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**AMES LABORATORY
RESEARCH AND DEVELOPMENT REPORT
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TID-4500, August 1, 1959

UNITED STATES ATOMIC ENERGY COMMISSION

Research and Development Report

ANNUAL SUMMARY RESEARCH
REPORT IN CHEMISTRY

July 1, 1959 - June 30, 1960

by

Ames Laboratory Staff

September 1960

Ames Laboratory
at
Iowa State University of Science and Technology
F. H. Spedding, Director
Contract W-7405 eng-82

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For the period July 1, 1959 - June 30, 1960

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ANNUAL SUMMARY RESEARCH REPORT IN CHEMISTRY

(July 1, 1959 - June 30, 1960)

Under the direction of F. H. Spedding, C. A. Goetz, C. V. Banks,
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Physical and Inorganic Chemistry1. Separation of Rare Earths by Ion Exchange (F. H. Spedding and J. E. Powell)1.1 Pilot Plant Separations

A quantity of xenotime sand left over from yttrium production was digested in the usual manner to provide source material for a run on the 30-inch diameter series of ion-exchange columns. The initially adsorbed band was about 34 feet long and contained about a thousand pounds of mixed rare earths. The band was displaced about five feet by an initial elution with HEDTA eluant in an attempt to divert any scandium which might be present in the mixture to a system of auxiliary resin beds. The elution was carried out at 60°C. Profiles showed that some scandium and a considerable amount of iron and titanium were present in the eluate which passed from the main system to the auxiliary beds. When about five feet of the rare-earth band had progressed off the main set of columns, the auxiliary beds were detached and coupled to a series of 6-inch diameter beds. Elution with HEDTA is being continued at 60° in hopes that the scandium will form a

compact band just ahead of lutetium so that it can be isolated free of rare earths and iron. Although the scandium appears to be segregating as expected, it is too early to ascertain just how much scandium is actually present in the system. The economic feasibility of the process will depend a great deal upon how much scandium is actually contained in xenotime, even though the major portion of the cost of the operation may be charged to the rare earths which are isolated simultaneously. The normal procedure in purifying the rare earths, erbium through lutetium has been to perform an initial concentration of this group with EDTA and then to finish the separation with HEDTA. Scandium, however, is not retained by cupric ion during elution with EDTA and has been lost, heretofore, in a large volume cupric-EDTA eluate. Elution from the beginning with HEDTA on hydrogen-form resin should conserve the scandium. Then, after scandium, lutetium, ytterbium, thulium and most of the erbium have been diverted to an auxiliary bed, the remaining rare earths can be resolved with EDTA in the usual manner.

1.2 Elution Sequences with Nitrilotriacetate (NTA)

In order to establish the behavior of certain common cations in the presence of the rare earths some preliminary elution studies were made. When 0.015 molar NTA was used at pH 9 the following sequence was noted:

Cu^{+2} , Th^{+4} , Ni^{+2} , Pb^{+2} , Al^{+3} , Zn^{+2} , Lu^{+3} , Yb^{+3} , Tm^{+3} , Er^{+3} ,
 Cd^{+2} , Ho^{+3} , Dy^{+3} , Y^{+3} , UO_2^{+2} , Sm^{+3} , Nd^{+3} , Pr^{+3} , Ce^{+3} , La^{+3} ,
 Mn^{+2} , Co^{+2} , Mg^{+2} , Be^{+2} , Sr^{+2} , Ba^{+2} .

The position of yttrium was not completely established because terbium, gadolinium and europium were not included in this study. At pH 8.7, however, the following partial sequence was observed:

Yttrium probably occurs between europium and samarium at pH 9 also.

Although cadmium was included in the mixture adsorbed in both experiments, the spectrograph did not detect it in the sequence of samples collected at pH 9. It should be noted that uranyl ion changed its position when the pH was changed.

2. The Solubilities of Some Rare-Earth Compounds (J. E. Powell)

2.1 Rare-Earth Glycolates

Mixtures of glycolic acid and ammonium glycolate have been used by several investigators to separate trace quantities of rare earths. In the case of macroseparations one needs to consider the solubilities of the individual rare-earth glycolate species in order to avoid undesirable precipitates in the resin beds.

A literature search revealed that the solubilities of a few rare-earth glycolates have been measured, but, in spite of a very interesting trend in the data, the work was never completed. Consequently, a series of glycolates was prepared from high purity rare-earth glycolate compounds by combining ammonium glycolate with individual chlorides, it was found that light-rare-earth glycolates generally separate from aqueous solution in anhydrous form. At 20°C the rate of formation is very slow, but as

the temperature is increased the anhydrous rare-earth glycolates precipitate more rapidly. The glycolates of the heavy rare earths, terbium through lutetium, and yttrium glycolate separate only in the form of dihydrates. Gadolinium glycolate is obtained anhydrous at 60°, but separates as the dihydrate at 20°. The solubilities of the rare-earth glycolates at 20° and 60° are given in Table I.

Table I. Solubilities of the Rare-Earth Glycolates in Water at 20° and 60°C.

Compound	Solubility (g compd/100 g H ₂ O)	
	20°	60°
La(gly) ₃	0.378	0.462
Ce(gly) ₃	0.381	0.495 (?)
Pr(gly) ₃	0.421	0.465
Nd(gly) ₃	0.447	0.449
Sm(gly) ₃	0.823	0.667
Eu(gly) ₃	0.841	0.811
Gd(gly) ₃	1.098	0.997
Gd(gly) ₃ · 2H ₂ O	1.021	1.004 (?)
Tb(gly) ₃ · 2H ₂ O	0.552	1.135
Dy(gly) ₃ · 2H ₂ O	0.323	0.695
Ho(gly) ₃ · 2H ₂ O	0.230	0.518
Er(gly) ₃ · 2H ₂ O	0.171	0.375
Tm(gly) ₃ · 2H ₂ O	0.140	0.322
Yb(gly) ₃ · 2H ₂ O	0.111	0.234
Lu(gly) ₃ · 2H ₂ O	0.093	0.225
Y(gly) ₃ · 2H ₂ O	0.220	0.462

The solubilities of the glycolate dihydrates of the heavy rare earths vary in a regular manner--decreasing with increased atomic weight from gadolinium to lutetium. The dihydrates are more soluble hot than cold. Yttrium glycolate dihydrate falls between dysprosium and holmium glycolates in molal solubility in agreement with the reported ionic radius for yttrium. The reasons for the strange solubility phenomena observed with the anhydrous light-rare-earth glycolates cannot be readily explained. Lanthanum, cerium and praseodymium glycolates are more soluble hot than cold, while the solubilities of neodymium and europium glycolates apparently do not vary with temperature to any extent. The anhydrous glycolates of samarium and gadolinium have inverse temperature coefficients of solubility, being more soluble in cold water than in warm water. Note that gadolinium glycolate dihydrate is probably not stable in water at 60° and slowly changes to the anhydrous form.

There is a break in the stability constant data reported by Artur Sonesson,¹ for rare-earth glycolates. This break occurs at gadolinium, corresponding to the point at which the glycolates begin to separate from solution as dihydrates (see Table II).

The differences in hydration, solubility and rate of formation suggest that glycolic acid might be useful in fractionally precipitating rare earths as well as in ion-exchange separations. It was thought that precipitation

¹ Artur Sonesson, *Acta Chem. Scand.*, 13, 998 (1959).

Table II. Stability Constants for Rare-Earth Glycolate Systems. Data of Artur Sonesson, *Acta Chem. Scand.*, 13, 998 (1959).

Rare Earth	b_1	b_2	b_3	b_4
La	155	37	11.5	1.8
Ce	225	46.5	13.3	2.5
Pr	270	57.5	16.1	3.6
Nd	320	69	16.8	3.4
Sm	360	94	22.5	3.9
Gd	300	90	23.0	4.2
Dy	330	91	26.5	3.8
Ho	350	86	27	3.3
Er	400	95	26	3.1
Yb	520	127	32	2.9

of dysprosium glycolate dihydrate in the presence of samarium glycolate would adequately demonstrate the feasibility of separating light and heavy rare earths by fractional precipitation with ammonium glycolate.

Five grams each of Dy_2O_3 and Sm_2O_3 were dissolved in a minimum amount of concentrated HCl (about 14-15 ml). This mixture was combined with 7/6 of the amount of ammonium glycolate required to form a mixture of dysprosium and samarium glycolates in a total volume of 500 ml. The mixture was stirred at 25°C for seven hours during which time a dysprosium-

rich precipitate of rare-earth glycolate dihydrate formed. The oxide recovered upon ignition of this precipitate weighed 5.1421 grams. The oxide recovered from the supernatant solution weighed 4.9255 grams.

The analyses of the two fractions are given below:

Experiment A	Weight (g)	%Dy ₂ O ₃	%Sm ₂ O ₃
Oxide from glycolate dihydrate ppt.	5.1421	84	16
Oxide rec. from supernatant soln.	4.9255	15	85

The single-stage separation factor for this procedure (ratio of Dy₂O₃ to Sm₂O₃ in the precipitate/ratio of Dy₂O₃ to Sm₂O₃ in solution) was 29.7.

As a further proof of the effectiveness of this process two additional experiments were performed. (B) 8.5 grams of Dy₂O₃ and 1.5 grams of Sm₂O₃ were converted to the neutral chlorides and treated with 7/6 the calculated amount of ammonium glycolate in a total volume of 850 ml. (C) 1.5 grams of Dy₂O₃ and 8.5 grams of Sm₂O₃ were converted to the neutral chlorides and treated with 7/6 the calculated amount of ammonium glycolate in a total volume of 150 ml. The precipitation time allowed in both cases was seven hours. The temperature was 25°C. The analyses of the products are given below:

Experiment B	Weight (g)	%Dy ₂ O ₃	%Sm ₂ O ₃
Oxide from glycolate dihydrate ppt.	7.0080	95	5
Oxide rec. from supernatant soln.	3.0053	57	43
Experiment C			
Oxide from glycolate dihydrate ppt.	6.6402	14	86
Oxide rec. from supernatant soln.	3.3758	17	83

The separation factor in experiment B was 14--only half as large as in experiment A. In experiment C the complete lack of separation was apparently due to an unfortunate circumstance. Very little material separated in the early stages of the experiment, but the bulk of the precipitate increased markedly during the last couple of hours. It is thought that the increase in precipitation rate was initiated by accidental seeding of the mixture with anhydrous samarium glycolate formed either by evaporation of moisture from spray thrown up by the stirrer or by evaporation at the meniscus on the walls of the beaker.

2.2 Rare-Earth Lactates

The interesting solubilities of the rare-earth glycolates suggested that a similar investigation should be made in the case of the lactates. At the present time all of the lactates, except those of lanthanum, cerium, praseodymium and neodymium, have been prepared by combining ammonium lactate and the rare-earth chloride in aqueous media. All the lactates have separated as the trihydrate and it appears that the light-rare-earth lactates are much more soluble than the heavy-rare-earth lactates. Since they are extremely soluble, lanthanum, cerium, praseodymium and neodymium lactates will have to be prepared in a different manner.

2.3 Rare-Earth Nitrilotriacetates

A series of rare-earth nitrilotriacetates have been prepared by combining rare-earth chlorides with ammonium nitrilotriacetate. In many cases the separation of a rare-earth nitrilotriacetate occurs

only after a long period of time. The degree of hydration varies with the rare earth involved as well as with the temperature at which the nitrilotriacetate was prepared. The solubilities of some of the species are given in Table III.

The composition of the stable hydrates of the lighter rare earths is not certain. The original compounds of La(NTA) contained 2.12 and 5.11 moles of H_2O . Upon equilibration at both 25° and 60° , these compositions were altered to the neighborhood of $La(NTA) \cdot 2.4H_2O$. In the case of cerium 2.34 and 5.00 waters were observed originally. After long equilibrations with water at 25° and 60° compositions ranging from $Ce(NTA) \cdot 2.2H_2O$ to $Ce(NTA) \cdot 2.4H_2O$ were found. With praseodymium the initial compounds contained 2.99 and 1.18 moles of water. After equilibration at 25° the compositions of the solids supposedly in equilibrium with the saturated solutions were observed to be $Pr(NTA) \cdot 5.10H_2O$ and $Pr(NTA) \cdot 5.07H_2O$. In spite of the similarity of the equilibrated solid phases the solubilities differed markedly, being 0.0959 and 0.0653 grams of $Pr(NTA)$ per 100 grams of water. At 60° the $Pr(NTA) \cdot 2.99H_2O$ and $Pr(NTA) \cdot 1.18H_2O$ compositions were altered to $Pr(NTA) \cdot 2.16H_2O$ and $Pr(NTA) \cdot 1.42H_2O$. Solubilities of 0.1178 and 0.214 grams $Pr(NTA)$ per 100 grams of water were noted.

Anomalies were also noted in the cases of dysprosium, holmium and erbium. The true tetrahydrated compounds remained tetrahydrates and gave reasonable solubilities, but in other cases certain peculiarities

Table III. The Solubilities of Some Rare-Earth Nitrilotriacetates

Compound	Solubility (g anh. R(NTA)/100 g H ₂ O)	
	25°	60°
La(NTA)·2.4H ₂ O	0.010-0.013	0.028-0.032
Ce(NTA)·2.2H ₂ O	0.024-0.027	0.046-0.052
Pr(NTA)·2.2H ₂ O	-----	0.118-0.214
Nd(NTA)·3H ₂ O	0.140	0.176
Sm(NTA)·3H ₂ O	0.080	0.118
Eu(NTA)·3H ₂ O	0.072	0.108
Gd(NTA)·3H ₂ O	0.084	0.119
Tb(NTA)·3H ₂ O	0.093	0.146
Dy(NTA)·3H ₂ O	0.154	0.193
Dy(NTA)·4H ₂ O	0.064	0.151
Ho(NTA)·4H ₂ O	0.058	0.127
Er(NTA)·4H ₂ O	-----	0.119
Tm(NTA)·4H ₂ O	0.052	0.102
Yb(NTA)·4H ₂ O	0.057	0.101
Lu(NTA)·4H ₂ O	0.058	0.103
Y(NTA)·4H ₂ O	0.054	0.131

were noted. A compound originally prepared as $\text{Dy(NTA)} \cdot 2.68\text{H}_2\text{O}$ changed to $\text{Dy(NTA)} \cdot 2.93\text{H}_2\text{O}$ at 25°C and gave a solubility of 0.154 grams Dy(NTA) per 100 grams of water. At 60° the observed composition was $\text{Dy(NTA)} \cdot 2.74\text{H}_2\text{O}$ and the solubility 0.193 grams per 100 grams H_2O . The increase in solubility with temperature appeared normal and the solubilities have been listed in Table III as those for the normal trihydrate of Dy(NTA) , although the compositions obtained for the neodymium, samarium, europium, gadolinium and terbium compounds were closer to that of a trihydrate. $\text{Ho(NTA)} \cdot 2.74\text{H}_2\text{O}$ changed to $\text{Ho(NTA)} \cdot 3.64\text{H}_2\text{O}$ yielding an apparent solubility of 0.3355 grams of Ho(NTA) per 100 grams of water at 25°C . At 60° the composition changed to $\text{Ho(NTA)} \cdot 1.64\text{H}_2\text{O}$ and the observed solubility was 0.1902. In the case of $\text{Er(NTA)} \cdot 1.96\text{H}_2\text{O}$ the composition changed to $\text{Er(NTA)} \cdot 2.76\text{H}_2\text{O}$ at 25° and $\text{Er(NTA)} \cdot 2.06\text{H}_2\text{O}$ at 60° . The solubilities observed were 0.2320 and 0.1940 grams Er(NTA) per 100 grams of water, respectively.

The apparent negative temperature coefficients of solubility for these non-stoichiometric hydrates of Ho(NTA) and Er(NTA) suggest that different hydrates or perhaps different mixtures of hydrates were in contact with the aqueous phase at the two experimental temperatures.

2.4 $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$

A paper, "The Solubilities of Lanthanum Chloride 7-Hydrate and Lanthanum Chloride 6-Hydrate in Water, and a Study of the Thermal De-

composition of Hydrated Lanthanum Chloride", by Jack E. Powell and Harvey R. Burkholder, was submitted for publication in J. Inorg. Nucl. Chem. :

Abstract--Thermal decomposition of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ results in the stepwise formation of $\text{LaCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot \text{H}_2\text{O}$, LaCl_3 and LaOCl . Under proper conditions either $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ may separate from aqueous solutions of lanthanum trichloride. The solubilities of the hexa- and heptahydrates at various temperatures are given.

3. Stability Constants of Rare-Earth Chelates (J. E. Powell)

The mercury electrode method for determining stability constants has been used to measure the stability constants of compounds formed between the rare-earths and some aminopolyacetate chelating agents. Data have been obtained at 20°C and an ionic strength of 0.1 for 1:1 hydroxyethylethylenediaminetriacetate (HEDTA), diaminodiethylethertetraacetate (ME), and ethyleneglycol-bis-(2-aminoethyl)ethertetraacetate(DE) complexes of the rare earths.

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

4.1 The Isotopes of Sulfur

Following up the encouraging results reported last period for the enrichment of sulfur isotopes by eluting a band of adsorbed HS^- ion down hydroxyl-form Permutit-SK anion-exchange resin with 0.03 N hydrochloric acid, an experiment was performed to establish the separation

factors for the following equilibria:

The nature of the experiment was to pass a solution of H_2S dissolved in water through a short bed of hydroxyl-form Permutit-SK resin until the bed was saturated with HS^- and the S^{33} and S^{34} contents of the effluent H_2S returned to normal. By measuring the number of equivalents of H_2S in each fraction collected, assaying each fraction for S^{32} , S^{33} and S^{34} by means of a mass spectrometer*, and knowing the capacity of the resin bed, it was possible to obtain $\text{S}^{33}\text{-S}^{32}$ and $\text{S}^{34}\text{-S}^{32}$ separation factors according to the method of Spedding, Powell and Svec.¹ The values obtained were $\alpha_{32}^{33} = 1.0061$ and $\alpha_{32}^{34} = 1.012$. From these two values it can be seen that α_{33}^{34} would be approximately 1.006, since $\alpha_{32}^{34} = \alpha_{32}^{33} \cdot \alpha_{33}^{34}$.

4.2 The Isotopes of Nitrogen

A series of experiments are being made to evaluate the effect of constitution on the $\text{N}^{15}\text{-N}^{14}$ separation factor in the ion-exchange reaction between an aqueous solution of an amine and Dowex 50. The method used is that of Spedding, Powell and Svec. Some tentative values are given in Table IV.

* Mass spectrometric assays were performed under the direction of Dr. H. J. Svec of this Laboratory.

¹ Spedding, Powell and Svec, J. Am. Chem. Soc., 77, 6125 (1955).

Table IV. N^{15} - N^{14} Separation Factors

Compound	Separation Factor
Ammonia	1.0257
Methylamine	1.0204
Ethylamine	1.0182
Propylamine	1.0208

The remarkable thing is that, after the notable drop in the separation factor upon adding one $-CH_2-$ unit, lengthening the chain further produces little change. Data for dimethyl-, trimethyl-, and diethylamines will be available soon, and it is planned to repeat the experiments with the primary amines, particularly the experiment with ethylamine.

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

5.1 Scandium

A paper, "Preparation and Properties of High Purity Scandium Metal", by F. H. Spedding, A. H. Daane, G. Wakefield and D. H. Dennison was submitted for publication in Trans. AIME.

Abstract--Preparation of pure scandium metal was accomplished by calcium reduction of the fluoride by two methods: a low temperature alloy process and direct reduction with subsequent distillation of the product.

The following properties were determined:

Melting point.....1839°K

Boiling point (calculated).....3000°K

Lattice constants at 298°K (hexagonal lattice)... $a = 3.308 \pm .001 \text{ \AA}$

... $c = 5.267 \pm .003 \text{ \AA}$

Calculated density at 298°K, grams per cm^3 ... $2.990 \pm .007$

Electrical resistivity, ohm-cm. 299°K. $23.1 \pm .2 \times 10^{-6}$

..... 373°K. $27.2 \pm .2 \times 10^{-6}$

Thermal coefficient at 299°K, ohm-cm per degree. 5.4×10^{-8}

Heat of sublimation at 298°K, Kcal per mole. 80.79

The vapor pressure was determined as a function of temperature between 1505°K and 1748°K, with the data fitted to a straight line yielding the equation:

$$\text{Log } P_{\text{mm}} = \frac{-1.718 \times 10^{-4}}{T^{\circ}\text{K}} + 8.298.$$

The preparation and purification of scandium metal has been continued. The optimum conditions for high vacuum distillation of crude scandium metal (containing from 2 to 5% Ta) have been determined. To achieve a reasonable rate of distillation and yet not overheat to induce large amounts of tantalum to dissolve into the melt, a temperature of 1625°C has been found to be optimum. Using a 35 mil wall tantalum still, over 120 grams of high purity scandium have been obtained in this work.

5.2 Yttrium

In a similar study with yttrium, conditions for lowering the oxygen content of distilled yttrium were examined. The conditions of this study are given in Table V. The oxygen and carbon content of the metal fed into the still does not appear to be a critical factor, but a lower condenser

Table V. Purity of Yttrium Metal Distilled* from Various Sources

Purity of Starting Material	Condenser Temperature °C	O ₂ Content of Distillate
970 ppm O ₂	1300	275 ppm
2030 ppm O ₂	1300	215 ppm
3070 ppm O ₂	1300	190 ppm
200 ppm C ppm O ₂	1300	280 ppm
300 ppm C ppm O ₂	1300	250 ppm
750 ppm C ppm O ₂	1300	250 ppm
1500 ppm C ppm O ₂	1300	150 ppm
800 ppm O ₂	1250	130 ppm
800 ppm O ₂	1300	220 ppm
800 ppm O ₂	1350	150 ppm
800 ppm O ₂	1400	275 ppm

* Temperature of still pot was 2000°C.

temperature is accompanied by generally lower oxygen contents. Using a two-inch-diameter still constructed from 35 mil tantalum, 250 grams of yttrium may be condensed in one hour at a still pot temperature of 2000°C. The distilled metal is more easily fabricated than higher oxygen material, with a 90% reduction in thickness achieved in cold rolling without intermediate annealing.

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

6.1 Melting Points

The melting point of cerium was re-measured by thermal analysis using samples prepared from special high purity cerium salts. A value of 795°C was obtained on two samples; this value is believed to be more nearly correct than the 804°C figure reported previously.

6.2 Transformations

Thermal analyses of samples of distilled scandium have shown a high temperature transformation in this metal, similar to the situation found for most of the rare-earth metals. The transformation is at 1335°C, and probably indicates a high temperature body-centered-cubic form of the metal, again by analogy with the rare-earth metals. Further evidence for the body-centered-cubic form of scandium is presented in the results of a study of the Sc-Ti alloy system presented below.

The h. c. p. -b. c. c. transformation in yttrium has been observed at 1459°C in resistivity studies, in which the resistivity is seen to increase regularly from a value of 60 microhm cms at room temperature. At 1459°, an abrupt increase in resistivity is seen, with a mid-range value of 225 microhm cms. Thermal analysis of distilled yttrium shows a value of 1455°C for this transformation.

6.3 Vapor Pressures of Holmium and Neodymium

The vapor pressure of holmium metal has been studied using the quartz

fiber balance version of the Knudsen method. By introducing several modifications, data were obtained over the pressure range 5.9×10^{-7} to 9 mm, with no apparent inconsistencies. For liquid holmium (above 1461°C), the vapor pressure may be expressed as:

$$\log p_{\text{mm}} = - \frac{1.4069 \times 10^4}{T^{\circ}\text{K}} + 7.802$$

Heats of sublimation and vaporization at the melting point are 69.1 ± 0.5 and 64.4 ± 0.6 Kcal/mole respectively indicating a heat of fusion of 4.7 Kcal/mole. The boiling point is 2583°C .

The decomposition pressure of HoC_2 was also examined in this study, and a value of 78 Kcal/mole was obtained for the heat of decomposition. However, attempts to corroborate this by other measurements have not succeeded, and the above figure must be considered tentative.

The vapor pressure of solid neodymium was studied using the Langmuir method. Combining third law data with the measurements, a value $\Delta H_{273}^{\circ} = 77$ Kcal/mole was obtained. However, since the sample area changed during the measurements, this value is also tentative.

6.4 Heat Capacities

The heat capacities of lanthanum and ytterbium have been determined from 0° to 1100°C . The enthalpy plots of these studies are given in Figs. 1 and 2, where the heats of transformation and fusion are indicated. The heat capacities of the high temperature solid and liquid forms of these metals appear to be constant and are given in Table VI. The low temperature data (0° to the high temperature transformation) have not been pro-

Figure 1.

Figure 2.

cessed to give the exact heat capacities in this region, but they are known to be temperature dependent.

The heat capacity of Yb has been measured in the range 15-350°K. There is a definite change of slope and a temperature-time hysteresis effect above 200°K to as far as our measurements have extended.

The enthalpy of yttrium has been measured from 0° to 1100°C, and the study will be extended to the liquid region (above 1500°C) when the new calorimeter is in operation. This is a drop calorimeter that operates in a vacuum, and should be capable of making measurements to above 1800°C.

6.5 Hardness Measurements

The hardness of annealed specimens of distilled rare-earth metals are given in Table VII.

6.6 Magnetic Properties

The perpendicular and parallel initial susceptibilities of $\text{Tm}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$

Table VI. Heat Capacities of Rare-Earth Metals

Metal	Temperature Range, °C	Heat Capacity Cp Cal/mole/deg °C
La	868° to 920° (b. c. c. region)	9.45
	920° to 1100° (liquid)	8.21
Yb	760° to 824° (b. c. c region)	8.63
	824° to 1100° (liquid)	8.80

Table VII. Hardness of Rare-Earth Metals

Metal	DPH after annealing	Rockwell H Hardness
La	37	55
Ce	24	3
Pr	37	38
Nd	35	50
Sm	45	63
Eu	17	(26)*
Gd	57	67
Tb	46	62
Dy	42	57
Ho	42	57
Er	44	63
Tm	48	69

Table VII. (cont.)

Yb	21	-4
Lu	77	86
Y	38	61
Sc	--	(60 ^{**})

* Rockwell L Scale

** Rockwell F Scale, Quenched from 860°C.

have been measured in the range 1.5-200°K using a dynamic mutual inductance method. The results do not agree with a statistical calculation of these properties using the crystal field approximation and two sets of crystal field constants available in the literature.

Tm metal has similarly been examined in the temperature range from 4-78°K by the mutual inductance technique, and found to exhibit a behavior at 55.8°K, the temperature of the maximum in the heat capacity, similar to that of Tb at its heat capacity maximum. Most interesting, however, is the large maximum in a plot of mutual inductance vs. temperature for Tm, in the region 27-30°K. This maximum exhibits hysteresis effects depending on whether measurements are made by cooling down through, or heating up through the region of the peak. The behavior corresponds to the effect observed in Tb corresponding to the bump in the heat capacity of Tb, below the maximum in the heat capacity of Tb. The heat capacity bump in Tb corresponding to the mutual inductance measurements which exhibited temperature hysteresis, however, also exhibited hysteresis. No corresponding anomaly has been observed in the heat capacity

of Tm in the range 27-30°K.

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

7.1 Corrosion Resistance of Low-Scandium Zirconium Alloys

The corrosion resistance to high temperature water of zirconium with small additions of scandium was examined.

Crystal bar zirconium with the following analysis was used:

	<u>ppm</u>
Fe	27
C	33
Al	25
Ti	8
N	10
Mg	25

The scandium added was distilled metal with a minimum purity of 99.8%.

The samples were prepared by arc melting under "gettered" argon with each sample turned four times and remelted. Samples of zirconium, 0.1 wt % Sc, and 0.5 wt % Sc were prepared, each weighing approximately 40 grams. They were reduced 50% in thickness by cold rolling and "coupons" 1" x 1/2" x 1/8" were cut out on a carborundum cut-off wheel. The surfaces were all prepared by grinding through successively finer papers to the final 600 grit paper. The samples were then placed in quartz test tubes and placed in steel bombs with freshly boiled distilled water added. The bombs were sealed and placed in a furnace at 310°C for 500 hours and then removed.

The results are vividly shown in Fig. 3. The possibility that some greater percentages of scandium would enhance the corrosion resistance of zirconium has not been eliminated, but the high cost of scandium and the poor results on low-percentage alloys seems to eliminate the need for any further experiments.

Zr

Zr-0.1 wt % Sc

Zr-0.5 wt % Sc

Fig. 3. Corrosion resistance of crystal bar zirconium with small additions of scandium.

7.2 Scandium-Titanium

A study of the scandium-titanium alloy system was begun to see if a predicted solid solubility existed in alpha forms of these metals, and to observe the effect of scandium on the beta form of titanium. The system has been examined by thermal analysis, x-ray and metallographic methods, and the essential features have been established:

- (1) There is a minimum in the solidus-liquidus curve at 1295°C at 49 wt % Sc.
- (2) There is a solubility of about 5 wt % of each of the metals in the alpha form of the other at about 850°C.
- (3) There appears to be complete solid solubility in the upper portion of the beta phases of these metals.
- (4) A monotectoid exists at approximately 55 wt % Sc and 1050°C, with the immiscibility loop extending from 18 to 55 wt % Sc, with a temperature range of 1050 to 1110°C at its maximum.

7.3 Yttrium-Nickel System

A paper entitled "Yttrium-Nickel System", by B. J. Beaudry and A. H. Daane was submitted for publication in Trans. AIME.

Abstract--The yttrium-nickel system has been investigated by metallographic, thermal and X-ray methods.

There are nine intermetallic compounds present: Y_3Ni , Y_3Ni_2 , YNi_2 , YNi_3 , Y_2Ni_7 , YNi_4 , and Y_2Ni_{17} which

undergo peritectic decomposition and YNi and YNi_5 which melt congruently. There are eutectics at 34.8, 57.5 and 93.3 a/o Ni which melt at 805, 950, and 1285°C, respectively. Crystallographic data are given for YNi , YNi_2 , YNi_3 , YNi_5 and Y_2Ni_{16} . The terminal solid solubility is low.

7.4 Yttrium-Manganese and Yttrium-Cobalt Systems

In a continuation of a study of the alloys of yttrium with the first transition group metals, the Y-Mn and Y-Co systems are being examined. The Y-Co system exhibits some similarity to the Y-Ni system, while the Y-Mn system differs in more details.

7.5 Laves Phases of Yttrium-Transition Elements

A paper, "Some Laves Phases of Yttrium with Transition Elements", by B. J. Beaudry, J. F. Haefling and A. H. Daane has been accepted for publication in Acta Cryst.

Abstract--Alloys containing 65.0, 66.7, and 68.0 a/o B were studied by X-ray diffraction powder techniques. YNi_2 has a composition range of approximately 0.7 a/o while YMn_2 , YFe_2 and YCo_2 are line compounds.

The lattice constants of the cubic Laves phases (C_{15} type) and YNi_2 are $a_0 = 7.680, 7.357, 7.216$ and $7.181 \text{ \AA}$, respectively.

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

8.1 Halides

As the rare-earth halides are directly involved in the preparation of the metals, a study has been under way to provide data such as melting points, crystal structures, vapor pressures etc. that are not known for all of these compounds.

Data obtained in this period are presented in Table VIII. Crystal structure studies of some of the rare-earth halides show the chlorides to have hexagonal or monoclinic structures as have been reported in the literature. For the difluorides SmF_2 , EuF_2 and YbF_2 , lattice constants of the f. c. c. phase are $5.86\text{\AA}$, $5.82\text{\AA}$ and $5.69\text{\AA}$ respectively.

8.2 YF_3 - Y_2O_3 System

In the preparation of yttrium by the reduction of YF_3 with calcium, trace amounts of oxygen in the YF_3 are known to contribute to the oxygen content of the product. It has been found to be extremely difficult to eliminate these last traces of oxygen from the fluoride, and to examine this problem, a study of the YF_3 - Y_2O_3 system was undertaken. The persistence of the oxygen in the fluoride appears to be due to a solid solubility of 2 mole % Y_2O_3 in the YF_3 . This solid solubility provides an environment for the oxygen that prevents direct contact with the fluorinating agent. Other features observed in this study are:

- (1) Confirmation of the solid transformation in YF_3 at 1050°C
- (2) A eutectoid at 1082°C and 34% Y_2O_3 .

Table VIII. Melting Points of Rare-Earth Halides

Halides	MP°C	Halides	MP°C
ScF ₃	1566	TmI ₃	1021
ScCl ₃	940 ± 40	LuI ₃	1050
ScBr ₃	950 ± 30	SmF ₂	1417
ScI ₃	920 ± 50	SmCl ₃	848 transition at 756°
NdI ₃	783	SmBr ₃	669
	transition at 580°	SmI ₂	520
TbI ₃	957	EuF ₂	1416
DyI ₃	978	TmCl ₂	697
HoI ₃	998	TmBr ₂	619
ErI ₃	1015	YbF ₂	1407
		YbI ₂	772

(3) A eutectic at 1116°C and 6% Y₂O₃

(4) A peritectoid at 1140°C and 37.5% Y₂O₃

(5) A transformation in α YOF at 556°C

X-ray studies of the high temperature forms of YF₃ and α YOF have given patterns that have not been indexed unequivocally, but the structures appear directly related to the low temperature forms of these compounds.

8.3 Thulium Diiodide

Previous work on thulium metal and some of its salts had suggested the existence of a divalent state of this element. This has been confirmed in studies in which TmI_2 was prepared by direct combination of the elements in a sealed tantalum crucible. X-ray diffraction showed the material to have the CdI_2 structure as has been reported recently by Asprey and Kruse of Los Alamos Scientific Laboratory. The paramagnetic susceptibilities of TmI_2 and TmI_3 were measured from room temperature to 200°C , and it was found that both compounds follow the Curie-Weiss law with values of Δ of 2° for TmI_2 and 11° for TmI_3 . Table IX shows the results of these measurements. It is quite apparent that in TmI_2 , thulium is in the divalent state and that it is isoelectronic with the Yb^{+3} ion.

8.4 Yttrium Triiodide

A report (IS-57) entitled, "The Determination of the Melting Point, the Vapor Pressure and the Decomposition Temperature of Yttrium Triiodide", by D. H. Dennison, F. H. Spedding and A. H. Daane, was distributed.

Abstract--Yttrium iodide was prepared by reacting yttrium metal turnings with ammonium iodide. The resulting salt was distilled into a melting point assembly and the melting point and vapor pressure were

determined by conventional techniques. Little decomposition of the iodide on a hot surface was observed under conditions that gave 100% decomposition of zirconium iodide.

Table IX. Magnetic Data of TmI_2 and TmI_3

Compound	Magnetic Moment Bohr Magnetons		Curie Const.	
	Expt.	Calc.	Expt.	Calc.
TmI_2	4.58	4.54	2.61	2.56
TmI_3	7.63	7.56	7.22	7.09

9. Preparation of Alkali Metals

A study of the preparation and properties of the alkali metals was prompted by a review of methods employed to prepare cesium and rubidium metals, in which reduction of the alkali oxide with an active metal of lower volatility appeared to be one of the methods of choice. As a somewhat parallel situation, it appeared likely that lanthanum could be used effectively as a reductant in such a reaction, much as in the reaction by which samarium, europium and ytterbium metals may be prepared from their oxides. To provide a more liable medium in which to react, cesium and rubidium fluorides were proposed as the reactant salts for test experiments. Mixed with lanthanum turnings and heated in a vacuum, these salts gave excellent results; additional experiments were carried

out on sodium and potassium fluorides and the results are given in Table X.

Table X. Conditions for Preparation of Alkali Metals

Metal	Temperature of Reduction °C	Yield %
Na	390	82
K	405	64
Rb	315	92
Cs	290	91

It was found that, although pyrex equipment may be used at 500°C, Cs and Rb attack this material slightly, with Na and K showing a somewhat greater effect.

This work is being continued to see if one of the alkali metals may be preferentially distilled out of a mixture of their fluorides in such a reaction. Preliminary experiments indicate that good separations of Cs and K may be realized; more quantitative experiments are being made on mixtures of CsF and RbF.

10. Surface Chemistry (R. S. Hansen)

10.1 Adsorption Kinetics

A paper, "The Theory of Diffusion Controlled Adsorption Kinetics with Accompanying Evaporation", by Robert S. Hansen was published. (J. Phys. Chem. 64, 637 (1960)).

Abstract--A quantitative theory is developed for diffusion controlled adsorption at the liquid-air interface with simultaneous

diffusion-controlled loss of solute into the vapor phase.

No essential complications result from inclusion of evaporational losses, and the general result is an integral equation equivalent to one given earlier by Ward and Tordai. A power series representation of the adsorption valid at small times and an asymptotic representation valid at large times are given, and the integral equation is solved numerically for adsorbates satisfying the Langmuir adsorption isotherm. The results explain the transient steady state observed recently by Hommelen in the surface tension of aqueous solutions of organic solutes. The infinite initial rate of adsorption predicted by diffusion-controlled adsorption theory is not in agreement with available data.

10.2 Gravimetric Adsorption Apparatus

A paper, "High Sensitivity-High Capacity Gravimetric Adsorption Apparatus", by Frank C. Edwards and Robert S. Hansen was submitted for publication in Rev. Sci. Instr.

Abstract--The Edwards-Baldwin magnetically controlled quartz fiber microbalance was adapted for gas adsorption studies. The gas adsorption apparatus consisted of an adsorption microbalance and a gas density microbalance completely enclosed except for a Bayard-Alpert valve connection to a dosing chamber. Sensitivity of the ad-

sorption balance was 0.1 microgram for loads as high as 10 gm, and of the gas density balance of the order of 0.01 mm of Hg with gases of molecular weight of about 100.

The important advantage of convenient external weighing inherent in magnetically compensated balances is retained. In addition, the balance is effectively a single piece of fused silica, cannot lose alignment except by breakage, and can tolerate any reagents, gaseous or liquid, which will not attack silica. For example, the balance section of the apparatus can be cleaned with hot nitric-sulfuric or chromic acids, and the entire apparatus can be baked out under evacuation at 300°C.

Design, construction, and operation of the balances are discussed in terms of mechanical theory of balance sensitivity.

Suitability of the apparatus constructed was demonstrated by the measurement of isotherms for the adsorption of ethyl bromide on a 832 cm² sample of cubic habit NaCl.

10.3 Measurement of Electronic Absorption Spectra (L. S. Bartell)

A quantitative procedure for deducing electronic absorption spectra of unimolecular layers of molecules on metal surfaces was worked out

and applied for the first time. Spectra were measured, by the use of a polarizing spectrometer for films a few angstrom units thick, both with crystalline and with dilutely dispersed films. Significant differences were observed according to the state of aggregation of the film on the surface. In some cases absorption maxima were observed that were not characteristic of the film material or of its known complexes in solution, but rather, apparently, of an adsorption complex with the underlying surface. The results promise to give new information regarding the electronic interactions of adsorbates and adsorbents that are responsible for adsorption forces.

10.4 Wetting of Solid Surfaces (L. S. Bartell)

A paper, "Wetting of Solids by Solutions as a Function of Solute Adsorption", by R. J. Ruch and L. S. Bartell was published in J. Phys. Chem., 64, 513 (1960).

Abstract--The wetting of flat platinum and chromium slides of small surface area by aqueous solutions of decylamine was measured as a function of the adsorption of the amine and the surface tension of the solutions. Adsorption at the solid-solution interface was measured in situ by an optical polarimetric method and wetting was determined concurrently by contact angle measurements employing the captive bubble technique. Adsorption and wetting results for platinum were sharply defined but those for chromium were somewhat obscured by erratic

kinetic effects. Multilayer adsorption was observed in all cases, and isotherms on platinum in basic solutions exhibited steps. The observed contact angles of the solutions on platinum rose from 0° to a maximum of about 90° as adsorption increased, and then fell, sometimes to 0° , as adsorption proceeded further. A model is proposed to explain the wetting results which provides a semi-quantitative scheme for computing the behavior of the contact angles from the adsorption isotherms.

11. Vapor Pressure of HCl-HBr System (J. D. Corbett)

The paper of "Pressure-Composition Data for the Liquid HCl-HBr System at Dry Ice Temperatures", by John D. Corbett and William J. Burkhard, has been accepted for publication in J. Inorg. Nucl. Chem.

Abstract--A simple, pressurized thermostat containing solid CO_2 has been used to achieve temperatures accurate to $< 0.01^\circ$ in the range -78.4 to -79.0°C . The vapor pressure of high purity HBr in this temperature range is given by $\log P_{\text{mm}} = -9.5915 \times 10^2 + 7.5316$. Similar equations are reported for the vapor pressures of eight mixtures of HCl and HBr and dew point pressures for four. The system shows moderate positive deviation from ideality.

12. Fused Salt Research (J. D. Corbett)

12. 1 Metal-Metal Halide Systems

12. 1. 1 Bismuth

Considerable progress has been made in the past year in the study of solutions of metals in their molten salts. An electromotive force study of the unusual solutions of bismuth metal in $\text{BiCl}_3(\lambda)$ has been completed. The results appear inconsistent with any of the suggested solute models, such as $(\text{BeCl})_n$ or $(\text{BiCl})_2 + \text{Bi}_2$.

12.1.2 Cadmium

The initial study of the formation of cadmium(I) compounds in fused salt systems has been completed. The manuscript "Stabilization of the Cadmium(I) Oxidation State. The System $\text{Cd}-\text{Cd}_2(\text{AlCl}_4)_2-\text{Cd}(\text{AlCl}_4)_2$ ". by John D. Corbett, William J. Burkhard and Leonard F. Druding has been accepted for publication in J. Am. Chem. Soc.

Abstract--The effects of added salts on the degree of solubility of cadmium metal in the molten cadmium(II) halides are reinterpreted in terms of acid-base reactions between the added halides and a solution of Cd_2X_2 in CdX_2 . At 335° , melts containing 67, 57 and 31 mole percent Cd_2^{+2} result when CdCl_2 , CdBr_2 and CdI_2 are reduced in the presence of two moles of the respective aluminum trihalides per mole of the dihalide. The presence of stable cadmium(I) salts in the diamagnetic, white to yellow products obtained on solidification of these melts is confirmed by the $\text{Cd}-\text{Cd}_2(\text{AlCl}_4)_2-\text{Cd}(\text{AlCl}_4)_2$ phase diagram and by the isolation of $\text{Cd}_2(\text{AlCl}_4)_2$. This salt decomposes to metal and a melt containing 65% Cd_2^{+2} at 227° and disproportionates in all solvents much more basic than benzene.

In the melts the increased stability of the cadmium(I) oxidation state when X^- is replaced by the larger and less basic AlX_4^- is considered to result from the decrease in the interaction of the more acidic cation, Cd^{+2} , with the anion, and in the solid, to a related decrease in the difference in lattice energies of the salts in the two oxidation states. The contrast between the light green color of the reduced tetrachloroaluminate melts and the opacity of those containing chloride ion is discussed.

In addition, the Raman spectrum of the melt containing 65% $Cd_2^{+2}(AlCl_4^-)_2$ has been recorded, verifying the structure deduced (above) by other means. The $+183\text{ cm}^{-1}$ displacement from Hg 5461A due to Cd_2^{+2} corresponds to a bond force constant about two-thirds of that in Hg_2^{+2} ; the known frequencies of $AlCl_4^-$ were also observed.

Present equilibria studies in acidic melts are being directed toward applications involving other low oxidation states and other acids.

12.1.3 Rare earths

The initial study of metal-metal halide systems for the praseodymium and neodymium chlorides and iodides has been completed. In contrast to the behavior in Ce-CeCl₃, where 9% metal solubility in molten CeCl₃ is the only interaction reported, all of the above systems form stable, solid subhalides. These are $PrCl_{2.3}$, $NdCl_2$, $NdCl_{2.27}$, $NdCl_{2.37}$, $PrI_{2.0}$, $PrI_{2.5}$ and $NdI_{1.95}$; all but the last two melt incongruently. The compound $PrCl_{2.3}$ disproportionates to $PrCl_3$ and Pr about 70° below its melting point, accounting for the earlier report of its nonexistence based on powder patterns of the quenched melts. The existence of lower halides of the

lanthanons appears far more general than formerly expected, since the surprising compounds LaI_2 and CeI_2 have also been obtained. These are isostructural with PrI_2 , while $\text{NdI}_{1.95}$ appears to have the (unknown) $\text{SmBr}_2(\text{SrBr}_2)$ structure. A simple fluorite structure results when about 15% of the neodymium in $\text{NdCl}_{2.27}$ is replaced by cerium or praseodymium. Up to 24% of what is presumed to be Ce^{+2} can be substituted for Nd^{+2} in the $\text{NdCl}_{2.37}$ phase. Some of the preliminary results have been published.¹

12.2 Ion Mobility Studies in Fused Salts (F. R. Duke)

The alkaline earth chlorides were subjected to study by the radio-tracer method. During the year, sufficient progress was made to enable us to fix the transport number of Ba^{++} in BaCl_2 at 0.2 ± 0.05 and the transport number of Sr^{++} in SrCl_2 at 0.4 ± 0.07 .

12.3 Reaction Mechanisms in Fused Salts

The heavy metal ion-catalyzed decomposition of BrO_3^- in fused alkali nitrates was studied. The reaction sequence found was:

$\text{M BrO}_3^- \xrightleftharpoons{\text{slow}}$ decomposition products (Br_2 , O_2 , and MO) where M^{++} is Zn^{++} , Cu^{++} , Co^{++} and Ni^{++} . In some of the cases the equilibrium constant for the first reaction was determined. The catalytic efficiency of the ions relative to one another was found to be: $\text{Zn}^{++} = \text{Ni}^{++} < \text{Co}^{++} < \text{Cu}^{++}$.

¹ Leonard F. Druding and John D. Corbett, "Rare Earth Metal-Metal Halide Systems. The Preparation of Neodymium(II) Halides", J. Am. Chem. Soc., 81, 5512 (1959).

Studies were continued on the reaction sequence $S_2O_7^{2-} + NO_3^- \rightleftharpoons NO_2^+ + 2SO_4^{2-}$ followed by $NO_2^+ + NO_3^- \rightarrow 2NO_2 + O$, the variable under study being the solvent. Mixtures of $NaNO_3$ and KNO_3 of varying composition constituted the solvent. As KNO_3 increased, the equilibrium was affected only slightly, but the rate of the second reaction was greatly diminished.

12.4 Complex Formation in Fused Salts

A paper, "Complex Formation Constants of Lead and Cadmium Ions with Chloride in Fused Lithium Perchlorate", by Frederick R. Duke and Walter W. Lawrence was submitted for publication in J. Chem. Phys.

Abstract--Complex formation constants involving lead and cadmium ions with chloride ion have been determined in a fused KNO_3 - $NaNO_3$ eutectic. It is of interest to compare the complex formation constants in a nitrate solvent with those in a perchlorate. Lithium perchlorate is the only stable fused perchlorate and it has been shown to dissolve insignificant amounts of water at low humidity. Therefore the constants were determined in fused $LiClO_4$. The experiments paralleled exactly those reported in fused nitrates.

12.5 Transport Numbers in Pure Fused Zinc Chloride

A report (IS-114) entitled, "Transport Numbers in Pure Fused Zinc Chloride", by Arnold Lunden was distributed.

Abstract--Using radioactive tracers, the transport numbers have been measured for both the cation and anion in molten zinc chloride. Due to non-ideal conditions, there was a pronounced tendency for the experiments to give too low values for t^+ and t^- . This tendency became stronger as the current density increased in the cell. An extrapolation to zero current gives $t^+ = 0.6 \pm 0.1$. There was no detectable temperature influence on the transport number in the region from 420° to close to the boiling point, while measurements in the region below 420°C were uncertain due to the growth of dendrites of deposited zinc metal.

No current transport by complex ions could be detected.

13. Fe(II)-Fe(III) Exchange (F. R. Duke)

A paper entitled, "The Effect of Some Organic Compounds on the Rate of the Fe(II)-Fe(III) Exchange", by Frederick R. Duke and Edward Wolf was submitted for publication in I.S.J. Sci.

Abstract--The electron exchange rate involving Fe(II) and Fe(III) in aqueous perchlorate solution was studied in the presence of some potential "bridge" catalysts. It was found that paraphthalic acid acted as an electron bridge, as has been shown for other reactions by Taube. However, benzoquinone and pyrazine, both good potential catalysts having the "conjugated" structure and good basic groups at either end of the conjugation were found to be inactive.

14. Mass Spectra of Volatile Inorganic Compounds (H. J. Svec)

14.1 Natural Abundance of the Cr Isotopes

Our study of the chromium isotopic abundances in natural sources is completed except for assays on one or two of the minerals on hand. In addition to the chromites for which results have already been reported, the scope of the original work was expanded to include chromites from the Miller and Holbrook chondrites. Further extension involving metamorphic minerals included chromiferous chlorite, garnet, micas and diopside. Secondary minerals included the clay-like bodies miloschite, alexandrolite and avalite and the crystallites merumite ($\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and crocoite (PbCrO_4).

Alexandrolite, found in rotten serpentine located in a deposit in Tulare County, California, was the only mineral in which the isotopic abundances were different at the 3 σ confidence level from those found in the chromites.

Indeed this was the only mineral demonstrating differences beyond the 95 percent confidence level although miloschite and avalite were found to be different at the 90 percent confidence level.

The results of this extended work on the chromium isotopes in natural materials does not alter our original conclusions regarding the atomic weight of chromium based on the earlier measurements. With the exception of chromium from alexandrolite, which is a rare mineral and not one of commercial interest, all terrestrial and the meteoritic chromium bearing samples examined, have absolute isotope abundances within the ranges indicated here,

Cr^{50}	4.352 ± 0.024
Cr^{52}	83.764 ± 0.036
Cr^{53}	9.509 ± 0.027
Cr^{54}	2.375 ± 0.018 ,

in which the uncertainty is $\pm 3\sigma$. From these data a chemical atomic weight (conversion factor 1.000275), based on physical nuclide masses related to $\text{O}^{16} = 16$, of $51.998_5 \pm 0.001_3$ is obtained. On the basis of physical nuclide masses related to $\text{C}^{12} = 12$, the physical atomic weight of chromium is $51.996_3 \pm 0.001_3$, in good agreement with the proposed new chemical atomic weight based on $\text{O}^{16} = 16$, the conversion factor 1.000275 and our new absolute abundance values.

A report of the isotope abundances in terrestrial chromites has been accepted for publication in Geochemica et Cosmochemica Acta.

14.2 The Mass Spectra of Stannane

Stannane, SnH_4 , has been studied to determine the ion fragmentation patterns of both singly and doubly charged ions employing 70 volt electrons. Appearance potential data has been used to estimate the energies of the Sn-H bonds in $\text{SnH}_3^+ - \text{H}$, $\text{SnH}_2^+ - \text{H}$, $\text{SnH}^+ - \text{H}$ and $\text{Sn}^+ - \text{H}$. The heat of formation of SnH_4 from the gaseous atoms, based on appearance potential data and the ionization potential of Sn^+ has been determined to be $281.4 \pm 4.7 \text{ kcal-mole}^{-1}$. The heat for formation from metallic tin and aqueous H^+ ions is $72.4 \pm 4.7 \text{ kcal-mole}^{-1}$.

As a result of these studies, serious doubt concerning the validity of previous studies¹ reported for germane and silane has arisen. A report of the results of this work has been accepted for publication in J. Inorg. Nucl. Chem.

14.3 The Mass Spectra of Hydrides of the Group IV-B and V-B Elements

The discovery of a discrepancy between the observed fragmentation of stannane and that expected on the basis of report for silane and germane has indicated the feasibility of an extension of the volatile hydride studies to check these compounds. Studies on arsine, stibnine, bismuthine and plumbane are underway and preliminary results have been obtained. Dimeric hydrides have been found for both arsenic and antimony with the formulae As_2H_4 and Sb_2H_4 . Ion fragmentation patterns have been obtained

¹ Neurt and Clasen, Z. Naturforsch , 71A, 410 (1952).

for these dimeric hydrides.

New methods for preparing the hydrides of these elements have been developed based on sodium borohydride reductions. Some progress has been made in the synthesis of bismuthine and plumbane although no mass spectral data have been obtained to date.

14.4 Other Volatile Inorganic Compounds

Successful synthetic methods have been developed for preparing the highly pure (99.5 + %) VOCl_3 and VOF_3 from mineral sources and some progress has been made with the mass spectral studies of these compounds.

The fragmentation of $^{29}\text{N}_2$ in the ion source of an electron bombardment mass spectrometer to produce atomic ions has been studied and the results compared with those for $^{28}\text{N}_2$ and $^{30}\text{N}_2$. It has been found that more $^{15}\text{N}^+$ ions than $^{14}\text{N}^+$ ions are produced from $^{29}\text{N}_2$ with the $^{15}\text{N}^+ / ^{14}\text{N}^+$ ratio being 1.04 ± 0.01 at electron energies below 45 volts and increasing to 1.09 ± 0.01 for 100 volt electrons. These results have been observed in both 180° and 60° magnetic deflection mass spectrometers in which magnetic scanning was employed. A comparison of the total number of atomic ions from $^{28}\text{N}_2$, $^{29}\text{N}_2$ and $^{30}\text{N}_2$ indicates that there is no difference, within the precision of the measurements. These measurements have not been explained yet in either terms of possible isotope effects or possible instrumental discriminations.

15. Isotope Dilution Analyses (H. J. Svec)

15.1 Nitrogen in Metals

A wet chemical procedure for determining the amount of nitrogen in a metal or alloy has been developed which utilizes the isotope dilution

technique. Ammonium sulfate, either enriched or depleted in ^{15}N is added to the metal sample during conventional solution procedures. Ammonium ions resulting from the hydrolysis of bound nitrogen in the metals, mixes with that of the tracer and the total is then oxidized to N_2 in which form the element is analysed in the mass spectrometer. The method has been tested on a variety of metals and alloys including thorium, lanthanum, yttrium, titanium, chromium, manganese, vanadium, various steels, nickel-chromium, ferrotitanium, ferromanganese and ferrochrom. The range of nitrogen in these materials was from 2 ppm to almost 6 percent. Average precision was generally better than ± 5 percent.

15.2 Oxygen in Inorganic Compounds

A study of the oxygen isotopes in a large group of inorganic reagents has been made. This element is quantitatively released from these compounds as O_2 by means of KBrF_4 . Results of these studies indicate a 4 percent spread in the $^{18}\text{O}/^{16}\text{O}$ ratio. It is possible to determine the role of fresh water in the preparation of these compounds. Table XI shows the results.

Table XI.

Salt	$^{34}\text{O}_2/^{32}\text{O}_2$ (absolute)	
Sodium peroxide	0.00401	} Assay uncertainty + 0.000005 - 0.000005
Sodium acetate	0.00397	
Sodium borate	0.00408	
Sodium carbonate	0.00393	
Sodium chlorate	0.00388	
Sodium perchlorate	0.00387	
Magnesium perchlorate	0.00395	
Ammonium molybdate	0.00399	
Sodium nitrate	0.00393	
Trisodium phosphate	0.00409	
Sodium sulfite	0.00394	

Sodium sulfate	0.00395		0.00002 (Value varies with weather conditions)
Rust on radiator (Chem. Bldg.)	0.00393		
ISU Chem. Dept. distilled H ₂ O	0.00393		
Atmospheric H ₂ O (Ames)	0.00393		
Atmospheric O ₂	0.00409		

Excess fresh water was used in one of the preparation steps for sodium carbonate, magnesium perchlorate, sodium nitrate, sodium sulfite and sodium sulfate. The low values for sodium chlorate and perchlorate indicate different rates of reaction for ¹⁶O and ¹⁸O in the electrolytic oxidations used to prepare these compounds.

An isotope dilution technique has been found feasible for the direct determination of oxygen in any of these compounds. Enriched tracers may be prepared by equilibrating concentrated solutions of these salts with enriched water. By mixing weighed amounts of tracer and salt and determining the resultant isotopic constitution of O₂ released with KBrF₄, accurate and precise oxygen assays are achieved. The method should be widely applicable to investigators working in the field of non-stoichiometric oxides and salts.

15.3 Oxygen Isotopes in the Boron Minerals of the Kramer Ore Body, Boron, California

A study of the oxygen isotopes in the various boron minerals found in the Kramer Ore Body at various levels in the open pit mine have been made. The results are given in Table XII, in order from the lowest levels to the top of the deposit.

Table XII.

Ore and Position	$^{34}\text{O}_2/^{32}\text{O}_2$
1. Probertite, veins in shale below entire ore body	0.00401
2. Borax, 2225' level	0.00405
3. Kernite-borax, shaly, 2250 level	0.00409
4. Kernite, 2275' level	0.00412
5. Lesserite, 2290' level	0.00405
6. Indcritite, 2300' level	0.00402
7. Ulexite, 2 foot layer above inderite, 2302' level	0.00402

Layers above (7) have been eroded away and are lost.

All these minerals are hydrates and were dehydrated before the oxygen isotopic assays were made. In all cases the water of crystallization had the same isotopic abundance as the anhydrous borates.

The time during which the first four layers were being deposited was characterized by a period in which the rate of evaporation was greater than the rate of influx of fresh water. Thus a concentration of ^{18}O in the lake water resulted with the minerals being deposited in isotopic equilibrium with the lake water. This period of evaporation was followed by one in which the rate of influx of fresh water was sufficient to lower the ^{18}O content of the waters with the resultant lowering of the ^{18}O content of the borate and water of crystallization oxygen.

16. Development of Methods for Isotopic Assay of Various Elements

(H. J. Svec)

16.1 Carbon and Nitrogen

As a result of attempts to separate the isotopes of C and N by anion chromatography, samples in the form of AgCN have been received. These are converted to a mixture of CF_4 and N_2 by heating with CoF_3 . The resultant mixture may be separated or may be used directly to assay both nitrogen and carbon using N_2^+ and CF_3^+ or CF_2^+ ion currents.

16.2 Oxygen and Nitrogen

The work of other laboratory groups with aquo complexes of various platinum chloride and ammine compounds presented the problem of assaying the aquo oxygen for its isotopes and the compounds for their N/O ratio. The first was accomplished by means of the KBrF_4 reaction while the latter was accomplished by the CoF_3 reaction. Both oxygen and nitrogen are quantitatively released from the platinum compound with both of the reagents but their individual use depends upon the rapidity required for reaction and problems associated with the outgassing of apparatus.

16.3 Silicon and Oxygen

Silicates and silica when heated with KBrF_4 or CoF_3 form SiF_4 and O_2 . These are used to assay for the respective isotopes using O_2^+ and SiF_3^+ ion currents.

16.4 Boron and Oxygen

When boric acid or boric oxide is heated with KBrF_4 or CoF_3 , BF_3

and O_2 are formed. O_2^+ and BF_2^+ ion currents are used to assay the isotopes of boron and oxygen in these compounds.

17. The Cohesion in Polyatomic Many-Electron Systems and the Physical Nature of the Chemical Bond (K. Ruedenberg)

Research on this problem has recently yielded the first known rigorous breakdown of molecular binding-energies in terms of physically significant fragments, on the basis of purely quantum-mechanical premises. It is hoped that this partitioning will be susceptible to empirical ordering schemes and interpretations.

During the period of this report, this work was pursued in several directions.

- (1) Particular difficulties were found to exist for a partitioning of the energy, the electron density and the electron pair density which would properly represent partial transfer of electrons between atoms with slightly different electronegativities. In the end, a satisfactory solution was found and applied in the case of the water molecule.
- (2) In view of the experiences gained with hand calculations carried out for the molecules H_2O , N_2 , CO_2 , a program is being constructed for the ISU Cyclone electronic computer, in order to be able to carry out the new analysis

for arbitrary molecular wavefunctions.

- (3) This computer program will be used to analyze those bona fide molecular wavefunctions which are presently available. The data for these molecules (about 50) are being assembled and prepared in a form suitable for the computer program.
- (4) Application of the theory to the H_2 molecule has led to the conclusion that certain common notions concerning the nature of the chemical bond must be revised:

It is known that: (1) by virtue of the virial theorem the molecular binding energy ΔE results from the potential energy drop $\Delta V = 2 \Delta E < 0$, and in spite of the kinetic energy increase $\Delta T = -\Delta E > 0$; (2) bond formation is closely connected with the overlap of atomic wavefunctions in the bond region.

Current opinion, fashionable in quantum-mechanical textbooks, regards the facts (1) and (2) as demonstrating that the quantum-mechanical overlap effect accumulates in the bond extra charge (as compared with a classical model) and that this extra charge, being attracted by both nuclei, gives rise to the negative potential ΔV . A quantitative analysis shows this inference to be invalid.

In actual fact, the overlap accumulation of charge leads to

a considerable increase in potential energy. It furnishes, however, a decrease in kinetic energy. The resulting low kinetic energy density in the bond region permits a high kinetic energy density near the nuclei without undue increase of the total kinetic energy. As a consequence, the valence electrons can cluster more tightly around the nuclei than in the free atoms before being held back by virtue of the uncertainty principle in the form of the virial theorem. In doing so they acquire the negative potential energy ΔV .

Thus the chemical bond owes its existence to a lowering of the kinetic energy in the bond region which, indirectly, creates the possibility of a closer approach of the valence electrons to the nuclei with a concomitant lowering of the potential energy.

Pyrometallurgy

1. Low Decontamination Separations (A. F. Voigt)

1.1 Distribution of Rare-Earth Metals Between Alloy Phases

It was observed earlier that the rare-earth metals are removed very effectively from a uranium-5 wt % chromium phase by extraction with a magnesium-48 wt % silver phase. These two phases are highly insoluble in each other at 1000°C, the temperature of the experiments, and a separation of phases can be achieved by allowing the molten mixture to stand at this temperature before solidification. The very much greater concentration of the rare-earth metal in the final Mg-Ag phase led to results which were not as consistent as they might have been, since a small amount of Mg-Ag trapped in the U-Cr phase on cooling would contribute more of the rare earth to the latter than was there as a result of its solubility. Thus, there is good reason to consider the distribution coefficients defined as $K_d = \frac{g_{RE}/g_{Mg-Ag}}{g_{RE}/g_{U-Cr}}$, as lower limits, or to consider the larger values obtained as being closer to the actual distribution coefficients or solubility ratios.

Analyses were made by radiochemical techniques. Samples of the rare-earth metals were irradiated in CP-5 at Argonne National Laboratory to produce Nd^{147} , Sm^{153} and Tb^{160} . The specific activities of the resulting metals were determined. The analyses were made by separating the rare earth from uranium and its daughter products and counting with a

gamma ray scintillation spectrometer. Gamma ray energies for counting were chosen as those which gave the highest sensitivity, 91 Kev for Nd^{147} , ~ 60 Kev for Sm^{153} and ~ 40 Kev for Tb^{160} .

The two phases were contacted in a rocking furnace for one hour at 1000°C , allowed to stand at temperature for 10 minutes, and water quenched. Samples were taken by sectioning the solid into discs. In all cases, equilibrium was approached from both directions by adding the rare earth to one of the two phases, analyzing a sample of that phase and equilibrating the remainder with the other alloy.

The results are presented in Tables XIII, XIV, and XV for neodymium, samarium and terbium respectively. In the cases of neodymium and samarium, two sets of experiments were run at different times. The rare-earth content of the U-Cr phase in the first set was very low after the extraction, resulting in low counting rates and poorer statistics.

Considering that the most probable errors would lower the distribution coefficients, the preferred values are 4×10^4 for Nd, 4×10^4 for Sm and 8×10^3 for Tb. Until techniques are found for eliminating the contamination of the U-Cr phase by trapped Mg-Ag, greater accuracy than this would be difficult to achieve.

Table XIII. Distribution of Neodymium Between Alloy Phases

Original		Analyses, mg Nd/g Phase Final		$K_d(\times 10^{-3})$	% Rem.	Ag in Final U-Cr Mg-Ag/g U-Cr
U-Cr	Mg-Ag	U-Cr($\times 10^3$)	Mg-Ag			
0.514		0.048	3.12	65	99.99	
	13.42	0.87	12.71	15		
	12.96	1.3	11.60	9		
0.566		1.25	3.42	2.7	99.78	
0.566		0.42	4.03	9.6	99.93	
	13.19	2.0	13.16	6.6		
(Nd added to both layers at time of mixing)		3.6	18.7	5.2		
0.984		7.3	6.0	0.81	99.25	0.6
0.994		9.1	5.6	0.61	99.08	1.06
0.996		11.8	5.7	0.48	98.81	1.01
0.997		0.14	5.7	40	99.99	0.004
	13.89	0.33	13.9	42		0.004
	13.41	35.	13.7	0.40		0.59
	13.44	2.5	13.6	5.4		0.023
	13.46	33.	13.1	0.49		1.38

Table XIV. Distribution of Samarium Between Alloy Phases

Analyses, mg Sm/g Phase					
<u>Original</u>		<u>Final</u>		<u>$K_d(\times 10^{-3})$</u>	<u>% Rem.</u>
<u>U-Cr</u>	<u>Mg-Ag</u>	<u>U-Cr($\times 10^3$)</u>	<u>Mg-Ag</u>		
0.424		0.040	2.37	59 ± 21	99.99
0.422		0.154	2.38	15 ± 9	99.96
0.417		0.053	2.28	43 ± 10	99.99
0.418		2.24	2.24	1 ± 0.3	99.46
	5.66	2.88	4.99	1.8 ± 0.5	
	5.54	7.52	5.24	0.70 ± 0.2	
	5.54	0.84	5.19	6.1 ± 0.6	
	5.21	1.98	5.19	2.6 ± 0.5	
0.312		0.057	1.82	32.	99.98
0.316		0.186	1.92	10.4	99.94
0.318		0.198	1.82	9.2	99.94
0.318		0.054	1.82	33.	99.98
	2.48	0.056	2.30	41.	
	2.48	0.044	2.23	51.	
	2.97	$2.93^{(1)}$	2.10	0.72	
	2.97	0.061	2.14	35.	

(1) Sample contaminated with relatively large amounts of silver.

Table XV. Distribution of Terbium Between Alloy Phases

Analyses, mg Tb/g Phase					
Original		Final		$K_d(\times 10^{-3})$	% Rem.
U-Cr	Mg-Ag	U-Cr $\times 10^3$	Mg-Ag		
0.702		0.612	4.08	6.68	99.91
0.845		6.28	4.02	0.64	99.26
0.845		16.7	4.08	0.24	98.02
0.612		1.60	3.82	2.4	99.74
	5.20	0.557	4.66	8.38	
	5.10	0.556	4.49	8.36	
	5.11	1.20	4.55	3.78	
	5.13	0.493	4.54	9.18	

1.2 Vapor Pressure Measurements

Two methods of measuring vapor pressures of components in alloys have been under study as ways of determining thermodynamic properties of importance in such systems, particularly activity coefficients and free energies. The two methods are the Knudsen diffusion technique and a modified dew-point method. In both methods radioactive tracers have been used as the means of detecting the vapor phase.

1.2.1 Knudsen Method

In the Knudsen method, the vapor diffusing from a cell with a small opening is collected on a cold planchet and counted. For the systems which were studied, in which zinc was the vaporized metal, the Knudsen method did not give reproducible results. In order to test the method,

pure zinc was used to see if the vapor pressure curve of zinc could be reproduced. The results showed extreme scatter due to lack of constant deposition. A wide variety of deposition methods was tried, including the use of planchets of different metals, cleaning and plating the planchets with various techniques and collection over a wide temperature range, but none of the techniques improved the results sufficiently. Radioautographic studies of the deposit showed that it was far from uniform. Since the apparatus in a test with silver gave results which were quite satisfactory and in agreement with published values, it appears that zinc is an element for which the Knudsen method is unusually difficult to apply. This is probably due to the fact that its vapor pressure is in the right range for the method (10^{-4} - 10^{-2} mm), in a temperature range (250-350°C) which is too low for proper collection of the vapor, even on cooling the planchet with liquid nitrogen.

1.2.2 Dew-Point Method

In the dew-point method, as modified for this purpose, the vapor above an alloy was made to condense on a cold finger in a closed system. The temperature of this finger was measured and the moment of condensation was detected with a gamma ray scintillation telescope which was focused on the condensation point by means of a collimating system. A knowledge of the vapor pressure of the pure component which vaporizes out of the mixture can then be used to determine the vapor pressure of that component above the mixture. This method has been applied to two systems, Zn-Mg and Zn-Al. In both cases results have been obtained for a number

of alloys across the phase diagram. Some of the results appear to be anomalous and additional data are being obtained. Most of the effort has been on the Zn-Mg system in which eight alloys have been run over the temperature range 550-725°C. The isotherm (activity of zinc vs. composition) at 823°K shows minima at 40 and 70 a/o zinc and a maximum at 50%. At higher temperatures, the first minimum disappears and the position of the maximum shifts closer to the second minimum so that at the highest temperature, 1000°K, there appears to be a sharp drop from a maximum at 70 to a minimum at 74 a/o. With the limited number of compositions examined so far, the positions of these maxima and minima are only approximate.

The Zn-Al system has been examined to compare results by this technique with published values.¹ For some compositions good agreement was obtained while for others our values were closer to the ideal Raoult's Law value for the vapor pressure of a component in a mixture. No anomalies or pronounced maxima or minima have been observed in this system.

¹ Schneidner and Stoll, Zeit. Electrochem. 47, 527, (1941).

Analytical Chemistry1. Analytical Procedures (C. V. Banks and J. S. Fritz)1.1 Analysis for Oxygen1.1.1 High Temperature Fluorination

The high temperature fluorination apparatus for the determination of oxygen in metals and salts was redesigned and a new apparatus constructed. The new apparatus is of a simpler design and permits a more accurate measurement of the gas evolved. It is considerably safer and has been operated by a specially trained technician for routine analysis.

A number of U_3O_8 , Ag_2O , and As_2O_3 standard samples were analyzed in an effort to determine the precision and accuracy of the method. The oxygen recovery on the U_3O_8 and As_2O_3 samples was essentially quantitative provided the reaction tube was freshly charged for each analysis. Subsequent analyses were usually low and results up to 8% low were obtained when five to eight analyses had been made without recharging the reaction tube. The results on the silver oxide samples were all about 6% low.

The results obtained on the standard samples indicated the method very likely would give low results unless the reaction tube is recharged after every run or at least after every two runs. The results can then probably be depended upon to within $\pm 2\%$. This is, of course, based on the assumption that the sample reacts quantitatively. For the purpose of estimating small amounts of oxygen in metal and salts, the above precision is satisfactory. Better precision could undoubtedly be obtained if much larger

samples were used and up to ten times as much oxygen measured. This would involve modifying the gas measuring system slightly but this can be readily done if the demand arises.

A number of yttrium fluoride samples to which known amounts of yttrium oxyfluoride were added were analyzed by the KBrF_4 method. The results were very low and indicated that oxygen present as the oxyfluoride was evolved so slowly the KBrF_4 method would not be suitable. Table XVII shows a comparison of the results obtained on several yttrium fluoride-yttrium oxyfluoride samples by the inert gas fusion and KBrF_4 methods.

The method has also been used for the determination of the oxygen to metal ratio in uranium dioxide and tungsten trioxide as well as for the determination of oxygen in niobium(V) chloride, niobium(V) oxychloride, and vanadium(II) iodide.

1.1.2 Inert Gas Fusion

In order to determine whether the inert gas fusion technique could be used for the determination of oxygen in yttrium fluoride, regardless of the form in which the oxygen was present, a series of standard samples of yttrium fluoride was prepared to which known amounts of yttrium oxide or yttrium oxyfluoride were added. The base material was yttrium fluoride which had been analyzed repeatedly and had been found to be homogeneous. Weighed amounts of Y_2O_3 or α -YOF were added to weighed portions of this material and the mixture blended thoroughly under an inert atmosphere. Attempts to grind the mixtures always resulted in increasing the oxygen content greatly even if the grinding was carried out under an inert atmos-

phere. Apparently the yttrium fluoride became warm and extracted oxygen from the container. This apparently does not occur in the blending process and homogeneous standards were obtained. The results obtained on the standards thus prepared are given in Tables XVI and XVII. The vacuum fusion results were performed by members of the Spectrochemistry Group.

Table XVI. Oxygen Recovery by Various Methods on Yttrium Fluoride Samples Containing Y_2O_3

Sample No.	% Oxygen, Theory	% Oxygen Recovered		
		Inert Gas Fusion	Vacuum Fusion	KBrF ₄
1	0.1003	0.1015	0.1025	0.0600
2	0.1301	0.1306	0.1380	0.0900
3	0.1693	0.1702	0.1650	0.1300
4	0.2194	0.2200	0.1990	---

Table XVII. Oxygen Recovery by Two Methods on Yttrium Fluoride Samples Containing α -YOF

Sample	% Oxygen, Theory	% Oxygen Recovered	
		Inert Gas Fusion	KBrF ₄
1	0.1001	0.0998	0.0119
2	0.1607	0.1587	0.0270
3	0.2173	0.2098	0.0635

The data obtained indicate the inert gas fusion technique can be used for the determination of oxygen in yttrium fluoride. A paper, "Determination of Oxygen in Yttrium and Yttrium Fluoride by the Inert Gas Fusion Method", by C. V. Banks, J. W. O'Laughlin and George J. Kamin, was accepted for publication in Analytical Chemistry.

The possibility of using the inert gas fusion method for the determination of oxygen in other metal salts is being investigated.

1.2. Solvent Extraction

An investigation of various organophosphorous compounds as extractants for uranium and other metals was continued. The compound bis-(di-n-hexylphosphinyl) methane (H_4HDPM) was studied in particular. A summary of the physical properties of H_4HDPM is given in Table XVIII.

Table XVIII. Physical Properties of Bis-(di-n-hexylphosphinyl) methane

Physical Form	White, waxy substance
Melting Point	33-35°C
Boiling Point	247°C at 2 mm Hg
Density at 25°	0.951 g/ml
n_{25}^D	1.4721
Dipole Moment	3.6D
Molecular Weight	448.6 (Theory), 445 calc. from m. p. depression
Solubility in H_2O at 25°C	.0154 g/l
Readily soluble in most organic solvents.	

An exact correlation of the distribution coefficient for various metals into H_4 HDPM is difficult because of the effect many factors such as temperature, diluent for H_4 HDPM, electrolyte concentration in aqueous phase, the mineral acid used, and its concentration have on the distribution coefficient. A qualitative summary of the extractability of various metals into H_4 HDPM is given in Table XIX.

Table XIX. Extractability of Various Metal Ions with
Bis-(di-n-hexylphosphinyl) Methane

From 1 <u>N</u> HCl				
Distribution Coefficient	0-0.01	0.01-0.1	0.1-50	50 or higher
Metal Ion	Ga	Al	Fe(III)	Au(III)
	Cu(II)	Ga	Zr	Bi(III)
	Fe(II)	Ph(II)		Hg(II)
	Mg	Zn		Mo(VI)
	Ni(II)			Th
	Sm			U(VI)
	V(V)			
	Y			

Table XIX (continued)

From 1 N HNO₃

Distribution Coefficient	0 - 0.01	0.01 - 0.1	0.1 - 50	50 or higher
Metal Ion	Al	Mg	Hg(II)	Au(III)
	Ca	Zn	Fe(III)	Bi(III)
	Cu(II)		Mo(VI)	Th
	Ga		Sm	U(VI)
	Pb(II)		Y	Zr
	Ni			
	V(V)			

The extraction of uranium(VI) was studied extensively and the magnitude of the distribution coefficient was found to increase steadily with the mole ratio of H₄HDPM to uranium up to values of the ratio of at least 12.

Spectral evidence indicates that the uranium(VI) is present in the organic phase as a uranium(VI) dinitrate-H₄HDPM complex. The effects of the dielectric constant of the solvent, the temperature, and the electrolyte concentration on the extraction of uranium with H₄HDPM are consistent with the extractant species being of an ion association type.

Other new organic extractants that are being synthesized and studied are: bis-(bis-2-ethylbutylphosphinyl)methane, bis-(bis-2-ethylhexylphosphinyl) methane, bis-(diphenylphosphinyl)- methane, 1,1-bis-(di-n-hexylphosphinyl)propane, and tri-n-octylphosphine sulfide.

1.3 Differential Spectrophotometry

The precise determination of concentration by differential spectrophotometric methods was investigated. The conclusion was reached that large increases in the relative precision of concentration measurements were possible without special instrumentation. Generally, the relationship between the uncertainty in absorbance, ΔA , and the relative uncertainty in concentration is given by the equation

$$\frac{\Delta C}{C} = \frac{\Delta A}{SC}$$

where S is the slope of the absorbance-concentration plot. The general rule for good precision is to make the product SC as large as possible while keeping the uncertainty in absorbance, ΔA , small. The latter requirement means the spectrophotometer should be read near the zero absorbance end of the scale. This can readily be accomplished while still reading a highly absorbing sample solution by balancing the instrument at zero absorbance with a slightly less concentrated reference solution.

The use of more precise instruments or using conventional instruments in such a manner as to make them more sensitive to slight changes in absorbance will not necessarily result in any decrease in the relative concentration error. The use of a relative method, i. e., comparing the absorbance of the sample with the absorbance of a known reference, can result in an appreciable increase in both precision and accuracy. An extended discussion of this subject will be included in the proposed Encyclopedia of Microscopy and Spectroscopy which will be edited by Professor

G. L. Clark of the University of Illinois.

1.4 Fused Salt Spectrophotometry

An increasing interest in fused salt chemistry and the availability of several spectrophotometers in this group suggested that the fabrication of equipment for the spectrophotometric measurement of fused salt systems be undertaken. A literature survey was conducted and the necessary apparatus for spectrophotometric measurements on fused salt systems designed and fabricated. The cell compartment of the Cary Model 12 spectrophotometer was adapted to permit spectrophotometric measurements on fused salt systems up to 500°C. Absorption spectra for uranium (III), uranium(IV), and uranium(VI) chlorides in fused LiCl-KCl eutectic were obtained and were similar to the reported spectra for uranium in this media.

An attempt was made to obtain the absorption spectrum of zirconium(II) chloride in a fused LiCl-KCl eutectic. No characteristic spectrum was obtained, however, apparently due to the insolubility of zirconium(II) chloride in the eutectic.

The absorption spectrum of niobium(V) and neodymium(III) have also been obtained. Future plans include an investigation of the spectra of niobium(III) and possibly the various oxidation states of vanadium.

1.5 Aluminum

The polarographic method for aluminum using the aluminum complex with Solochrome Violet RS (Sodium salt of 5-sulfo-2-hydroxy- α -benzene

azo-2-naphthol)¹ was found to be satisfactory for the determination of aluminum in aluminum-yttrium alloys.

1.6 Cerium

Although a number of methods for the determination of small amounts of cerium have been proposed, none have been found to be particularly reliable or versatile. An investigation of the determination of cerium as the carbonate complex either polarographically or, for smaller amounts of cerium, spectrophotometrically, was undertaken. The polarographic method proposed by Dolezol and Novak was found quite satisfactory and the same general procedure and reagents could be used for the preparation of samples for the spectrophotometric determination of cerium as the carbonate complex. In the latter case, tartrate is not used as a masking agent, however, as it reportedly interferes with the spectrophotometric determination. The spectrophotometric method is considerably more sensitive than the polarographic method with the lower concentration limit approximately 5×10^{-6} molar in cerium while the polarographic limit is approximately 2×10^{-4} molar. Preliminary work indicates that the above two methods are both reliable.

1.7 Chromium

The spectrophotometric determination of chromium with diphenylcarbazide² has been applied to samples of lithium chloride-potassium chloride

¹ Anal. Chem., 22, 1264 (1950).

² Chemist Analyst, 83, 555 (1958).

eutectic mixtures containing chromium, zinc, zirconium, and magnesium. No separations are necessary.

1.8 Copper-Aluminum Mixtures

The method of Rush and Yoe¹ for the spectrophotometric determination of zinc and copper using zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene) was adapted to the determination of copper in the presence of aluminum by changing the pH from 5.2 to 10 and masking the aluminum with tartaric acid. The absorbance is read at 600 m μ .

1.9 Indium

A method was developed for the separation and determination of indium in indium-tin alloys containing less than five percent indium. The indium is first separated from the tin using an anion exchange resin in 0.5 M hydrochloric acid. The indium complex with 5,7-dichloro-8-quinolinol is then extracted into 1,2-dichlorobenzene and the absorbance measured. A manuscript describing this procedure is being prepared for publication.

1.10 Magnesium

It was found that magnesium can be determined in lithium chloride-potassium chloride samples by titration with EDTA to the Eriochrome Black T end point if the uranium, thorium, zirconium, and chromium, also present in the samples, are first extracted with TOPO.² Any zinc present in the samples is masked with cyanide before the titration.

¹ Rush and Yoe, Anal. Chem., 26, 1345 (1954).

² ASTM Special Technical Publication No. 238, (1958).

1. 11 Thiocyanate-Chloride Mixtures

Pyridine and copper(II) react with thiocyanate in slightly acid solution to form a green complex, $\text{Cu}(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_2$. The complex is extracted into chloroform or a chloroform-tributyl phosphate mixture and the absorbance is measured at $410 \text{ m}\mu$. The absorbance conforms to Beer's law in the range of one to 10 milligrams of thiocyanate per 100 ml of solvent. Chloride does not interfere. Chloride and thiocyanate displace the chloranilate ion from mercury(II) chloranilate in slightly acid solution forming the undissociated mercury(II) chloride. The free chloranilate ion is determined spectrophotometrically at $530 \text{ m}\mu$. Beer's law is followed from one-tenth to five-tenths of a millequivalent of chloride per 100 ml of solution. The chloride is then determined by difference. An alternative procedure is to destroy the thiocyanate by boiling the solution with alkaline peroxide after which the chloride is determined with mercuric chloranilate.

1. 12 Thorium-Zirconium-Uranium Mixtures

Uranium and zirconium both interfere with the spectrophotometric determination of thorium with thorin and the interference is not completely removed by the extraction of thorium into mesityl oxide. The ion exchange separation of thorium proposed by Neitzel, Wessling, and DeSesa¹ was tried and found to be satisfactory for the separation of thorium from uranium and zirconium in eutectic mixtures of lithium chloride and potassium

¹ Neitzel, Wessling, and DeSesa, USAEC Report WIN-62.

chloride.

1.13 Tungsten Bronzes

Work is in progress to develop methods for the determination of tungsten and the alkali metal in tungsten bronze samples. It has been found that the tungsten can be determined by reduction to the metal with hydrogen. The alkali metal can be determined by decomposing the sample with nitrosyl chloride at 500 to 1000°C. Lithium can then be determined spectrophotometrically with thorin while sodium and potassium can be weighed as the chlorides.

1.14 Uranium-Molybdenum Mixtures

It was found that uranium and molybdenum could both be determined as the thiocyanate complexes by measuring the absorbance of the solution at both 320 and 500 m μ . Both complexes follow Beer's law at 320 m μ but only the molybdenum absorbs at 500 m μ .

1.15 Uranium-Tantalum-Zirconium-Zinc

The method most satisfactory for the determination of uranium seems to be the arsenazo method following the extraction of uranium into a mixture of tributyl phosphate and isooctane. Niobium in amounts up to one milligram and tantalum up to 200 milligrams can be masked with sodium fluoride.

1.16 Zinc

The polarographic method for the determination of zinc in the presence of uranium in an acetic acid-ammonium acetate solution¹ was studied

¹ Anal. Chem., 25, 983 (1953).

and found to be satisfactory for the determination of zinc in lithium chloride-potassium chloride samples containing thorium, uranium, zirconium, chromium, magnesium, and zinc.

1.17 Zinc-Lead-Copper Mixtures

The lead is removed by precipitation as lead sulfate after which the zinc can be titrated with EDTA using Eriochrome Black T as the indicator under the following conditions. A trial run must be made to locate the approximate end point. A new aliquot is taken and slightly less EDTA is added. The indicator is then added and the titration completed. Satisfactory results were obtained.

1.18 Zinc-Uranium Mixtures

The interference of uranium in the polarographic determination of zinc was eliminated by extracting the uranium into TOPO from a nitrate solution. The zinc does not extract if chloride is absent.

1.19 Ion Exchange (J. S. Fritz)

A paper entitled, "Ion Exchange Separation of Metal Cations", by James S. Fritz and Shirley K. Karraker was published in Anal. Chem. 32, 957 (1960).

Abstract--Metal cations can be conveniently separated into groups by elution of a cation exchange column with an ethylenediammonium perchlorate solution. Most divalent ions are eluted from the column with 0.1 M eluent.

Then trivalent metal ions (plus barium and lead) are eluted with 0.5 M ethylenediammonium perchlorate.

Bismuth, thorium and zirconium remain quantitatively on the column after this treatment. The effect of temperature and of certain complexing anions on the separations was studied.

Dilute hydrofluoric acid has been used to separate metal ions from hydrogen-form cation exchange columns. Using an 8 cm column and 0.1 M HF as the eluting agent, the following metal ions are quantitatively eluted from the column in 180 ml or less: Al(III), Cd(II), Mo(VI), Nb(V), Sc(III), Sn(IV), Ta(V), Ti(IV), U(VI), W(VI), and Zr(IV). Most other metal ions are not eluted at all under these conditions. The following metal ions are partially eluted and thus interfere with a quantitative separation: Ga(III), rare earths(III), Mg(II). The elution behavior of Fe(III), Cd(II) and Th(IV) is much different from the hydrogen-form column than previously found from an ethylenediammonium-form column. Quantitative separation of several mixtures has been achieved.

Work on the anion exchange separation of metal ions from water-alcohol-hydrochloric acid systems is being completed. In this work we found that metal ions are taken up by an anion exchange column at much lower hydrochloric acid concentrations if an appreciable quantity of a water-miscible organic solvent is present. Further, the distribution coefficients of

most metal ions are appreciably higher in partly nonaqueous media, and some metal ions (such as thorium(IV) and rare earths(III) are absorbed which are not taken up at all from aqueous hydrochloric acid solutions. The order of alcohols in increasing the uptake of metal ions by the ion exchange resin is as follows: 2-propanol > ethanol > methanol. Many mixtures have been separated using eluting agents of different composition for the various metal ions.

1.20 Titration of Mercaptans with Mercury(II)

A paper entitled "Titration of Mercaptans with Mercury(II)" by James S. Fritz and Thomas A. Palmer was accepted for publication in Anal.

Chem.

Abstract--A rapid and precise titrimetric method for the determination of mercaptans is described. Samples (0.3 to 1 mmole) are titrated with mercury(II) perchlorate in neutral aqueous or acetone medium. The end point is detected either visually using thio-Michler's ketone (4, 4' Bis(dimethylamino) thiobenzophenone) as the indicator, or potentiometrically using the mercury indicator electrode. Smaller amounts of mercaptans in hydrocarbon solution are titrated photometrically.

The absorbance of the Hg(II) thio-Michler's ketone complex at 580 m μ is used to follow the course of the titration. A study of potential interferences show that chloride, acetonitrile and carbon disulfide do not interfere

in the visual indicator method for the determination of mercaptans. Large amounts (at least 20 to 1 molar ratio of added compound to thiol) of bromide, alkyl sulfide, thiophene, organic sulfide and styrene oxide can be tolerated. The important interferences are elemental sulfur, sulfide, iodide, cyanide and thiocarbonyl compounds. Acidic solutions of thiols must be neutralized prior to the addition of acetone to prevent mercaptal formation which leads to low, erratic results.

1.21 Titration of Metal Ions with EDTA

Several new metal indicators of the naphthyl azoxine type have been synthesized and tested for their usefulness in titrations of metal ions with EDTA. Of these, the 4-sulfo-1-naphthyl azoxine and 6-sulfo-2-naphthyl azoxine are especially good. These indicators are as good as naphthyl azoxine in weakly acid solutions, but have the advantage that they are equally useful in alkaline solution.

1.22 Determination of Bismuth

The possible interference of foreign metal ions in the EDTA titration of bismuth(III) using Xylenol Orange indicator has been investigated. Using a low pH and fluoride, tartrate or sulfate as a masking agent, a highly selective procedure for determination of bismuth has been developed. Using a back titration with bismuth(III), iron(III) can be determined in the presence of considerable quantities of fluoride.

2. Analytical Research (C. V. Banks)

2.1 Composition and Stability of Some Metal-5-Sulfosalicylate Com-

A paper, "Composition and Stability of Some Metal-5-Sulfosalicylate Complexes", by C. V. Banks and R. S. Singh has been accepted for publication in J. Inorg. and Nuclear Chem. in 1960.

Abstract--The 5-sulfosalicylate complexes of Al(III), Cr(III), U(VI), Ni(II), Co(II) and Mn(II) have been investigated by the potentiometric method. The Al(III)-and U(VI)-5-sulfosalicylate systems were also investigated spectrophotometrically. It was found that Al(III) forms 1:1, 1:2 and 1:3 complexes at pH values of 3.8, 5.5 and 8.5, respectively and that U(VI) forms 1:1 and 1:2 complexes at pH values of 4.5 and 7.5, respectively. The stability constants for Be(II)- and Cu(II)-5-sulfosalicylate complexes have been recalculated. The log k values found by the potentiometric method for the step-wise stability constants are as follows:
Al, 13.20, 9.63, 6.06; Cr, 9.56; U, 11.14, 8.06; Ni, 6.42, 3.82; Co, 6.13, 3.69; Mn, 5.24, 3.00; Be, 11.71, 9.10; Cu, 9.52, 6.93.

2.2 Silver/Bis(1,10-Phenanthroline)Silver(I) Nitrate Electrode

A paper, "Silver/Bis(1,10-Phenanthroline)Silver(I) Nitrate Electrode", by C. V. Banks and Patrick G. Grimes was submitted for publication in J. Am. Chem. Soc.

Abstract--The silver/bis(1, 10-phenanthroline)silver(I) nitrate electrode ($\text{Ag}/\text{AgP}_2\text{NO}_3$) which responds to the activity of the nitrate ion and the square of the concentration of free-base 1, 10-phenanthroline (activity coefficient taken as one) was developed for measuring the stability constants of the weak alkali metal-1, 10-phenanthroline complexes.

2.3 Reaction of 1, 10-Phenanthroline with Some M(I) and M(II) Ions

A paper, "Studies with a Silver/Bis(1, 10-Phenanthroline)Silver(I) Nitrate Electrode. I. Reaction of 1, 10-Phenanthroline with Some M(I) and M(II) Ions", by Charles V. Banks, Patrick G. Grimes and Richard Fullerton, was submitted for publication in J. Am. Chem. Soc.

Abstract--The reactions of the hydrogen ion and some alkali metal and divalent metal ions with 1, 10-phenanthroline have been studied. The stability constants of the complexes formed have been measured by means of a silver/bis(1, 10-phenanthroline)-silver(I) nitrate electrode. The log k values found for the step-wise stability constants are as follows: H, 5.27, 2.83, 3.97; Li, 2.32, 3.05; Na, 2.15, 3.25; K, 2.09, 2.84; Zn, 6.31, 6.09, 4.77; Cd, 5.75, 5.09, 3.07; Cu, 7.53, 6.07, 4.99; Co, 7.01, 5.43, 4.50. The proposed method should prove particularly useful for studying the weaker complexes, the stability constants of which cannot be conveniently determined by other methods.

2.4 Nickel(II) Complexes

A paper, "4-Carboxy 1, 2-Cyclohexanedionedioxime Complexes of Nickel(II) in Alkaline Media", by C. V. Banks and Joseph LaPlante was submitted for publication in J. Am. Chem. Soc.

Abstract--The reactions of 4-carboxy-1, 2-cyclohexanedione-dioxime and nickel(II) were studied in alkaline media. Spectrophotometric studies indicate the presence of 1:1 complex ion, NiD^- . Magnetic susceptibility measurements on a series of solutions of varying ratios of vic-dioxime and nickel(II) showed that the 1:1 complex ion was diamagnetic and that two paramagnetic complexes, probably NiD_2^{-4} and NiD_3^{-7} , are present in solution. The stability constants for the three complexes were calculated from spectrophotometric and magnetic susceptibility data. The log k values were found to be $\log k_1 = 28.74$, $\log k_2 = 0.76$, and $\log k_3 = 3.67$, respectively.

2.5 Acetylation of Phenols, Thiols and Amines (J. S. Fritz)

A paper entitled, "Acetylation of Phenols, Thiols and Amines", by George H. Schenk and James S. Fritz was published in Anal. Chem. 32, 987 (1960).

3. Service Analyses (C. V. Banks)

A total of 10561 service analyses were made during the period of this report.

Spectrochemistry

1. Analytical Emission Spectroscopy (V. A. Fassel)

1.1 Oxygen, Nitrogen, and Hydrogen Content of Metals

One of the most difficult and challenging problems facing analytical chemists today is the accurate determination of oxygen and nitrogen in metals in the 1 to 50 ppm range. Since it is becoming increasingly apparent that impurity concentrations of these elements at these levels may still exert significant effects on the physical properties of many metals, this deficiency in our analytical abilities is serious. The spectrometric techniques developed in our laboratory have now been applied successfully to determining oxygen, nitrogen and hydrogen down to 50 ppm. Considerable experimental work is now in progress to extend the sensitivity down to 10 ppm. A technique based on extracting the gaseous element contents with a high-current d-c arc discharge in pure argon followed by excitation of the gases with a microwave driven discharge appears particularly promising for lowering the detection limit for nitrogen.

A paper entitled "Emission Spectrometric Determination of the Gaseous Elements in Metals. VI. Oxygen in Vanadium", by Velmer A. Fassel and Lawrence L. Altpeter was published in Spectrochim. Acta 16, 443-9 (1960).

Abstract--The oxygen impurity content of vanadium metal can be determined spectrometrically by liberating it as carbon monoxide with a d-c carbon-arc discharge in pure argon. The arc discharge dissociates the evolved carbon monoxide and excites the emission

spectrum of oxygen. The intensity ratios of the line pairs $I_{O\ 7772\ \text{\AA}}/I_{Ar\ 7891\ \text{\AA}}$ and $I_{O\ 7775\ \text{\AA}}/I_{Ar\ 7891\ \text{\AA}}$ are related to the oxygen concentration. It is shown that the rate and degree of evolution of the oxygen content is sensitively dependent on the environmental conditions in the graphite supporting electrode. Oxygen concentrations in the range from 0.004 to 0.5 weight per cent can be determined with a coefficient of variation of ± 5 to 6 per cent of the amount present.

1.2 Total Oxygen Content of Metallic Halides

The possibilities of determining the total oxygen content of metal halides by emission spectrometric techniques has been under study and a method for the determination of the total oxygen content of yttrium fluoride has been devised. This procedure is based on the emission spectrometric techniques discussed in the preceding section. The fluoride samples are formed into briquets and placed into specially designed graphite electrodes which form the anode of high current d-c arc discharges in pure argon. If powdered graphite is admixed with the fluoride and if the excitations are conducted at reduced pressures, most of the oxygen content of the sample is evolved in 45 seconds. The intensity ratio of the line pair $I_{O\ 7775\ \text{\AA}}/I_{Ar\ 7891\ \text{\AA}}$ is related to the oxygen content. The concentration range 0.03 to 0.8 weight per cent oxygen is covered by the calibrations. The average of duplicate observations show a coefficient of variation of $\pm 5\%$ of the amount present.

1.3 Rare Earths

The arc and spark emission spectra of many of the rare earths are exceedingly complex, because both the neutral atom and ion spectra are excited to a high degree. On the other hand, the temperature distribution in conventional flames is so low that atomic spectra can be excited with adequate sensitivity in only Yb and Eu. When aerosols of aqueous solutions containing the rare earths are introduced into flames, the more stable reaction products are the rare-earth monoxide molecules. Their presence in the flame is signalled by the emission of strong band spectra characteristic of these species. Unfortunately, these spectra overlap to a high degree and are thus generally of little utility for the analysis of rare-earth mixtures. In order to achieve a higher degree of dissociation of these molecules we have explored the application of "hot" flames. The most intense atomic spectra have been obtained when absolute ethanol solutions of rare-earth perchlorates are aspirated into oxy-acetylene flames. Useful spectra of all the rare earths except Ce have now been observed and their analytical applications are being explored.

2. X-ray Fluorescence Spectroscopy (Scandium in Ores and Minerals)

An x-ray fluorescent spectrometric procedure has been devised for the direct determination of the scandium content of ores, minerals, ore concentrates, and rare-earth mixtures. No sample treatment is required other than blending the powdered sample with vanadium oxide and silicon carbide in the ratio 5:3:3. The intensity ratio of the $Sc_{K\alpha}/V_{K\alpha}$ is related

to the scandium concentration. A lithium fluoride crystal is used with a gas-flow proportional counter as the detector. Correction factors have to be applied if the sample contains appreciable amounts of Er and Ta. The concentration range 0.1 to 100 percent scandium oxide can be covered. The coefficient of variation is about ± 3 percent of the amount present.

3. Infrared Spectroscopy

For several years a project has been conducted in this Laboratory on the utilization of nitrogen-15 for the characterization of the nitrogen vibrational modes in organic compounds. The results of some of these studies have been reported.¹ More extensive studies of benzamide have been completed and the following papers have been submitted for publication in Spectrochim. Acta.

"Use of Nitrogen-15 for the Characterization of Infrared Bonds Arising from Nitrogen Vibrations", by Lindsley S. Gray, Jr., Velmer A. Fassel and Richard N. Kniseley.

Abstract--The infrared spectra of the nitrogen-14 and nitrogen-15 analogs of n-hexyl nitrite, benzenediazonium chloride and p-N,N-dimethylaminoazobenzene have been examined in the region from 4000 cm^{-1} to 450 cm^{-1} .

¹ Spectrochimica Acta, 16, 514-517 (1960).

The data thus obtained have been used to assign the bands which are characteristic of vibrational modes involving nitrogen movement. These data and assignments are presented in tabular form.

"Vibrational Spectra of Nitrogen Containing Compounds. I. Benzamide",
by R. N. Kniseley, Velmer A. Fassel, Lindsley S. Gray and Edward
Farquhar.

Abstract--The infrared spectra of benzamide- N^{15} and benzamide- N^{14} have been employed in assigning some of the vibrational modes of the parent compound. These studies indicate that the Amide I band is basically a C=O stretching vibration, whereas the Amide II band is a mixed vibration involving both a C-N stretching and a NH_2 deformation mode. In the solid state spectrum of benzamide the Amide II band actually falls at a higher frequency than the Amide I band. Other vibrational modes involving significant nitrogen or amide hydrogen motion are also assigned.

4. Vacuum Ultraviolet Spectroscopy

A comprehensive literature search has been completed and a bibliography is now in preparation. This bibliography covers the following subjects: (a) emission and absorption spectra of atomic and molecular species (b) absorption coefficients (c) spectral characteristics of light

sources providing continua and line radiation (d) useful window materials (e) analytical applications, and (f) ultraviolet and vacuum ultraviolet photochemistry.

5. High Temperature-High Vacuum Analytical Studies

A paper entitled "Determination of Oxygen in Yttrium Fluoride by a Vacuum Distillation Technique", by Virginia M. Horrigan, Velmer A. Fassel and John W. Goetzinger, was published in Anal. Chem., 32, 878 (1960).

Abstract--A conventional vacuum-fusion gas analysis unit is used for the determination of oxygen in yttrium fluoride. The yttrium fluoride is distilled from the furnace, leaving the less volatile oxygen-containing compounds to be reduced by the carbon crucible. Recoveries of oxygen are quantitative when a liquid reaction medium is provided for the reduction. The effect of platinum as the bath medium on the rate of carbon monoxide evolution is discussed.

6. Misidentifications in Rare-Earth Arc Spectra

A paper, "Misidentifications in the Arc Spectra of the Rare Earths", by R. Kniseley, V. A. Fassel and F. Lentz was submitted for publication in Spectrochim. Acta.

Abstract--The MIT Wavelength Tables contain a number of errors in the listing of the emission lines of the rare-earth elements. These errors consist of either misidentifications of the spectral lines or discrepancies

in the assigned intensities. Both types of errors apparently arose from the unrecognized presence of rare-earth impurities in the rare earths whose spectra were investigated. These misidentifications are listed in tabular form along with the correct assignments as determined by a careful examination of the spectra of highly purified rare earths.

7. Spectroscopic Service Analyses

During the period covered by this report, 5,930 samples were analyzed or examined by optical emission, X-ray fluorescence, and infrared absorption spectrometric techniques. In addition, 528 samples were analyzed for their O, N, or H content by vacuum fusion, vacuum distillation, or carrier-gas fusion manometric techniques. A number of new methods of analysis were developed.

Radiochemistry

1. Photo-Production of Beryllium-7 (A. F. Voigt)

Research is being continued on the production of the nucleus Be^7 by the gamma irradiation of light elements. The detection of this nucleus is by gamma-ray scintillation spectrometer observation of the 475 Kev gamma ray which it emits in 12% of its decays, and by its 53-day half-life. Thus far it has been observed in the $\text{Be}^9 (\gamma, 2n)$, $\text{B}^{10} (\gamma, p2n)$ and $\text{C}^{12} (\gamma, \alpha n)$ process. In each case the yield is extremely small and, for the first two cases at least, far less than one would expect on the basis of statistical models of nuclear reactions.

The observation of this nucleus at other laboratories as a spallation product in high energy nuclear reactions of heavier elements adds considerable interest to this study of its production at energies near thresh-

hold by a photo process. The study is being continued to obtain better data for qualitative evaluation of theory. Other nuclei such as O^{16} are also being studied since the 46 Mev maximum energy of the synchrotron beam is theoretically sufficient to produce Be^7 by the photo disintegration of such nuclei.

2. Production of Calcium-47 by Synchrotron Irradiation

There is considerable interest in the 4.7 day Ca^{47} as a tracer for medical and biological research. One of the principal drawbacks to its development is that by most methods of producing it, there are simultaneously produced undesirably large amounts of 150 day Ca^{45} . For medical use this long lived tracer is a distinct hazard. One way of producing Ca^{47} , the γ, n reaction on Ca^{48} , would lead to fairly pure Ca^{47} if the companion reaction $Ca^{46} (\gamma, n) Ca^{45}$ is not too important. The relative abundance in normal calcium of Ca^{46} is 0.0032% and of Ca^{48} , 0.18%. From normal calcium, the γ, n reaction would thus give a pronounced advantage to Ca^{47} relative to Ca^{45} but the specific activity would be low, possibly too low for medical applications. However, the use of enriched Ca^{48} would remove this drawback.

At the suggestion of the Oak Ridge National Laboratory and with their cooperation the irradiation of highly enriched Ca^{48} (95.6% Ca^{48} , < 0.1% Ca^{46}) was tried. A 69-hour irradiation of a small sample of $Ca^{48}CO_3$ was performed; the Ca^{47} was counted and the counting rate corrected to approximately absolute counting conditions. For this irradiation, a yield of $12.2 \mu c/mgCa^{48}$ was obtained from 37.2 mg of $Ca^{48}CO_3$ or $0.77 \mu c/$

mgCa⁴⁸. This sample has been followed for 21 half-lives of Ca⁴⁷, which is a decay factor of 2×10^6 . No indication of any Ca⁴⁵ has been seen. Due to the low Ca⁴⁶ content of this material any Ca⁴⁵ would be more likely to originate from the $\gamma, 3n$ reaction on Ca⁴⁸ than from the γ, n reaction on Ca⁴⁶.

The maximum beam energy for the irradiation was 46 Mev and by comparison with copper foils irradiated at the same time the integrated cross section was calculated to be 29 Mev millibarns ($\pm 20\%$).

3. Gamma Radiolysis of Carbon-14 Labelled Isobutane

A paper entitled "Gamma Radiolysis of Carbon-14 Labelled Isobutane" by Joseph Kivel and Adolf F. Voigt was submitted for publication in International Journal of Applied Radiation and Isotopes.

Abstract--The decomposition of liquid and gaseous carbon-14 labelled isobutane by cobalt-60 gamma radiation has been studied. Results are presented in terms of the G values of the radiation products. The specific activity of propane produced from isobutane-2-C¹⁴ was found to be about 1.5 times greater than that from isobutane-1-C¹⁴. Similar results were obtained for propylene. Carbon-14 activity was not found in the methane product when isobutane-2-C¹⁴ was irradiated. The isobutane yield was unaffected by changing the labelled compound. The yield of neopentane was considerably greater than that of isopentane. Effects

of temperature on hydrogen and methane formation are given and explained in terms of molecular and radical processes. Several mechanisms are presented for the formation of these radiation products.

4. Half-Life of Antimony-125

A paper, "Half-Life of Antimony-125" by E. H. Klehr and A. F. Voigt was submitted for publication in J. Inorg. Nucl. Chem.

Abstract--The half-life of Antimony-125 separated from uranium fission products has been determined to be 2.6 ± 0.1 years by measurements on a Lauritsen electroscope over a 5-year period.

5. Photonuclear Reactions (D. S. Martin, Jr.)

The cross sections of the $A^{10}(\gamma, p)Cl^{39}$ and $A^{40}(\gamma, pn)Cl^{38}$ reactions as a function of photon energy were determined by induced radioactivity measurements up to 42 Mev with the Iowa State University synchrotron. The photon beam was monitored with a transmission ionization chamber which was calibrated by relating its response to a standard chamber, whose prototype was built by the National Bureau of Standards. The ultimate calibration of the prototype chamber was by means of a beam calorimeter at the NBS. The results are given in Table XX. It should be noted that the calibration of the X-ray beam by a Victorean thimble in a paraffin block gave somewhat different results but the method is believed to be less reliable. An interesting feature was the high energy tail on the (γ, p) cross section curve.

Table XX. Cross sections of the $A^{40}(\gamma, p)Cl^{39}$ and $A^{40}(\gamma, pn)Cl^{38}$ reactions

Reaction Method	(γ, p)		(γ, pn)	
	NBS	Vic.	NBS	Vic.
Threshold (Mev)	13	13	19	19
Peak Energy (Mev)	23	22.5	27	26
σ (E_{Max})(mb)	14.8	18.6	1.0	1.4
σ (40 Mev)(mb)	3.5	0	0.5	0
σ (40 Mev) (Mev-mb)	173	180	7.3	7.9

6. Szilard-Chalmers Processes

Some additional techniques were tested with the tris(dipivaloylmethane) holmium compound, $Ho(dpm)_3$, in search for a Szilard-Chalmers process which might be employed with a rare-earth element. The compound has been dissolved in a benzene and water emulsion in anticipation that, following

irradiation, when the emulsion was broken, the target compound would remain in the benzene layer, and the recoil radioactive Ho^{164} ions would concentrate in the aqueous phase. However, in these experiments a substantial enrichment has not been obtained.

7. Isotopic Exchange Reactions

The first acid hydrolysis for cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ was studied at 25°C and 35°C . Its equilibrium constant, K_1 , is 3.3×10^{-3} moles/l, and its rate constant, k_1 , is $2.5 \times 10^{-5} \text{ sec}^{-1}$ at 25°C . An ion exchange separation process was used to separate the $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and the combined complexed chloride from free Cl^- in isotopic exchanger reactions with Cl^{36} .

The acid hydrolysis provides the only means for the exchange between the chloride ligands of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and Cl^- . The acid hydrolysis of the first hydrolysis product, $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})]^+$ has an equilibrium constant of 4×10^{-4} moles/l at 25°C . The exchange between free chloride and the chloride ligand of this species occurs by a process which is chloride independent and which is characterized by a first order rate constant, $k_2 = 3.6 \times 10^{-5} \text{ sec}^{-1}$. It appears likely this exchange also occurs by only the acid hydrolysis process.

Extensive experiments with the acid hydrolysis of trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ have been completed. In contrast to the cis-compounds, only a first acid hydrolysis with the equilibrium constant of 3.6×10^{-4} moles/l at 25° and a rate constant of $9.8 \times 10^{-5} \text{ sec}^{-1}$ has been observed for this compound. The exchange of the chloride ligands for this compound occurs by the acid

hydrolysis process but also a process first order in chloride occurs.

This feature is especially interesting because no similar reaction has been observed with eight different chloride ligands for platinum(II) complexes.

Other exchange studies have dealt with the two inert ligands cis to ethylene in trichloro(ethylene)platinate(II) complexes. The change rate appears to follow a very complex law which includes the product of the concentration of the original complex and its hydrolysis product.

Additional experiments with the exchange between platinum in $[\text{Pt}(\text{en})_2]^{++}$ and $[\text{Pt}(\text{en})_2\text{Cl}_2]^{++}$ (where (en) = ethylenediamine) have further confirmed the rate law $R = k [\text{Pt}(\text{en})_2^{++}] [\text{Pt}(\text{en})_2\text{Cl}_2^{++}] \text{Cl}^-$ with $k \approx 700 \text{ M}^{-2} \text{ min}^{-1}$ at 25°C .

8. Chemical Equilibria and Kinetics

The equilibrium constant for the first acid hydrolysis of $[\text{PtCl}_4]^-$ at 25°C is 3.0×10^{-2} at $\mu = 0$ and 1.5×10^{-2} at $\mu = 0.318$. The equilibrium constant for the second acid hydrolysis is 1.0×10^{-3} at $\mu = 0$ and 5.4×10^{-4} at $\mu = 0.318$. A tentative value of 7.0 was found for $\text{p}K_{11}'$ where K_{11}' is the dissociation constant of $[\text{PtCl}_3(\text{H}_2\text{O})]$. Tentative values are $\text{p}K_{21}' = 5.2$ and $\text{p}K_{22}' = 8.3$ where K_{21}' and K_{22}' are the first and second acid dissociation constants for $[\text{Pt}(\text{Cl}_2)(\text{H}_2\text{O})]$.

The ultraviolet spectra of solutions of $[\text{PtCl}_4]^-$ have been recorded at intervals of time following the addition of either NaOH or NH_3 . Although the interpretation is complicated by minor side reactions which change the spectrum irreversibly, rather substantial information has

been obtained about the direct substitution reactions of OH^- and NH_3 for Cl^- in the complexes. The replacement of Cl^- by OH^- appears to occur by the acid hydrolysis step and the introduction of a second OH^- into the complex can be observed. The substitution of NH_3 occurs much more rapidly and the introduction of subsequent NH_3 molecules to give cis-
 $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and eventually $\text{Pt}(\text{NH}_3)_4^{++}$ has been demonstrated to be more rapid still.

A program is underway for the evaluation of equilibrium constants by methods which employ digital computers for the analysis of data from titration curves.

9 . Activation Analyses and Analytical Application of Radiotracers

A paper, "Neutron Activation Analysis for Iridium in Platinum", by L. S. Jowanovitz, F. B. McNatt, R. E. McCarley and D. S. Martin, Jr. was accepted for publication by Anal. Chem.

Abstract--A procedure is given for a high sensitivity neutron activation analysis for Ir in Pt which permits the use of $\text{Pt}^{195\text{m}}$ as a tracer. The standard deviation of seven analyses of a 0.04 ppm sample was 10%. The activation of $\text{Pt}^{195\text{m}}$ as an internal standard was unsatisfactory and an external standard is recommended. The effectiveness of separation procedures of Ir from Pt have been evaluated with the high sensitivity of the radiochemical procedure. The fractional crystallization

of K_2PtBr_6 is proposed as the best means for the purification of platinum from an indium impurity.

Activation analysis have been made for Ta in yttrium metal which has been melted in Ta crucibles and which has been resublimed. In the latter over 5% Ta was found, however, it was shown that when the metal was dissolved in acid, the Ta remained quantitatively in the insoluble residue. The Ta content in the resublimed metal was close to the limit of detection and a tentative value of 70 ppm was obtained; however, the details of the analysis need improvement and additional analyses will be required.

10. Diffusion in the Solid State

A paper entitled, "Diffusion of Ag^+ , Cl^- and Cd^{++} in Silver Chloride Single Crystals", by R. F. Reade and D. S. Martin, Jr. was accepted for publication in J. Applied Physics.

Abstract--The diffusion rates of silver, chlorine and cadmium ions in single crystals of silver chloride have been investigated by means of a modification of the surface counting method. The diffusion coefficient of the silver ion from 200°C to 400°C was represented by the equation $D = 9.36 \exp(-1.01 \text{ ev}/kT) \text{ cm}^2/\text{sec}$. Estimates of chloride ion activation energies gave a value of 1.57 ev between 350° and 400°C and a value of 0.37 ev below 280°C. The silver and chloride ion diffusion data have been compared with results of workers who used section-

ing methods. The diffusion coefficient of the cadmium ion may be expressed by the equation $D = 32.8 \exp(-1.36 \text{ ev/kT}) \text{ cm}^2/\text{sec} + 2.35 \times 10^{-5} \exp(-0.56 \text{ ev/kT}) \text{ cm}^2/\text{sec}$.

X-Ray Chemistry

1. Structure and Magnetic Properties of $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ (R. E. Rundle)

A paper, "Structure and Magnetic Properties of $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ ", by P. H. Vossos, L. D. Jennings and R. E. Rundle, was published in *J. Chem. Phys.* **32**, 1590 (1960).

Abstract--A new complex ion Cu_2Cl_6^- ion has been found. The triplet state appears to be the ground state for this ion from magnetic susceptibility data, and the compound has a Neel temperature of 5.9°K . The compound has implications as to the nature of ferromagnetic interactions in halides.

2. Ethylenediamine Platinum Tribromide

A paper, "The Crystal Structure of Ethylenediamine Platinum Tribromide, EnPtBr_3 ", by R. E. Rundle and T. Ryan has been submitted for publication in *J. Am. Chem. Soc.*

Abstract--Pt(II) and Pt(IV) are found in equal amounts to give an average valence of three. The structure has an interesting disorder and dichroism which are explained in part by the structure. Pt(II) and Pt(IV) appear to have very nearly the same radius in forming bonds to halogens.

3. The Crystal Structure of Dimethyl Zinc (R. E. Rundle)

Dimethyl zinc was found to be tetragonal with $a = 6.86$, $c = 4.20 \text{ \AA}$, space group $P-4_2/mmm$ $Z = 2$, Zn at 000, $\frac{1}{2} \frac{1}{2} \frac{1}{2}$; C at $\pm (xx0) (\frac{1}{2} x x, \frac{1}{2} - X)$, with $X = 0.199$. Zn - C = $1.93 \text{ \AA}$. There is no evidence for the weak association of molecules as found in trimethylindium.

4. The Crystal Structure of $\text{LiCuCl}_2 \cdot 2\text{H}_2\text{O}$ (R. E. Rundle)

A complete three-dimensional refinement with asymmetric temperature factors has been carried out on the IBM 704, with very low standard deviations in atom positions. The structure is interesting for its magnetic properties, and a neutron diffraction investigation is underway.

5. The Crystal Structure of bis-Metabromobenzoylmethane (R. E. Rundle)

This β -diketone exists in the crystal in the enol form with an intramolecular hydrogen bond. Crystal counter data for the single crystal have been obtained and a full 3-D least-square refinement with asymmetric temperature factors has been made using the IBM 704. $R = 6\%$ for the final structure, and standard deviations are $0.01 \text{ \AA}$ or less for all bonds. The

system appears to be symmetrical, with O-H-O = $2.40 \text{ \AA}$. Because this interesting part of the structure may be statistically symmetrical here, the corresponding chloro-compound is under study.

6. The Crystal Structure and Magnetic Properties of CrCl_2 from X-Ray Powder Data

This orthorhombic structure contains infinite, planar

 chains as in CuCl_2 . This is in accord with expectations with crystal field and MO theories of valence. The chains are known to involve antiferromagnetic interactions from the work of Wollan, et al., at Oak Ridge. The magnetic susceptibility has been found to be very peculiar at low temperature, with no simple Néel temperature. A calorimetric study is in progress.

7. A New Type of Ferromagnetic Interaction in Bridged Halides

An MO (molecular orbital) treatment of the planar ion CuCl_4^- shows that the magnetic electron would occupy an MO which is partially on the halide ligands. When coupled into chains, as in CuCl_2

, each bridge chlorine will receive electron density from two magnetic centers into two orthogonal p-orbitals. The coupling can then be shown to be due to coulomb integrals of the form that leads to Hund's rule of maximum multiplicity, and a ferromagnetic chain is expected. The same mechanism explains the ferromagnetic sheets in the MX_2 halides, where M is a transition metal and X is Cl, Br or I.

8. The Crystal Structure of Triethylenediamine-nickel(II) Nitrate,

A paper, "The Crystal Structure of Triethylenediamine-nickel(II) Nitrate, $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3(\text{NO}_3)_2$ ", by L. N. Swink and M. Atoji was accepted for publication in Acta Crystallographica.

Abstract--The crystal structure of triethylenediamine-nickel(II) nitrate, $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3(\text{NO}_3)_2$, is hexagonal D_6^6 -P6₃22 with two chemical formulae in a unit cell of dimensions $a = b = 8.87 \text{ \AA}$ and $c = 11.41 \text{ \AA}$, confirming results previously reported. The packing of the $[\text{Ni}(\text{en})_3]^{++}$ and $(\text{NO}_3)^-$ groups in the crystal is of extreme interest. Two nitrate ions are stacked one above the other to form a close packing with the complex ions. Although this configuration would seemingly give rise to electrostatic instability, a stable crystalline field is achieved, apparently by interactions involving the hydrogen atoms, some of which participate in forming a weak bifurcated hydrogen bond of the type, $\text{O} \cdots (\text{H}-\text{N})_2$. The configuration of $[\text{Ni}(\text{en})_3]^{++}$ is D-*lll* or L-*ddd* type with $\text{Ni}-\text{N} = 2.12 \text{ \AA}$, $\text{N}-\text{C} = 1.50 \text{ \AA}$ and $\text{C}-\text{C} = 1.50 \text{ \AA}$. The configuration of the $\text{Ni}(\text{en})$ ring is a gauche-gauche-gauche type with the azimuthal angles of 46° and 56° . Considerable distortion of the octahedral coordination in $[\text{Ni}(\text{en})_3]^{++}$ is observed. The N-O distance in NO_3^- is $1.21 \text{ \AA}$. The optical properties and the infrared spectrum of the compound are also discussed.

9. Slow Neutron Scattering Cross Sections (M. Atoji)

"Slow Neutron Scattering Cross Sections of Terbium, Ytterbium and Lutetium", by M. Atoji was submitted for publication in Phys. Rev.

Abstract--The coherent neutron scattering cross sections of terbium, ytterbium, and lutetium as determined from the neutron diffraction measurements on TbC_2 , YbC_2 , and Lu metals are found to be 7.2 ± 0.4 , 20.0 ± 0.4 and 6.70 ± 0.37 barns, respectively, all with amplitude of positive phase. The total scattering cross sections of Tb , Yb and Lu and the magnetic scattering cross sections of Tb^{+3} and Yb^{+3} are evaluated for thermal neutron energies. The neutron diffraction data also show the Debye temperatures of Yb and Lu metals to be $109 \pm 5^\circ\text{K}$ and $161 \pm 7^\circ\text{K}$, respectively.

10. The Neutron Diffraction Studies of CaC_2 , YC_2 , LaC_2 , CeC_2 , TbC_2 , YbC_2 and UC_2

The results of a complete-matrix least-squares treatment on the neutron diffraction data of CaC_2 , YC_2 , LaC_2 , CeC_2 , TbC_2 , YbC_2 and UC_2 are shown in Table XXI.

Table XXI.

	Z-parameters in the CaC_2 -type structure	C-C distances in Å
CaC_2	0.4067 ± 0.0007	1.191 ± 0.009
YC_2	0.3967 ± 0.0002	1.275 ± 0.002
LaC_2	0.4009 ± 0.0009	1.303 ± 0.012
CeC_2	0.4011 ± 0.0003	1.283 ± 0.004
TbC_2	0.3960 ± 0.0007	1.293 ± 0.009
YbC_2	0.3947 ± 0.0007	1.287 ± 0.009
UC_2	0.3881 ± 0.0006	1.340 ± 0.007

11. X-Ray Absorption Factors for Ellipsoidal Crystals (D. R. Fitzwater)

A paper, "X-Ray Absorption Factors for Ellipsoidal Crystals", by

D. R. Fitzwater has been accepted for publication by Acta Crystallographica.

Abstract--The absorption factor integral for a general ellipsoidal crystal was transformed to spherical polar coordinates. The resulting exponential in the integral was expanded in a power series and the triple integration was carried out term by term. The process was stopped after the fifth order term but could be carried further. Four integrals could not be directly integrated and were evaluated by series expansions and integrations. The resulting series were tabulated as a function of one parameter. The termination of the absorption factor series with the fifth order term gives results for a sphere with $< 2\%$ error for $\mu R = 1.0$.

The ellipsoidal crystal is a good approximation to many real crystal forms, and ellipsoidal absorption factor corrections should be satisfactory for film accuracies with many crystal forms. In addition, grinding an anisotropic crystal quickly produces ellipsoids and may not produce spheres even after continued grinding. The size of the final spheres, if any, may also be too small. Consequently, very accurate ellipsoidal corrections are useful for counter work with such crystals.

12. Anisotropic Structure Factor Calculations

A paper, "Anisotropic Structure Factor Calculations", by D. R. Fitzwater was submitted to Acta Crystallographica.

Abstract--A general treatment of the general form of the anisotropic structure factor was derived. The use of this form speeds up the structure factor and least squares calculation and eliminates the use of specially written "patches" to handle special symmetry in such a program.

13. Electron Diffraction Measurements (L. S. Bartell)

13.1 High Precision Electron Diffraction Unit

A high precision electron diffraction unit has been completed, tested and found to attain the new standards of performance for which it was designed. A series of molecular structure determinations has been initiated, and final results are available for CH_4 and CD_4 . Despite the fact that the latter molecules are not favorable cases for accuracy of bond lengths because of the large amplitudes of vibration and weak scattering powers of the hydrogens, the standard errors for the bond lengths appear to be only about $0.001 \text{ \AA}$. This represents the highest accuracy yet attained by electron diffraction. Moreover, the following aspects were all unequivocally demonstrated and measured for the first time by electron diffraction:

- (a) An isotope effect on bond lengths
- (b) An isotope effect on amplitude of vibration
- (c) An asymmetry of vibration of bonded atoms which yielded the cor-

rect value for the spectroscopic anharmonicity.

(d) The diffraction bond length was rigorously reduced to the (absolute) equilibrium r_e for the first time for a polyatomic molecule and found to agree with the spectroscopic r_e .

13.2 Monomethyl- and Dimethylphosphine

A paper, "Electron Diffraction Study of Monomethyl and Dimethylphosphine", by L. S. Bartell was published in J. Chem. Phys. 32, No. 3, 832-34 (1960).

Abstract--The structural parameters of gaseous monomethyl- and dimethylphosphine were determined by the sector-microphotometer method of electron diffraction.

Center of gravity bond distances and standard errors

for the two molecules were, respectively: $r_{CP} = 1.858 \pm$

0.003 A and 1.853 ± 0.003 A; $r_{CH} = 1.094 \pm 0.008$ A and

1.097 ± 0.007 A; $r_{PH} = 1.423 \pm 0.007$ A and $1.445 \pm$

0.02 A. The angles P-C-H were $109.6 \pm 1^\circ$ and $109.8 \pm$

0.7° . In dimethylphosphine the angle C-P-C was $99.2 \pm$

0.6° . The methyl groups were found to be in staggered

conformations. The distances and root-mean-square am-

plitudes of vibration agreed well with the values deter-

mined in recent studies of phosphine and trimethylphosphine.

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- IS-48 J. R. Bohn, R. E. Uhrig and Glenn Murphy. A Method of Specimen Corrosion Protection for High Temperature Creep Testing.
- IS-50 R. Kniseley, V. A. Fassel and F. Lentz. Misidentifications in the Arc Spectra of the Rare Earths.
- IS-57 D. H. Dennison, F. H. Spedding and A. H. Daane. The Determination of the Melting Point, the Vapor Pressure, and the Decomposition Temperature of Yttrium Tri-Iodide.
- IS-66 Robert L. Hammel and Robert E. Uhrig. An Autographic Elevated Temperature Creep Testing Facility.
- IS-67 Toshihiro Okada. Note on the Determination of the Magnetoresistance Tensor of a Crystal Having the Symmetry O_h or O .
- IS-107 C. D. Wirkus and D. R. Wilder. Uranium Glass I. Fundamental Considerations.
- IS-115 O. N. Carlson, F. A. Schmidt and R. L. Wells. A Study of the High-Temperature Air-Oxidation of Yttrium Metal.
- IS-125 R. L. Hammel. Creep of Tantalum Under Cyclic Elevated Temperatures.
- IS-138 Robert Uhrig. A Proposed Model for High Temperature Creep of Tantalum.

2. Publications

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APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
University of Arizona General Stores Building Fifth Street and Mountain Avenue Tucson, Arizona	5 gm ytterbium oxide
Monsanto Chemical Company Mound Laboratory Miamisburg, Ohio	1 lb cerium metal
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	2 metal cylinders lanthanum and cerium 50 gm lanthanum metal 50 gm neodymium metal
Michigan State University P. O. 39530 East Lansing, Michigan	20 gm cerium metal
H. B. Nicholas B-11 Research Building Iowa State University Ames, Iowa	10 gm yttrium oxide 10 gm lanthanum oxide 10 gm cerium oxide 10 gm neodymium oxide 10 gm dysprosium oxide 4 gm samarium oxide 2 gm gadolinium oxide 2 gm erbium oxide 2 gm ytterbium oxide 1 gm praseodymium oxide 1 gm holmium oxide 1 gm thulium oxide 1 gm terbium oxide 1 gm lutetium oxide
Mr. Sebastian Amer Box 122, Station A Ames, Iowa	20 gm Er_2O_3
Dr. Milton Burton Department of Chemistry University of Notre Dame Notre Dame, Indiana	10 gm Dy_2O_3 25 gm La_2O_3 25 gm Gd_2O_3 25 gm Y_2O_3 4 gm Lu_2O_3
Mr. Pierre Pelen French Embassy 2535 Belmont Road N. W. Washington, D. C.	samples of uranium metal (natural)

<u>Destination</u>	<u>Item</u>
University of California Receiving Department 2000 Carleton Street Berkeley 4, California	25 gm ytterbium metal 25 gm thulium metal 50 gm samarium metal
Dr. Masao Atoji Oak Ridge National Laboratory Oak Ridge, Tennessee	30 gm lutetium metal 30 gm ytterbium metal 30 gm terbium metal 2 glass vials of thorium carbide-thorium deuteride x-ray powder samples 46 gm lutetium carbide 110 gm thorium carbide 42 gm ytterbium dicarbide 30 gm Lu_2O_3 30 gm Yb_2O_3
Dr. Richard J. Weiss Materials Research Laboratory Ordnance Materials Research Office Watertown 72, Massachusetts	1 pc gadolinium metal appx. 10cm x 5cm x 0.1cm
Iowa State University Room 142 Research Building Ames, Iowa	200 ml 5% rare-earth chloride solutions: YCl_3 , NdCl_3 , GdCl_3 , DyCl_3 and YbCl_3 1500 ml 5% gadolinium chloride solution
J. C. Jamieson R. 21, 5641 S. Ingleside Avenue Chicago 37, Illinois	100 gm cylinder cerium metal
Mr. Warren DeSorbo General Electric Company Schenectady, New York	50 gm crystal bar vanadium
Dr. Glenn A. Crosby University of New Mexico Albuquerque, New Mexico	10 gm Sm_2O_3 10 gm Dy_2O_3
Mr. Dave Drennen Battelle Memorial Institute Columbus 1, Ohio	50 gm crystal bar hafnium metal
Mrs. Mary E. White Massachusetts Institute of Technology Cambridge 39, Massachusetts	1 gm yttrium metal

<u>Destination</u>	<u>Item</u>
Professor Paul A. Beck University of Illinois Urbana, Illinois	100 gm crystal bar wire appx. 1/16" diameter vanadium
Phillips Petroleum Company Atomic Energy Division Idaho Falls, Idaho	18 pc. 1" x 1/2" x 1/8" yttrium metal
Argonne National Laboratory Bailey Road Lemont, Illinois	250 gm distilled yttrium metal
Acct. Prop. Affr. Warehouse 335 Fort Belvoir, Virginia	5 gm praseodymium metal 5 gm samarium metal 5 gm neodymium metal 5 gm dysprosium metal 5 gm terbium metal 5 gm gadolinium metal 5 gm holmium metal
Veterinary Physiology & Pharmacology Room 100, Vet Physiology Ames, Iowa	1200 ml 5% dysprosium chloride solution 0.5 gm gadolinium oxide 0.5 gm dysprosium oxide 0.5 gm ytterbium oxide 0.5 gm yttrium oxide
Brookhaven National Laboratory Warehouse 100 Upton, L. I., New York	3 pc. thulium metal
Mr. W. E. Jardner Atomic Energy Research Establishment Harwell, Didcot Berks, England	5 gm crystal bar vanadium
Dr. Alvin Boltax Nuclear Metals Inc. Concord, Massachusetts	1 - 1" x 0.35" x 0.03" thorium metal