A.E.C. RESEARCH AND DEVELOPMENT REPORT

This document contains 24
pages and 0 figures No. 100
of 317 copies. Series a

**AMES
LABORATORY
IOWA STATE
COLLEGE**

RESTRICTED DATA

This document contains restricted data as defined in the Atomic Energy Act of 1946. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

**CHEMISTRY. QUARTERLY SUMMARY RESEARCH REPORT
JANUARY, FEBRUARY, AND MARCH, 1955**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ISC-606
1

UNITED STATES ATOMIC ENERGY COMMISSION

QUARTERLY SUMMARY RESEARCH REPORT IN CHEMISTRY

For January, February, and March, 1955

by

Ames Laboratory Staff

Photostat Price \$ 4.80

Microfilm Price \$ 2.70

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

June 10, 1955

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

QUARTERLY SUMMARY RESEARCH REPORT IN CHEMISTRY

For the period January, February, and March, 1955

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

Previous quarterly research reports in this series are:

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

~~CONFIDENTIAL~~

ISC-606

3

CHEMISTRY-GENERAL

<u>Standard Distribution</u>	<u>Copies</u>
AF Plant Representative, Wood-Ridge.	1
Alco Products.	2
Argonne National Laboratory.	3 - 8
Armed Forces Special Weapons Project (Sandia).	9
Army Chemical Center	10
Arthur D. Little, Inc.	11
Atomic Energy Commission, Washington	12 - 16
Battelle Memorial Institute.	17
Bettis Plant (WAPD).	18 - 19
Brookhaven National Laboratory	20 - 21
Carbide and Carbon Chemicals Company (C-31 Plant)	22 - 23
Carbide and Carbon Chemicals Company (K-25 Plant).	24 - 26
Carbide and Carbon Chemicals Company (ORNL).	27 - 32
Chicago Patent Group	33
Chief of Naval Research.	34
Columbia University (Hassialis).	35
Division of Raw Materials, Washington.	36
Dow Chemical Company, Pittsburg.	37
Dow Chemical Company (Rocky Flats)	38
duPont Company, Augusta.	39 - 41
duPont Company, Wilmington	42
General Electric Company (ANPD).	43 - 45
General Electric Company, Richland	46 - 51
Goodyear Atomic Corporation.	52 - 53
Hanford Operations Office.	54
Iowa State College.	55
Knolls Atomic Power Laboratory	56 - 59
Los Alamos Scientific Laboratory	60 - 61
Mallinckrodt Chemical Works.	62
Materials Laboratory (WADC).	63
Mound Laboratory	64
National Advisory Committee for Aeronautics, Cleveland	65
National Bureau of Standards	66
National Lead Company, Inc., Winchester.	67
National Lead Company of Ohio.	68
Naval Medical Research Institute	69
Naval Research Laboratory.	70
New Brunswick Area Office.	71
New York Operations Office	72
North Americal Aviation, Inc.	73 - 74
Nuclear Metals, Inc.	75
Patent Branch, Washington.	76
Phillips Petroleum Company (NRTS).	77 - 80
Pratt & Whitney Aircraft Division (Fox Project).	81

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

4

ISC-606

Standard Distribution (Continued)

Copies

Public Health Service.	82
Rohm and Haas Company.	83
Sandia Corporation.	84
Sylvania Electric Products, Inc.	85
Tennessee Valley Authority (Walthall).	86
USAF Project RAND.	87
U. S. Naval Postgraduate School.	88
U. S. Naval Radiological Defense Laboratory.	89
UCLA Medical Research Laboratory.	90
University of California Radiation Laboratory, Berkeley.	91 - 92
University of California Radiation Laboratory, Livermore.	93 - 94
University of Rochester.	95
Virginia-Carolina Chemical Corporation.	96
Vitro Engineering Division.	97
Vitro Laboratories.	98
Western Reserve University (Fiedell).	99
Technical Information Service, Oak Ridge.	100 - 314

Speical Distribution

Chicago Operations Office, TSD.	315
Document Library.	316 - 319

~~CONFIDENTIAL~~

TABLE OF CONTENTS

Page

CHEMISTRY

Physical and Inorganic Chemistry

1. Separation of Rare Earths by Ion Exchange.	7
1.1 Production of Heavy Rare Earths and Yttrium.	7
1.2 Further Investigation of EDTA as an Eluant for Heavy Rare Earths.	8
1.3 Separation of Isotopes by Ion-Exchange	8
2. Rare Earth Metallurgy.	8
3. The Lower Oxidation States of Gallium.	10
3.1 Gallium Iodide	10
3.2 Gallium Bromide.	10
4. Metal-metal Salt Solutions	11
5. The Chemistry of Niobium	11
6. Adsorption Studies.	12

Pyrometallurgy

1. Metallurgical Separation of Fuel and Fission Products. .	12
2. Uranium Alloy Studies	13

Analytical Chemistry

1. Titanium	13
2. Yttrium.	13
3. Service Analyses	13
4. Determination of Rare Earths in Thorium.	13

Spectrochemistry

1. Development of Spectroscopic Methods of Analysis	14
2. Spectroscopic Service Analyses	14

TABLE OF CONTENTS (Continued)

PageRadiochemistry

1. Synchrotron Studies.	14
1.1 Tellurium and Antimony Activities.	14
1.2 Other Photonuclear Processes	14
2. Szilard-Chalmers Reactions	15

X-Ray Chemistry

1. Transition Metal Complexes	16
APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY. . . .	18
1. Reports for Cooperating Laboratories.	18
2. Papers Published in Scientific Journals	19
APPENDIX II: LIST OF SHIPMENTS.	20

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

Physical and Inorganic Chemistry

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

1.1 Production of Heavy Rare Earths and Yttrium

Pilot plant scale production of pure rare earths was continued during this period with special emphasis on the purification of yttrium. Table I is a summary of the more noteworthy fractions obtained during this period.

Table I

Noteworthy Fractions of Highly Pure Rare Earths Produced during January, February, and March, 1955

Description of Fraction	Weight R_2O_3 (grams)
>99.9% Y_2O_3 ; cont. only traces of Dy and/or Tb	25,848
>99.95% Tb_4O_7 ; cont. <0.03% Y, <0.03% Gd	1,369
>99.9% Sm_2O_3 ; cont. <0.01% Eu, <0.05% Gd, <0.05% Nd	5,892
>99.9% Yb_2O_3 ; cont. only traces Lu and/or Tm	775
>99.9% Tm_2O_3 ; cont. <0.025% Yb, <0.02% Er	294
>99.9% Gd_2O_3 ; cont. traces Tb, Eu and Sm	201
>99.95% Lu_2O_3 ; cont. <0.01% Sc, <0.01% Yb	33

The first kilogram lot of highly pure Tb_4O_7 was produced. Due to the extreme scarcity of purified terbium salts, the market price of Tb_4O_7 has been about \$2000 per gram; consequently, a

*Names indicate group leaders in charge of work.

portion of this pure material is being allocated to the Ames loan collection where it will be made available to interested scientists, who wish to study the properties of pure terbium, on a loan basis or at a nominal cost.

Fifty kilograms of greater than 99.95% Y_2O_3 was homogenized and is being supplied to the A.E.C. for research purposes.

1.2 Further Investigation of EDTA as an Eluant for Heavy Rare Earths

It was discovered in the course of our pilot plant operations that Lu, Yb, Tm and Er tend to leak through a copper ion retaining band, if 5 gm./liter EDTA eluant is used at a pH above 8.2. Small column runs are being made to determine the maximum pH which can be tolerated.

1.3 Separation of Isotopes by Ion-Exchange

Nitrogen-15 isotope has been enriched to a value exceeding 96%, starting from normal ammonia containing 0.365% N^{15} and 99.635% N^{14} , by eluting an adsorbed ammonium band down a series of hydrogen-cycle resin beds with dilute sodium hydroxide eluant. The first part of the elution was performed upon an 8-ft. long adsorbed band on a series of 4-in. diameter resin beds and the enriched material from this series was used to obtain the final enrichment of 96% on a series of 2-in. diameter resin beds. The final band on the 2-in. columns was only 5 inches long. The isotopic concentration at the front edge of the final band was 99.94% N^{14} and the concentration at the rear edge was 96.0% N^{15} . Calculations for the HETP for the last 2 1/2 inches of the band indicated a plate height of only 0.17 mm at the steady state.

A communication "A Laboratory Method for Separating Nitrogen Isotopes by Ion Exchange" by F. H. Spedding, J. E. Powell and H. J. Svec was published in J. Am. Chem. Soc. 77, (1955).

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

The volatility of most of the heavy rare earth metals has made it possible to prepare the volatile ones by reducing their oxides with lanthanum metal, obtaining a high yield of very pure metal as a sublimate. Most of the heavy rare earth metals have been prepared by this method for the determination of precision lattice constants with the following results:

<u>(hexagonal, except for Ce & Yb)</u>	<u>a Å</u>	<u>c Å</u>
Sc	3.3112	5.2281
Y	3.6474	5.7306
Ce	5.1612	-- (f.c.c.)
Pr	3.6725	11.8354
Nd	3.6579	11.7992
Gd	3.6360	5.7826
Dy	3.5903	5.6475
Ho	3.5773	5.6158
Er	3.5588	5.5874
Tm	3.5374	5.5546
Yb	5.4862	-- (f.c.c.)
Lu	3.5031	5.5509

In the study of the lanthanum-carbon alloy system, a 7.9% carbon alloy, corresponding to a composition of LaC, was found to consist of nearly one phase which was found to have a body centered cubic lattice, with $a = 8.86 \text{ Å}$. At 14 and 20% carbon, a tetragonal structure previously reported for LaC₂ was observed, with indications that no higher carbide existed. Evidence indicated that no new phase existed between LaC and LaC₂.

Niobium crucibles have been used for melting yttrium metal; spectroscopic analyses show from 1 to 2% niobium in the yttrium.

3. The Lower Oxidation States of Gallium (J. D. Corbett)

3.1 Gallium Iodide

A paper entitled "The Lower Oxidation States of Gallium I. The GaI_3 - GaI_2 - GaI System" by J. D. Corbett and R. K. McMullan (ISC-581) submitted for publication in the J. Am. Chem. Soc.

Abstract

Gallium(II) iodide has been observed to disproportionate into gallium(III) iodide and gallium(I) iodide, instead of the trihalide and the metal that are obtained with gallium(II) chloride. A phase diagram and powder patterns confirm the existence of the two lower iodides. Gallium(II) iodide is only moderately stable at the melting point of 211° ; gallium(I) iodide is sufficiently unstable that in the presence of excess gallium only a limiting composition of $\text{GaI}_{1.19}$ is obtained at a melting temperature of 265° . Gallium(I) iodide can be isolated from the limiting mixture by a solvent extraction. The demonstration of the existence of the gallium(I) oxidation state in this system tends to favor the formulation $\text{Ga(I)}[\text{Ga(III)I}_4]$ for the diamagnetic gallium(II) iodide.

3.2 Gallium Bromide

Work on the gallium bromide system has shown it to be similar to that of the chloride. The limiting liquid composition is near $\text{GaBr}_{1.92}$. A combination of extensive supercooling and a slow transition in the solid state occasionally enables two melting points to be observed for GaBr_2 , at 152° (metastable) and at 164° .

The large solubility of GaCl_2 in benzene (4.4 wt %) seems to indicate considerable acid-base interaction between the components,

as might be expected for a $\text{Cl}_2\text{Ga-GaCl}_2$ configuration. Such a solution yields precipitates when simple amines and ethers are added. The nature of these complexes is being investigated; specific reagents for chelation across the metal-metal bond are being considered.

4. Metal-metal Salt Solutions (J. D. Corbett)

A paper entitled "The Solubility of Some Metals in Their Molten Salts" (ISC-565) by J. D. Corbett and S. von Winbush has been accepted for publication.

Abstract

The apparent solubilities of six metals in their respective molten halides have been measured, using the salts SnCl_2 , SnBr_2 , PbCl_2 , TlCl , AgCl , GaCl_2 and AlI_3 . A comparison of the lead and tin data with known metal solubilities in alkaline earth and cadmium(II) halides shows a generally decreasing solubility with decreasing electropositive character of the metal. In contrast to the intensely colored or darkened systems usually obtained in such systems, the Al-AlI_3 and Ga-GaCl_2 systems are colorless, and the formation of subhalides seems reasonable. A seemingly significant correlation can be obtained between the solubility of aluminum in AlI_3 and a theoretical calculation of the stability of AlI . The reaction of gaseous tin(II) or lead(II) chloride and excess tin or lead metal in the temperature ranges of 550 to 950° and 500° to 575° respectively does not appear to result in the formation of any subhalide.

Redetermination of solubilities in the tin and thallium systems by means of loss in weight of the metal has resulted in much more satisfactory values than those found previously by direct analysis. These are, in mole per cent dissolved metal, Sn-SnCl_2 , 500° , 0.0032% ; Sn-SnBr_2 , 500° , 0.068% ; Tl-TlCl , $550-650^\circ$, 0.009% . Examination of the Zn-ZnCl_2 system indicates the formation of unknown amounts of a colorless subhalide in the melt that disproportionates on quenching to give a black solid. The amount seems considerably more than the 10^{-4} mole per cent dissolved metal obtained by von Hevesy and Lowenstein (1) by a "titration" of a colored melt.

5. The Chemistry of Niobium (J. D. Corbett)

Reduction of solutions of Nb_2O_5 in 48% HF by active metals produces blue to black solutions containing one or more lower oxidation states of niobium; these in turn appear to reduce hydrogen ion fairly rapidly. The Nb_2O_5 solutions in HF show a distinct aging effect in that freshly prepared solutions are much more resistant to reduction.

(1) G. von Hevesy and E. Lowenstein, Z. anorg. Chem., 187, 266 (1930).

The preparation of pure anhydrous niobium(V) iodide has recently been achieved. The compound can be sublimed in a small pressure of iodine; heating in vacuum produces a number of lower iodides.

6. Adsorption Studies (Robert S. Hansen)

A paper, "The Theory of Vibrating Jets in Liquids of Variable Surface Tension" (ISC-552) by Robert S. Hansen was submitted for publication.

Abstract

The theory of jet oscillations in a liquid of time dependent surface tension has been analyzed. To the extent that surface tension change can be represented as linear over a single wavelength, the wavelength is approximately that given by the non-time dependent equations with surface tension constant at the mean value over the wavelength. A high frequency low-amplitude oscillation will be superimposed on the principal jet motion, which should, however, present negligible complications under usual experimental conditions.

Pyrometallurgy

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

During this period this part of the program on metallurgical separation has been concerned with the preparation and subsequent treatment of artificial fission product-uranium mixtures, the so-called "fissium". Various fission product elements were made radioactive and then incorporated into uranium metal which was subsequently melted and extracted with molten metal.

In one series of experiments magnesium and its alloys with tin, zinc and aluminum were used as the extractants on fuel which had molybdenum as the only fission product present. The ratio of counting rates of molybdenum in the extractant to that in the uranium phase per gram of each, varied from 10^{-3} to 10^{-1} but in no case was molybdenum removed in appreciable amounts.

Other experiments with silver and cerium as extractants were similarly low in the molybdenum removal obtained. Silver gave low removal of ruthenium, effective removal of rare earths and partial removal of zirconium. Cerium gave very high removal of rare earths and partial removal of both zirconium and ruthenium.

The extraction of ruthenium into cerium is in agreement with data reported last quarter. It now appears definite that about half of the ruthenium can be extracted into cerium in a single pass. To our knowledge this is the first pyrometallurgical procedure which will remove ruthenium from uranium.

2. Uranium Alloy Studies (A. H. Daane)

The immiscibility of samarium and uranium has been studied, and analyses indicate that the samarium layer contains 2.5% uranium, and the uranium layer contains at least 0.2% samarium, and perhaps as much as 2.5%.

In the study of the uranium-antimony system, it has been found that USb_2 is the last intermetallic compound on the antimony rich side of the system. This compound melts at about $1425^\circ C$, and decomposes at an appreciable rate in a vacuum at $1250^\circ C$. X-ray diffraction studies show the compound to be tetragonal with the structure reported by Ferro (2). The compound nearest the uranium axis of this system appears to be U_5Sb_3 , with a hexagonal lattice. A more complete x-ray study of this compound is in progress.

Analytical Chemistry

1. Titanium (C. V. Banks)

A satisfactory method has now been developed for determining as little as 50 micrograms of titanium per gram of niobium.

2. Yttrium (C. V. Banks)

Since yttrium metal is prepared by the co-reduction of yttrium and zinc fluorides with calcium, it is necessary to determine zinc in the yttrium metal before and after the dezincing process. The polarographic determination of zinc in these samples has proved to be both convenient and satisfactory.

3. Service Analyses (C. V. Banks and J. S. Fritz)

A total of 2993 service analyses were made during the period of this report.

4. Determination of Rare Earths in Thorium (J. S. Fritz)

Starting with a 5 to 1 molar ratio of thorium to lanthanum, we have been able to achieve virtually quantitative separation of these elements by use of a cation exchange column. EDTA is added in excess over the amount required to complex thorium and the pH of the solution is made sufficiently low so that lanthanum will be retained by the column but the thorium-EDTA complex will not be taken up. We expect to use this method as a preliminary separation for the determination of ppm quantities of rare earths in thorium metal.

Spectrochemistry

1. Development of Spectroscopic Methods of Analysis (V. A. Fassel)

The following emission spectroscopic analytical methods were completed this quarter:

1. Determination of Zr, Mo, Nd, and Ru in U-Cr eutectic reactor fuel before and after extraction with Ag, Mg, or other metals or alloys, or after removal of surface layers of the molten eutectic.
2. Determination of Tb_4O_7 in complex rare earth oxide mixtures.
3. Analysis of U-Nb binary alloys in the range 0.1 to 3% Nb.

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

1,379 samples were analyzed or examined by emission or fluorescence spectroscopic techniques. The samples consisted primarily of rare earth column fractions, metallurgical samples and purified Nb, Ta, and Zr oxides.

Radiochemistry

1. Synchrotron Studies

1.1 Tellurium and Antimony Activities (A. F. Voigt)

The decay schemes of synchrotron-produced Te^{127} , Te^{129} , Sb^{127} and Sb^{129} are under study. In the case of the two tellurium activities, it was found that tellurium 127 has a single beta ray of energy 0.695 Mev and Te^{129} has two betas with energies of 1.01 Mev and 1.46 Mev and a 0.450 Mev gamma. The abundance ratio of the betas is about 1 to 4 respectively.

1.2 Other Photonuclear Processes (D. S. Martin)

Yield determinations of photonuclear reactions by the x-rays from the 70 Mev electrons in the Iowa State College synchrotron have been continued. Yield values have been averaged from a number of determinations for several photonuclear reactions induced in iron by the 70 Mev bremsstrahlung. These values are:

$$\frac{Fe^{54}(\gamma, pn)Mn^{52m}}{Fe^{54}(\gamma, 2n)Fe^{52}} = 10.4$$

$$\frac{\text{Fe}^{54}(\gamma, \text{pn})\text{Mn}^{52\text{m}}}{\text{Fe}^{57}(\gamma, \text{p})\text{Mn}^{56}} = 1.02 *$$

$$\frac{\text{Fe}^{54}(\gamma, \text{pn})\text{Mn}^{52\text{m}}(21 \text{ min.})}{\text{Fe}^{54}(\gamma, \text{pn})\text{Mn}^{52}(6\text{d})} = 2.60$$

$$\frac{\text{Fe}^{57}(\gamma, \text{p})\text{Mn}^{56}}{\text{Fe}^{19}(\gamma, \text{n})\text{F}^{18}} = 3.5 *$$

The high yield of $\text{Mn}^{52\text{m}}$ compared to Mn^{52} is consistent with the lower spin assignment for Mn^{52} . The last ratio was obtained by irradiation of the compound $\text{FeSiF}_6 \cdot 6(\text{H}_2\text{O})$.

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

Irradiation by the 70 Mev bremsstrahlung of racemic tris-(ethylenediamine)cobalt(III), $[\text{Co}(\text{en})_3]^{+++}$, salts have been undertaken to determine the retention by the complex of the $\text{Co}^{59\text{m}}$ activity. About 60% of the activity was recovered as Co^{++} and about 14% was carried by a recrystallization of the nitrate target compound. However, additional fractional crystallizations continued to give large reductions in the activity carried by the crystals. It was found that purification was much more satisfactory with the fractional crystallization of the bromide. Hence, a nitrate target was converted rapidly to the bromide following an irradiation. Retention by the complex ion was less than 10%. Aging of the nitrate crystals for 1 day at 110°C resulted in an increase of the retention to 60% of the activity. Longer aging yielded no additional retention.

As^{74} Additional experiments were performed concerning the fate of activity in the irradiation of tetraphenylarsonium chloride. Earlier experiments had shown that 15-30% of the activity was precipitated with $\text{Mg}(\text{NH}_4)\text{AsO}_4$ in the presence of As^{III} carrier. Oxidation of the As^{III} carrier by H_2O_2 and a precipitation of $\text{Mg}(\text{NH}_4)\text{AsO}_4$ carried an additional 40% of activity. At least 30% was not accounted for. In other experiments in which AsCl_3 carrier was distilled from the solution of the target compound containing $\text{AsO}_4^{=}$ carrier, 80-90% of the activity was removed, 15-20% could then be precipitated with $\text{Mg}(\text{NH}_4)\text{AsO}_4$. Less than 4% of the activity was carried by recrystallizations of the target compound. There was no increase in the retention of activity by the target crystals when they were aged one week at 110°C .

X-Ray Chemistry1. Transition Metal Complexes (R. E. Rundle)

The theoretical molecular orbital treatment of transition metal complexes has been extended to tetrahedral complexes with most interesting results. These considerations were started due to our concern with the tetrahedral FeCl_4^- ion structure (see ISC-574).

Briefly, the directed theory of valence of Pauling and Slater, based on a valence bond treatment of molecules, would require that tetrahedral complexes of transition form either d^2sp tetrahedral bonds, or sp^3 tetrahedral bonds. If d-bonding were important, and if d-orbitals could be made available for bonding by pairing, then d^2sp -bonds should be expected. On the other hand, if d-bonding contributes little, as in quite ionic bonds, then sp^3 bonding should occur, with unpairing of the transition metal 3d-electrons in all five 3d-orbitals.

For example, in Fe^{+3} tetrahedral complexes, the two types should be as follows:

"Ionic" Complexes		"Covalent" Complexes	
3d ↑ ↑ ↑ ↑ ↑	4s — 4p — — —	3d ↑ — — — —	4s — 4p — — —
five unpaired electrons contributing to spin only magnetic moment	orbitals used in bonds to ligand	one unpaired electron contributing to spin - only moment	d^2sp orbitals used in bond formation.

In this case, in contrast to the octahedral case, there is disagreement between the molecular orbital and simple valence bond approaches. For strictly tetrahedral symmetry, the proper symmetry orbitals for ligands and metals are formed and combine according to the approximate scheme shown on the following page. Here it is seen that even with considerable d-bonding through the $3d-f_2$ type orbitals, and essentially non-bonding, triply degenerate f_2 level (now mixed with 4p of the metal and with ligand orbitals) arises near the e-level from the metallic 3d. This leaves 5-orbitals which are essentially non-bonding. Hence, in Fe^{+3} tetrahedral complexes, even where there is considerable d-bonding, five unpaired electrons (in the 5-non-bonding orbitals) are expected.

FeCl_4^- has five unpaired electrons, in agreement with the m.o. treatment, and detailed calculations are now underway to see how much covalent character there is to the Fe-Cl bonds in this treatment. For this case there will be the additional complication of π -type interactions.

Since this case seems to be an important example of a difference between valence bond and molecular orbital approaches we are pursuing it further. It seems advisable to make tetrahedral complexes of several transition metals using $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, and to examine their magnetic susceptibilities and spectra to see if these compounds which should be relatively covalent, and uncomplicated by π -bonding, fit the molecular orbital picture. Such a program is just getting underway.

A full 3-dimensional Patterson has been made of $\text{Fe}_3(\text{CO})_{12}$ and interpretation is now being made.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-535 R. D. Cooper and D. J. Zaffarano. Photodisintegration of Light in Nuclear Emulsions. UNCLASSIFIED.
- ISC-541 J. S. Wiley and M. Smutz. Separation of Thorium and Radium-228 by Solvent Extraction. SECRET.
- ISC-565 J. D. Corbett and S. von Winbush. The Solubility of some Metals in their Molten Halides. UNCLASSIFIED.
- ISC-566 J. A. Happe and D. S. Martin, Jr. Some Isotopic Exchange Reactions of Manganese. UNCLASSIFIED.
- ISC-567 R. F. Mitchell and D. S. Martin, Jr. High Specific Radio-activities of Osmium from Photonuclear Reactions. UNCLASSIFIED.
- ISC-568 D. E. Griffith and M. Smutz. Purification of Uranium by Solvent Extraction. SECRET.
- ISC-571 J. S. Fritz and M. Johnson. Volumetric Determination of Zirconium. UNCLASSIFIED.
- ISC-572 B. A. Rogers, L. Ried, Jr. and P. E. Palmer. The Rachinger Conversion Rule. UNCLASSIFIED.
- ISC-573 Ames Laboratory Staff. Engineering. Quarterly Summary Research Report. October, November, and December, 1954. SECRET.
- ISC-578 W. A. Rhinehart, D. J. Zaffarano and R. C. Prior. An Accurate Digital Count-to-Analog Voltage Converter Employing a Reliable Decade Scaler. UNCLASSIFIED.
- ISC-581 J. D. Corbett and R. K. McMullan. The Lower Oxidation States of Gallium. I. The $\text{GaI}_3\text{-GaI}_2\text{-GaI}$ System. UNCLASSIFIED.
- ISC-583 L. S. Ring, Jr. The Photodeuteron/Photoproton Yield from Sulfur. UNCLASSIFIED.
- ISC-529 Ames Laboratory Staff. Engineering. Quarterly Summary Research Report. July, August, September, 1954. SECRET.
- ISC-530 Ames Laboratory Staff. Chemistry. Quarterly Summary Research Report. July, August, September, 1954. CONFIDENTIAL.

- ISC-506 Ames Laboratory Staff. Metallurgy. Quarterly Summary Research Report. April, May, June, 1954. SECRET.
- ISC-532 Compiled by P. Chiotti and O. N. Carlson. Hanford Slug Program. Quarterly Summary Research Report. July, August, September, 1954. SECRET.
- ISC-533 Ames Laboratory Staff. Physics. Quarterly Summary Research Report. July, August, September, 1954. UNCLASSIFIED.
- ISC-549 F. H. Spedding, J. E. Powell and D. M. Provow. Determination of the Equilibrium Constant for the Exchange of Nitrogen Isotopes Between Ammonium Hydroxide Solution and Ammonium Ion Adsorbed on Dowex-50. SECRET.
- ISC-553 G. H. Beyer and R. B. Edwards. Flooding Characteristics of a Pulse Extraction Column. UNCLASSIFIED.
- ISC-558 C. L. Hammer and A. J. Bureau. A Method for the Prompt Destruction of the Electron Beam in a Conventional Synchrotron. UNCLASSIFIED.
- ISC-559 H. J. Hettel and V. A. Fassel. Determination of Fractional Part Per Million Amounts of Certain Rare Earths in Zirconium Metal. UNCLASSIFIED.
- ISC-561 C. L. Hammer and A. J. Bureau. A Method for the Prompt Destruction of the Electron Beam in a Conventional Synchrotron. II. UNCLASSIFIED.

2. Papers Published in Scientific Journals

- Goodman, L. and H. Shull.
Molecular Calculations. III. A Modification of the Naive Semi-empirical M O Method. J. Chem. Phys. 23, 33-43, (January, 1955)
- Johansson, S. A. E.
Experiments on the Direct Photonuclear Effect. J. Am. Chem. Soc. 77, 1393, (March, 1955).
- Johansson, S. A. E.
Experiments on the Direct Photonuclear Effect. Phys. Rev. 97, 434-443, (January, 1955).

- Margoshes, M. and V. A. Fassel
The Infrared Spectra of Aromatic Compounds. I. The
Out-of-Plane C-H Bonding Vibrations in the Region 625-900
cm⁻¹. Spectrochim. Acta, 7, 14-24. (1955).
- Margoshes, M. and V. A. Fassel
Infrared Functional Groups Analysis of Aryl Silanes.
Anal. Chem. 27, 351-355, (March, 1955).
- Morinaga, H.
Effects of Isotopic Skin and Selection Rules on Photo-
nuclear Yields. Phys. Rev. 97, 444-446, (January, 1955).
- Peterson, D. and R. Davis
Vapor Pressures and X-ray Diffraction Patterns of Some
Compounds in the Thorium Nitrate-Water System. Phys. Rev.
97, 434-443, (January, 1955).
- Pohm, A. V., R. C. Waddell, J. P. Powers and E. N. Jensen
The Beta Spectrum of Cl³⁴. Phys. Rev. 97, 432-433,
(January, 1955).
- Vander Haar, R., C. V. Banks and R. Vander Wal
Magnetic Studies of Nickel(II) and Palladium(II) Complexes
with Some of Its Alloys. J. Am. Chem. Sci. 77, 324-325.
(January, 1955)
- Wilder, D. R. and E. S. Fitzsimmons
Further Study of Sintering Phenomena. J. Am. Ceram. Soc.
38, 66-71, (February, 1955).
- Williams, J. T.
The Vanadium-Zirconium Alloy System. J. of Metals. 7,
345-350, (February, 1955).

APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
Dow Chemical Company Midland, Michigan	229 g uranium alloys
Astrophysical Lab, Vatican Observ. Attn: The Rev. Joseph Junkes S. J. Castel Gondolfo, Rome, Italy	2 g terbium oxide

<u>Destination</u>	<u>Item</u>
Dr. E. A. Martell Institute of Nuclear Studies University of Chicago Chicago, Illinois	100 g yttrium oxide better than 90%
Monsanto Chemical Company Mound Laboratory Miamisburg, Ohio Attn: Dr. L. Timms	1 g lanthanum oxide 1 g cerium oxide 1 g praseodymium oxide 1 g neodymium oxide 1 g samarium oxide 1 g gadolinium oxide 100 mg terbium oxide 100 mg ytterbium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg thulium oxide 100 mg lutetium 500 mg dysprosium oxide
Mallinckrodt Chemical Works St. Louis, Missouri Attn: Mr. Leaders	200 lbs zirconium tetrafluoride
National Lead Co. of Ohio Fernald, Ohio Attn: J. Ciborski	150 lbs zirconium tetrafluoride
Argonne National Laboratory Lemont, Illinois	50 lbs zirconium tetrafluoride
Dr. Geoffrey Wilkinson Chemical Laboratories of Harvard Univ. 12 Oxford Street Cambridge 38, Massachusetts	10 g erbium oxide 10 g dysprosium oxide 10 g ytterbium oxide
University of Minnesota Room 126, Chemistry Minneapolis, Minnesota	1 g lanthanum oxide 1 g cerium oxide 1 g praseodymium oxide 1 g neodymium oxide 1 g samarium oxide 1 g gadolinium oxide 1 g yttrium oxide 1 g erbium oxide 1 g ytterbium oxide 100 mg holmium oxide 100 mg dysprosium oxide 100 mg thulium oxide 100 mg lutetium oxide

<u>Destination</u>	<u>Item</u>
Nuclear Metals, Incorporated 155 Massachusetts Avenue Cambridge 39, Massachusetts	10 g lanthanum oxide 10 g neodymium oxide 10 g gadolinium oxide 10 g erbium oxide
Department of Biophysics Army Medical Service Walter Reed Army Medical Center Graduate School Washington 12, D. C.	50 g yttrium oxide 99% pure
Mr. Herbert Fleischman Saturnium Corporation, Inc. California, Kentucky	1 g lanthanum oxide 1 g cerium oxide 1 g praseodymium oxide 1 g neodymium oxide 1 g samarium oxide 1 g ytterbium oxide 1 g gadolinium oxide 1 g erbium oxide 1 g yttrium oxide 100 mg holmium oxide 100 mg dysprosium oxide 100 mg thulium oxide 100 mg lutetium oxide
Metals Research Laboratories Electro Metallurgical Company 4625 Royal Avenue Niagara Falls, New York	1 g lanthanum oxide 1 g cerium oxide 1 g praseodymium oxide 1 g neodymium oxide 1 g samarium oxide 1 g gadolinium oxide 1 g erbium oxide 1 g ytterbium oxide 1 g yttrium oxide 100 mg holmium oxide 100 mg dysprosium oxide 100 mg thulium oxide 100 mg lutetium oxide
Westinghouse Electric Corporation Attn: Purchasing Department Research Laboratories East Pittsburgh, Pennsylvania	19 g cerium metal 50 g gadolinium metal 70 g neodymium metal 50 g samarium metal
Brookhaven National Laboratory Upton, Long Island, New York	20 g lutetium oxide
Oak Ridge Institute of Nuclear Studies, Inc. Oak Ridge, Tennessee	2 g lutetium oxide

<u>Destination</u>	<u>Item</u>
Supply Officer Naval Research Laboratory Washington 25, D. C.	54 g lanthanum metal 51 g neodymium metal 52 g praseodymium metal 50 g gadolinium metal
Brookhaven National Laboratory Upton, Long Island, New York	5 g neodymium metal
Mallinckrodt Chemical Works St. Louis, Missouri	50 mg thulium oxide 50 mg lutetium oxide
Knolls Atomic Power Laboratory Attn: W. L. Robb Schenectady, New York	40 g yttrium metal
Dr. Daniel Laszlo, Chief Division of Neoplastic Diseases Montefiore Hospital New York 67, New York	25 g yttrium oxide, 99.9%
Dr. S. Jaffe Air Reduction Co., Inc., Research Laboratory Murray Hill, New Jersey	2 g thulium oxide (pure)
U. S. Bureau of Mines Raw and Precious Metals Experiment Station Reno, Nevada	1 g lanthanum oxide 1 g cerium oxide 1 g praseodymium oxide 1 g neodymium oxide 1 g samarium oxide 1 g gadolinium oxide 1 g yttrium oxide 1 g erbium oxide 1 g ytterbium oxide 100 mg holmium oxide 100 mg dysprosium oxide 100 mg thulium oxide 100 mg lutetium oxide 100 mg terbium oxide
Carbide and Carbon Chemicals Co. X-10 Plant, P. O. Box P Oak Ridge, Tennessee	400 g yttrium oxide 400 g neodymium oxide
Brookhaven National Laboratory Upton, Long Island, New York	50 g cerium metal (high purity)
Supply Officer Naval Research Laboratory Washington 25, D. C.	100 g thorium metal

<u>Destination</u>	<u>Item</u>
University of California	100 g ytterbium oxide
Attn: H. S. Allen	100 g erbium oxide
Los Alamos Scientific Laboratory	100 g dysprosium oxide
Los Alamos, New Mexico	
Litton Industries	3 thulium buttons
Beverly Hills, California	
General Electric Company	50 lbs yttrium oxide (high-
ANP Department	est purity)
Cincinnati, Ohio	1 lb samarium metal
	best grade available

1-24

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~