest and J. F. Smith  

Hammer, C. L. and R. H. Good, Jr.  

Hansen, R. S., R. E. Minturn and D. A. Hickson  

Henry, R. M. and D. S. Martin, Jr.  
Comparative Yields of (γ,2n) and (γ,pn) Processes for Fe⁵⁴ by 70 Mev. Bremsstrahlung.  Phys. Rev. 107, 772-774 (1957).

Jennings, L. D., R. M. Stanton and F. H. Spedding  

Levine, H. B.  

Moser, H. C. and A. F. Voigt  

Pearson, G. J., P. O. Davey and G. C. Danielson  
Thermal Conductivity of Nickel and Uranium.  Iowa Acad. of Sci. 64, 461-465 (1957).

Powell, J. E. and M. A. Hiller  

Ray, A. E. and J. F. Smith  

Schupp, F. D., C. B. Colvin and D. S. Martin, Jr.  

Segel, S. L. and R. G. Barnes  

Shaw, W. C., D. E. Hudson and G. C. Danielson  
Smith, J. F., C. E. Carlson and F. H. Spedding

Spedding, F. H.

Spedding, F. H., R. J. Barton and A. H. Daane
The Vapor Pressure of Thulium Metal. J. Am. Chem. Soc. 79, 5160-5163 (1957).

Spedding, F. H., A. H. Daane and K. W. Herrmann

Strittmatter, R. C., G. J. Pearson and G. C. Danielson
Measurement of Specific Heats by a Pulse Method. Iowa Acad. of Sci. 64, 466-470 (1957).

Svec, H. J. and D. S. Gibbs
## APPENDIX II: LIST OF SHIPMENTS

<table>
<thead>
<tr>
<th>Destination</th>
<th>Item</th>
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<tr>
<td>University of Arizona&lt;br&gt;Tucson, Arizona</td>
<td>11 gm praseodymium oxide&lt;br&gt;11 gm neodymium oxide&lt;br&gt;11 gm samarium oxide&lt;br&gt;11 gm lanthanum oxide&lt;br&gt;11 gm cerium oxide&lt;br&gt;11 gm gadolinium oxide&lt;br&gt;1 gm yttrium oxide&lt;br&gt;11 gm dysprosium oxide&lt;br&gt;11 gm holmium oxide&lt;br&gt;11 gm erbium oxide&lt;br&gt;11 gm ytterbium oxide&lt;br&gt;1 gm thulium oxide&lt;br&gt;1 gm lutetium oxide&lt;br&gt;1 gm terbium oxide</td>
</tr>
<tr>
<td>H. A. Schimming&lt;br&gt;University of Wisconsin&lt;br&gt;Madison, Wisconsin</td>
<td>20 gm terbium metal&lt;br&gt;100 gm terbium oxide</td>
</tr>
<tr>
<td>University of California&lt;br&gt;Los Alamos Scientific Laboratory&lt;br&gt;Los Alamos, New Mexico</td>
<td></td>
</tr>
<tr>
<td>Argonna National Laboratory&lt;br&gt;Lemont, Illinois</td>
<td>50 gm praseodymium metal</td>
</tr>
<tr>
<td>University of Denver&lt;br&gt;Denver, Colorado</td>
<td>2 samples of special reagent (1 gm each)</td>
</tr>
<tr>
<td>Purdue University&lt;br&gt;Lafayette, Indiana</td>
<td></td>
</tr>
<tr>
<td>Dr. James L. Kassner&lt;br&gt;University of Alabama&lt;br&gt;University, Alabama</td>
<td>1 disc each of gadolinium and erbium metals&lt;br&gt;4.82 gm dysprosium metal&lt;br&gt;3.63 gm ytterbium metal&lt;br&gt;4.31 gm holmium metal&lt;br&gt;4.21 gm terbium metal</td>
</tr>
<tr>
<td>University of California Radiation Laboratory&lt;br&gt;Livermore, California</td>
<td></td>
</tr>
<tr>
<td>Mrs. Mary E. White&lt;br&gt;High Voltage Laboratory&lt;br&gt;Cambridge 39, Massachusetts</td>
<td></td>
</tr>
</tbody>
</table>
Bell Telephone Laboratories
Murray Hill, New Jersey

Dr. Joseph G. Graca
Iowa State College
Ames, Iowa

Lincoln Laboratory
Lexington, Massachusetts

Physics Department
Georgetown University
Washington, D. C.

Huffman Microanalytical Laboratory
Wheatridge, Colorado

Mr. Arnold Gahler
Metals Research Laboratories
Niagara Falls, New York

Dr. Frank Benner
National Research Corporation
Cambridge, Massachusetts

State University of Iowa
Iowa City, Iowa

Dr. Henry J. Gomberg
Phoenix Memorial Laboratory
University of Michigan
Ann Arbor, Michigan

Union Carbide Nuclear Company
Oak Ridge, Tennessee

Carnegie Institute of Technology
Pittsburgh, Pennsylvania

Physikalisches Institut der
Technischen Hochschule
Munich, Germany

<table>
<thead>
<tr>
<th>Destination</th>
<th>Item</th>
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<tbody>
<tr>
<td>Bell Telephone Laboratories</td>
<td>2 lb dysprosium metal</td>
</tr>
<tr>
<td></td>
<td>2 lb neodymium metal</td>
</tr>
<tr>
<td></td>
<td>4.683 gm scandium metal</td>
</tr>
<tr>
<td></td>
<td>200 cc lutetium chloride solution</td>
</tr>
<tr>
<td></td>
<td>200 cc of each of the following rare earth solutions in ethylenediaminetetraacetic acid (equivalent to 5% chloride):</td>
</tr>
<tr>
<td></td>
<td>lanthanum</td>
</tr>
<tr>
<td></td>
<td>gadolinium</td>
</tr>
<tr>
<td></td>
<td>praseodymium</td>
</tr>
<tr>
<td></td>
<td>samarium</td>
</tr>
<tr>
<td></td>
<td>100 gm yttrium oxide</td>
</tr>
<tr>
<td></td>
<td>100 gm samarium oxide</td>
</tr>
<tr>
<td></td>
<td>1 gm yttrium metal</td>
</tr>
<tr>
<td></td>
<td>5 gm special hafnium oxide</td>
</tr>
<tr>
<td></td>
<td>3 samples yttrium fluoride</td>
</tr>
<tr>
<td></td>
<td>2 samples of niobium metal</td>
</tr>
<tr>
<td></td>
<td>4 samples of yttrium metal</td>
</tr>
<tr>
<td></td>
<td>10 gm terbium oxide</td>
</tr>
<tr>
<td></td>
<td>50 gm praseodymium oxide</td>
</tr>
<tr>
<td></td>
<td>2 gm special N15 sample</td>
</tr>
<tr>
<td></td>
<td>2 gm holmium metal</td>
</tr>
<tr>
<td></td>
<td>2 gm erbium metal</td>
</tr>
<tr>
<td></td>
<td>2 gm thulium metal</td>
</tr>
<tr>
<td></td>
<td>2 gm ytterbium</td>
</tr>
<tr>
<td></td>
<td>50 gm cerium metal</td>
</tr>
<tr>
<td></td>
<td>4 gm cerium metal</td>
</tr>
<tr>
<td></td>
<td>4 gm praseodymium metal</td>
</tr>
<tr>
<td></td>
<td>2 gm praseodymium metal</td>
</tr>
<tr>
<td></td>
<td>2 gm samarium metal</td>
</tr>
<tr>
<td>Destination</td>
<td>Item</td>
</tr>
<tr>
<td>----------------------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>General Electric Co.</td>
<td>1 lb praseodymium metal</td>
</tr>
<tr>
<td>Cincinnati, Ohio</td>
<td>1 lb erbium metal</td>
</tr>
<tr>
<td></td>
<td>1 lb neodymium metal</td>
</tr>
<tr>
<td></td>
<td>1 lb ytterbium metal</td>
</tr>
<tr>
<td></td>
<td>1 lb dysprosium metal</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>