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ISC-834

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For July - December, 1956

Ames Laboratory Staff

March 15, 1957

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
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Semi-Annual Summary Research Report in Chemistry

For the period July - December, 1956

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

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

Physical and Inorganic Chemistry

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

1.1 Pilot Plant Separations

A number of runs were made on six-inch columns using R_2O_3 from gadolinite as a source, resulting in some noteworthy fractions of pure rare earths.

A series of twelve columns, each ten feet long and thirty inches in diameter, has been installed. To date, one run with these columns has been completed. From all indications, the thirty-inch diameter columns perform as well as six-inch columns.

1.2 Use of Hydroxyethylethylenediaminetriacetic Acid for the Resolution of Heavy Rare Earth Mixtures

It has been established that HEDTA can be used to separate Lu, Yb, Tm, Er and Ho from each other on ion-exchange columns, after a mixture of these elements has been isolated from crude R_2O_3 sources by using EDTA and ion-exchange columns. This reagent is still being studied in hope that it will prove superior to EDTA for resolving the heavy rare earth elements.

2. The Separation of N^{15} and N^{14} by Ion-Exchange (F. H. Spedding and J. E. Powell)

A number of grams of 99.7% N^{15} were prepared by the elution of ammonium ion down a series of cation-exchange columns with dilute sodium hydroxide.

*Names indicate group leaders in charge of work.

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

3.1 Semi-Continuous Reduction

The scale-up of operations for preparing rare earth metals has continued. It has been possible to carry out preparations of 35 moles of metal in one reduction using a tantalum reaction chamber that is heated in a graphite inductor in an argon atmosphere. The metal and calcium fluoride slag are tapped into a water-cooled mold by means of a fusible plug in the bottom of the reaction chamber. At the present time, efforts are being directed toward determining the optimum operating conditions to give the best yield and purity of metals. When yttrium and the higher melting rare earth metals are prepared, it is found that about 2% of the rare earth metal is dissolved in the slag. As the pouring temperature is raised, the miscibility gap in the slag-metal system becomes smaller, and more of the product metal is dissolved in the slag, lowering the yield.

3.2 Samarium and Ytterbium

The increasing interest in the rare earth metals has made it desirable to have available methods of producing all of them in quantity. Since the method of preparing samarium, europium and ytterbium is not the same as that used for the other rare earth metals, a special effort has been made to scale up the preparation of these metals. The process developed at this Laboratory consists of reducing the oxides with lanthanum or misch metal. This process is expensive, partly because induction heating is used. The reduction might be carried out, at an obvious saving, by using a steel retort with external heating, in much the same manner as calcium and magnesium are prepared. It was found that metal could not be prepared by this means, at a reasonable rate at 1100°C (the temperature limit of the retort). However, this method and these conditions could be employed to redistill rare earth metals and alloys.

It was found that aluminum will reduce Sm_2O_3 to give an aluminum-samarium alloy, but pure samarium metal could not be obtained easily as a product of this reduction.

3.3 De-Oxidation of Rare Earth Metals

Contamination of rare earth metals by oxygen has been evident, both in metallographic studies and in chemical analyses of the metal in which an insoluble residue of rare earth oxide is obtained from a bromine-alcohol treatment of the metal sample. Preliminary

results indicate that melting the metal in vacuum with boron greatly reduces the amount of insoluble residue, presumably as a result of elimination of a volatile boron oxide. This method is being studied further to see if it can be utilized to obtain a better quality of metal.

4. Properties of Rare Earth Metals and Alloys (F. H. Spedding, A. H. Daane and L. D. Jennings)

4.1 Europium (F. H. Spedding and A. H. Daane)

The melting point of europium has been determined by thermal analysis and found to be $826^{\circ}\text{C} + 10^{\circ}\text{C}$, with no solid state transformations apparent between room temperature and the melting point. By radiographing the metal in the furnace at various temperatures the linear coefficient of thermal expansion was found to be $26 \times 10^{-6} \text{ deg}^{-1}$, and the expansion on melting was found to be 4.8%. For comparison, cerium was observed to expand about 0.3% on melting.

4.2 Samarium Oxides (F. H. Spedding and A. H. Daane)

Attempts have been made to prepare lower oxides of samarium by heating mixtures of samarium metal and Sm_2O_3 in various ratios. The only result of note is that large transparent crystals of the "B" form of Sm_2O_3 (monoclinic) were formed, having on their surfaces droplets of samarium metal, suggesting a possible disproportionation of a lower oxide, stable at higher temperatures. Analysis of the transparent crystals showed them to have the composition Sm_2O_3 , within the limits of error of the analysis.

4.3 Lanthanum-Yttrium Alloys (F. H. Spedding and A. H. Daane)

Alloys of lanthanum with yttrium have been prepared, whose microstructures indicate the presence of two phases at a composition 60 atomic per cent lanthanum, 40 atomic per cent yttrium. However, X-ray diffraction studies have shown only one phase having the double "C" axis structure of normal lanthanum. Alloys of these metals are being studied in more detail.

4.4 Lanthanum-Carbon System (F. H. Spedding and A. H. Daane)

Thermal analyses of lanthanum-carbon having a composition near 50 atomic per cent carbon have indicated the existence of LaC as a stable phase over a limited temperature range.

4.5 Vapor Pressure of Thulium (F. H. Spedding and A. H. Daane)

The study of the vapor pressure of thulium and of thulium over thulium-neodymium alloys has been completed. This study shows thulium and neodymium to form extensive terminal solid solutions with a relatively narrow two-phase region where these solid solutions co-exist. The thulium-rich alloys appear to be nearly ideal solutions, as indicated by the vapor pressure measurements, but there is a distinct departure from ideality at the neodymium-rich end.

4.6 Magnetic Properties of Erbium (F. H. Spedding and L. D. Jennings)

We have examined the susceptibility of a swaged erbium rod by the Gouy method. The measurements were made on an unannealed rod in the hope that the specimen was uniformly polycrystalline. The results, interpreted according to the molecular field theory, yielded an effective magnetic moment of 9.85 ± 0.1 Bohr magnetons per atom and a paramagnetic Curie temperature of $43.3^\circ \pm 0.5$. The error arises primarily from non-uniformity of the sample.

4.7 Thermal Properties of Terbium (F. H. Spedding and L. D. Jennings)

A large λ anomaly was found in the heat capacity of terbium at $227.65 \pm 0.1^\circ\text{K}$. There is a small rounded anomaly at 221° which is practically obscured by the primary anomaly. The small anomaly shows thermal hysteresis; the lower the temperature to which the sample has been cooled, the higher is the heat capacity through the anomaly. If the sample is cooled more than about 10° below the anomaly, however, the heat capacity becomes reproducible through it. We have found that, for the rare earths from gadolinium to erbium, this hysteresis is displayed for all anomalies below the one highest in temperature. At 300°K , $S = 17.55 \pm .05$ e.v., a value consistent with the hypothesis that the magnetic entropy is given by $R \ln(2J+1)$, where J is the value of the angular momentum appropriate for the tripositive ion. The enthalpy is 2264 ± 2 calories per mole at 300°K .

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

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

A paper entitled "A Non-Visual Method for Transport Numbers for Pure Fused Salts" by F. R. Duke and J. P. Cook was submitted for publication in Iowa State College Journal of Science.

Abstract

A method for determining pure salt transport numbers not requiring visual observation of the operating transport cell is described. The basis of the method is the change in distribution of the salt in a porous cell with the passage of a direct current, analogous to the Hittorf method in aqueous solution. A modification of the method is described for high temperature work with slightly volatile salts. The method is illustrated by its application to AgNO_3 .

5.2 Transport Numbers in Fused Salts (F. R. Duke)

A paper entitled "Transport Numbers and Structures in Fused AgNO_3 - NaNO_3 Mixtures" by F. R. Duke, R. W. Laity and Boone Owens was submitted for publication in J. ELECTROCHEM. SOC.

Abstract

The transport numbers of the ions in NaNO_3 - AgNO_3 mixtures are very closely proportional to the mole fractions. The transport number of the nitrate ion remains essentially constant. It is thus concluded that there are no complex species in NaNO_3 or AgNO_3 and that all cations present are structurally in identical positions. This argues strongly against any concept except complete dissociation in this nitrate system.

In the case of the KNO_3 - AgNO_3 system, we find that the mobility of each ion is a function of the composition. We attribute this to differences in molar volume; thus, the nitrate ions are farther apart in KNO_3 than in AgNO_3 and consequently, K^+ cannot move as well in AgNO_3 as it can in KNO_3 . We assume complete dissociation on the basis of the NaNO_3 - AgNO_3 work.

The PbCl_2 - KCl system is one in which the mobility of the chloride ion decreases as the composition varies from pure PbCl_2 to pure KCl . In mixtures, K^+ has a lower mobility in PbCl_2 than it does in KCl . The mobility of Pb^{++} is found to decrease as the composition varies from pure PbCl_2 to KCl , and may become negative (similar to that of an anion) after the composition reaches about 50 mole per cent KCl .

The results obtained thus far on AgCl - KCl mixtures indicate that no appreciable complexing of Cl^- with Ag^+ occurs in these melts. Up to about 25 mole per cent KCl , the Ag^+ mobility remains virtually constant.

Data were obtained on pure KCl and pure NaCl transport numbers. We found 0.80 for K^+ in KCl and 0.85 for Na^+ in NaCl.

5.3 Solubility of Water (F. R. Duke)

Work has been completed on the solubility of water in $Li^+-K^+-Na^+NO_3^-$ mixtures. The water is dissolved (as monomer) only if Li^+ is present. The solubility dependence on Li^+ is not linear, but varies according to the square of the Li^+ . Thus, indications are that two Li^+ are necessary to dissolve one water. Larger ions than Li^+ in the alkali series do not dissolve water. It is believed that the short distance of the Li^+-H_2O (ion-dipole) interaction is responsible for the action of Li^+ in dissolving water. The solubility of water in $LiClO_4$ has been determined and is comparable to that in the nitrate.

5.4 Complex Formation in Fused Salts (F. R. Duke)

It was found that $PbCrO_4$, $CdCrO_4$ and $BaCrO_4$ were insoluble in $NaNO_3$. Then, upon the addition of ions such as Cl^- and Br^- , some chromates dissolved. By measuring the solubility of chromates in $NaNO_3$ as a function of chloride ion concentration, it has been established that $PbCl^+$, $PbCl_2$ and $PbCl_3^-$ are fairly stable species. $PbBr^+$ and $PbBr_2$ have also been found and their dissociation constants determined; also, $BaCl^+$ was found to be an extremely weak complex. This work has also been done using $LiClO_4$ as solvent; the complexes are more stable in this solvent. We have now set up an apparatus for making potential measurements which should give further information on complex ions, particularly of salts where no convenient insolubility is found.

5.5 Metal-Metal Halide Systems (J. D. Corbett)

The solubilities of the three metal-metal halide systems were determined and are shown in Table I.

Table I

<u>System</u>	<u>Temp. °C</u>	<u>Mol. %</u>
Pb-PbI ₂	438	0.024
	597	0.15
	698	0.41
Cd-CdI ₂	410	0.63
	600	1.54
Sb-SbI ₃	201	1.69
	300	3.5
	398	5.4

The first two solubilities were measured by determining the weight loss of the metal when equilibrated with a known amount of salt; the third, by direct measurement of the weight of metal following sublimation of the salt. Transport of antimony metal as a gaseous subhalide by SbI_3 vapor has been observed at as low as 300°C with a salt pressure of 10^{-2} mm. This effect has required a modification of the techniques used in solubility measurement in this system; saturation of the salt is now achieved by diffusion of the dissolved subhalide through a sintered glass disk. Similarly, the Cd-CdI_2 measurements have been carried out in ampoules approaching zero free volume about the salt, so as to avoid transport of metal to cooler walls of the container.

The Ga-GaBr_2 system definitely contains the subhalide GaBr , stable in the solid phase. A criterion has been established as to whether a given subhalide can be separated from the metal-metal halide solution. It appears as if the eutectic in the hypothetical phase diagram for normal halide-subhalide must be exceeded in order for the latter to be a stable solid. This is observed in the systems from which GaI and GaBr have been isolated, but not with Ga-GaCl_2 and all other metal-metal halide systems. The bismuth halide systems may also be exceptions.

6. Adsorption Studies (R. S. Hansen)

A paper entitled "Idealized Models for Adsorption from Solution. I. van der Waals' Adsorption from Regular Solutions" by Robert S. Hansen and Ursula H. Mai, was submitted for publication in J. PHYS. CHEM.

Abstract

The theory of ideal van der Waals' adsorption from regular solutions of equal sized molecules is developed, and explicit limiting forms for high and low concentrations of preferentially adsorbed components and for slightly soluble systems are given. Salient properties of the model are the following: (1) one component is preferentially adsorbed over the entire concentration range, (2) adsorption of the preferentially adsorbed component is proportional to $\ln^{-1/3} \frac{1}{a}$, where a is the component activity at low concentrations and to $(1-x)$, where x is the component mole fraction at high concentrations, (3) in slightly soluble systems the adsorption is proportional to $\log^{-1/3} x'/x$ over the entire concentration range except for minor corrections. Comparisons with available experimental data are given.

Work on the inference of adsorption from differential double layer capacitance measurements has been extended, and the adsorption of a representative series of organic compounds from aqueous perchloric acid solution on mercury has been measured. This study has led to the following hypotheses.

1. The standard free energy of adsorption of an organic compound by mercury (standard states based on unit activity coefficients at infinite dilution on the monolayer and in solution) is proportional to the difference in optical polarizability between the organic molecule and the volume of solvent it displaces.

2. The difference in interaction free energy between an adsorbate molecule at infinite dilution in a monolayer and the same molecule in a complete monolayer is approximately one half the difference in interaction free energy between this molecule at infinite dilution in bulk solution and in pure liquid adsorbate. Further tests as to the validity of these hypotheses are in progress. Equipment permitting the oscillographic tracing of complete capacitance-potential curves in single sweep operations has been constructed. While less accurate than the technique commonly used, it shows promise for rapid survey work.

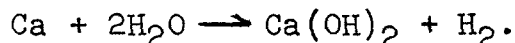
7. Metal-Water Reactions (H. J. Svec)

7.1 Calcium-Water Vapor

A paper entitled "Metal-Water Reactions. IV. Kinetics of the Reaction Between Calcium and Water Vapor" by Harry J. Svec and Charles Apel was submitted for publication in J. ELECTROCHEM. SOC.

Abstract

Calcium metal was reacted with water vapor in the temperature range 20 to 70°C and at water vapor pressures of 18 to 93 mm Hg. The experiments indicated that the only products were calcium hydroxide and hydrogen and that the reaction proceeded according to the equation



A manometric study of the reaction showed that it followed the logarithmic rate law. The rate constant K was observed to be linearly dependent on water vapor pressure below 70°C and to decrease with increasing temperature in the range 20-50°C. At 70°C the rate constant was observed to be independent of water vapor pressure. The activation energy was found to be -7.52 kcal/mole in the pressure dependent range.

7.2 Magnesium-Water Vapor

A paper entitled "Metal-Water Reactions. V. Kinetics of the Reaction between Magnesium and Water Vapor" by Harry J. Svec and Dale S. Gibbs was submitted for publication in J. ELECTROCHEM. SOC.

Abstract

The rate of reaction between magnesium and water vapor was studied in the temperature range between 425 and 575°C and in the water vapor pressure range between 31 and 208 mm Hg. The reaction took place according to the linear rate law. The rate constants were found to be linearly dependent on the water vapor pressure. The activation energy for the reaction was found to vary with both temperature and water vapor pressure, increasing as the temperature was increased and the water vapor pressure was decreased. This type of variation is explained on the basis of a change from a surface to a vapor phase reaction due to the very large increase in the vapor pressure of magnesium metal in the temperature range between 500 and 600°C.

7.3 Reactions with Calcium, Strontium and Barium

A paper by Harry J. Svec and H. G. Staley entitled "Metal-Water Reaction. VI. Anomalous Reactions of Water Vapor with Calcium, Strontium and Barium" was submitted to J. AM. CHEM. SOC. as a Communication to the Editor.

Pyrometallurgy

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

1.1 Extraction of Fission Products with Silver

Experimental work on pyrometallurgical processing has been concerned with studies on the removal of specific single fission product elements from uranium metal by extraction with silver. The technique involves adding to the uranium an amount of the fission product similar to that expected in a spent fuel and containing tracer at a specific activity high enough to be detected by autoradiographic methods. The metal samples are then examined by a series of autoradiographs and portions thus shown to be uniform are analyzed radiochemically for the tracer element.

The elements studied have been cerium and zirconium, two elements which were not giving reproducible results in the previous extractions of mixed fission products. In both cases, when the added element was initially alloyed with the uranium, it was found by autoradiography that the element concentrated in spots at the interface between the uranium and the tantalum crucible. When these spots were machined off, the remainder of the melt seemed quite uniform. Concentration at the crucible interface occurred again when these alloys were melted with silver and, in the case of cerium, high activity was also found at the uranium-silver interface. Samples of the apparently homogeneous portions of the two phases were analyzed.

Two extraction experiments with cerium as the fission product gave distribution coefficients of 42 ± 14 and 3900 ± 1400 and decontamination factors of 32 ± 10 and 1150 ± 400 , respectively. Although the results were considered fairly consistent in each extraction, results of the two extractions were vastly different. The major difference between the two experiments was the length of time the sample was molten, which was 7 minutes for the first experiment and 24 minutes for the second. During the longer period of the second melt, half of the original silver volatilized. This would explain part, but by no means all, of the discrepancy. In order to reduce this volatilization and permit the use of longer heating times, the apparatus was changed to allow the addition of an inert gas. A third experiment under 0.2 atmospheres of argon was not too successful, apparently because the argon contained impurities which reacted with the cerium, removing it from the uranium by oxidative slagging rather than by extraction.

These three extractions of cerium are compared in Table II which shows the mode of removal of cerium from uranium, whether by extraction or by other processes which are grouped under "per cent reacted."

Table II. Removal of Cerium from Uranium

<u>Melt</u>	<u>Per Cent Removed</u>	<u>Per Cent Extracted</u>	<u>Per Cent Reacted</u>
I	97	66	31
II	99.9	93	7
III	91-96	18	78-85

In similar experiments on uranium which contained zirconium, the system was again heated under argon. Activity was found at the uranium-tantalum interface but not at the uranium-silver or silver-tantalum interfaces. The radiochemical analyses showed that much of the zirconium had reacted but little had been extracted, probably because of the fact that the argon was not sufficiently pure. Steps have been taken to purify the argon adequately in future extractions.

Two extractions are compared in Table III.

Table III. Removal of Zirconium from Uranium

<u>Melt</u>	<u>Per Cent Removed</u>	<u>Per Cent Extracted</u>	<u>Per Cent Reacted</u>
I	94 + 1	2.8 + 0.7	91 + 1
II	88 ± 3	8 ± 2	80 ± 4

1.2 Removal of Fission Products from Silver Extractant

The removal of these elements, particularly cerium, from the silver layer by treatment with fused salt mixtures is also being studied. The salt baths used have been various mixtures of alkali chlorides with silver chloride. In the case of each alkali chloride used, lithium, sodium or potassium, the removal of cerium was better than 99.5% complete and in many cases better than 99.8%. The concentration of silver chloride in the mixture did not seem to influence the results particularly, and it can be concluded that cerium can be removed from the silver with essentially 100% effectiveness by treatment with these fused salt mixtures.

2. Corrosion Studies (A. H. Daane)

In the attempt to develop metals with good corrosion resistance to low melting uranium-thorium-aluminum alloys, the survey of possible container and coating materials was continued. Tantalum, niobium and zirconium failed after a relatively short time in contact with the molten alloys; a boride coating on 304 stainless steel was somewhat better but far from a practical solution.

3. Uranium-Antimony System (A. H. Daane)

Studies of uranium-rich alloys show the α - β transformation raised to 674°C, with the β - α transformation occurring at 652°C; the β - γ transformation occurs isothermally at 781°C. There appears to be a eutectic near 0.1 w/o antimony as indicated by photo-

micrographs, but thermal analyses show no detectable lowering of the solidus in this region. There does appear to be a high temperature eutectic between the compounds U_5Sb_3 and USb .

Analytical Chemistry

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

1.1 Analysis of Niobium-Uranium Alloys (C. V. Banks)

A paper entitled "Differential Spectrophotometric Determination of Uranium and Niobium" by C. V. Banks, K. E. Burke, J. W. O'Laughlin and J. A. Thompson was submitted for publication in ANAL. CHEM.

Abstract

A differential spectrophotometric method is described for the determination of both uranium and niobium in binary alloys of these metals. Uranium is determined by reading the absorbance of uranium(VI) in 50 per cent (v/v) sulfuric acid at 420 millimicrons against a standard uranium reference solution. Niobium does not interfere. Niobium is determined by reading the absorbance of the complex formed with hydrogen peroxide in concentrated sulfuric acid against a niobium reference solution prepared in the same manner. The maximum absorbance of perniobic acid under these conditions occurs at 360 millimicrons. Uranium(VI) has an absorbance minimum at this wavelength and a correction for this small absorbance is subtracted from the observed absorbance.

1.2 Neodymium-Erbium Mixtures (C. V. Banks)

A paper entitled "Differential Spectrophotometric Determination of Neodymium-Erbium Mixtures" by C. V. Banks, J. L. Spooner and J. W. O'Laughlin was submitted for publication in ANAL. CHEM.

Abstract

Differential spectrophotometric methods for the determination of neodymium and erbium in neodymium-erbium mixtures are described. These methods permit an analysis accurate to two parts per thousand for either neodymium or erbium, provided a sample containing 80 mg. of the

element to be determined is available. When as little as 7 mg. of the component to be determined is available, an analysis accurate to one per cent can be performed. The problems which arise when two or more substances absorb at the same wavelength are discussed and a method for the accurate determination of very small molar absorptivities is described.

1.3 Titration of Acid Mixtures in Acetone (J. S. Fritz)

A paper by James S. Fritz and Stanley S. Yamamura entitled "Differentiating Titration of Acid Mixtures in Acetone" was submitted to ANAL. CHEM. for publication.

Abstract

A wide variety of organic acids can be titrated in acetone using a tetraalkylammonium hydroxide in benzene-methanol as the titrant. Weakly acidic substances can be titrated and the products of titration are soluble. The titrations can be followed potentiometrically using a glass-modified calomel electrode system. In this study, the titration of phenols, carboxylic acids, enols, imides and sulfonamides were considered. In each class, the compounds selected for titration contained a variety of electron-withdrawing functional groups. The number and position of these groups relative to that of the acidic group were varied. By studying the individual titration curves of the acids, it was possible to predict the feasibility of quantitatively differentiating acids in mixtures. In general a differentiating titration is feasible if the potential at the start of the inflection of the stronger acid and the potential at the beginning of the curve of the weaker acid differ by more than 100 millivolts.

1.4 Complexometric Titrations (J. S. Fritz)

A paper by James S. Fritz, Marlene Johnson Richard and Ann Sutton Bystroff entitled "Complexometric Titrations Following Cupferron Separation of Interferences" was submitted for publication in ANAL. CHEM.

Abstract

The cupferron complexes of tri- and tetra-valent metals can be extracted from water into an immiscible organic solvent and thus separated from most divalent metal ions. Using a 1:1 mixture of benzene and isoamyl alcohol, the

separation is quantitative in a single extraction. The optimum pH range for this extraction is approximately 0.3 to 1.0. The divalent metals remaining in the aqueous phase may be determined by titration with Enta (ethylenediamine-tetraacetic acid). Data are given for the titration of magnesium, calcium, manganese, zinc, cadmium, lead, cobalt and nickel following separation from iron, thorium, zirconium, titanium, tin or bismuth. Separation from aluminum, copper, or rare earths is incomplete by this method.

2. Analytical Reagents (J. S. Fritz)

2.1 Titration with EDTA

A paper by James S. Fritz and Marlene Johnson Richard entitled "Potentiometric Titrations with Ethylenediaminetetraacetate" was submitted for publication in ANAL. CHEM.

Abstract

The potentiometric titration of metal ions with Enta (ethylenediaminetetraacetate) was studied using a mercury metal indicator electrode of the type recently proposed by Reilley. Bismuth, cadmium, calcium, copper, lead, mercury, rare earths, thorium, yttrium and zinc may be titrated directly with 0.05 M. Enta if a trace of mercury(II) is present. Metal ions such as aluminum, iron(III), nickel and zirconium react too slowly to be titrated directly with Enta, but can be determined by adding an excess of Enta and back-titrating with copper(II) or mercury(II). These determinations can be made more selective by varying the pH and through the use of certain masking agents. At pH 4.5, calcium and magnesium do not interfere in any of the titrations; at pH 2.1 thorium can be determined in the presence of lanthanum. Cadmium, copper, lead and zinc can be determined in the presence of iron(III), thorium, titanium(IV), zirconium and uranium(VI) using citrate as a masking agent. If sulfo-salicylate is added, rare earths can be determined in the presence of uranium(VI) or aluminum.

2.2 Titration Using Azoxine Indicators

A paper entitled "Complexometric Titrations Using Azoxine Indicators" by J. S. Fritz, W. J. Lane and Ann Sutton Bystroff was submitted for publication in ANAL. CHEM.

Abstract

7-(1-naphthylazo)-8-hydroxyquinoline-5-sulfonic acid (for which the trivial name naphthyl Azoxine is proposed) and several related compounds have been prepared and shown to be valuable as metal ion indicators in complexometric titrations. In acid solution using naphthyl Azoxine indicator, cadmium, cobalt, copper, lead, nickel, rare earths, thorium, yttrium and zinc can be accurately titrated with 0.05 M. Enta (ethylenediaminetetraacetate). In many cases a small amount of copper must be present in order for the indicator to function properly. Calcium and magnesium do not interfere if the pH is 5.5 or less. Using citrate as a masking agent, zinc and other divalent metals can be titrated in the presence of uranium(VI), thorium or zirconium. The use of tartrate, fluoride, iodide or thiourea as masking agents in certain cases also increases the selectivity of the method.

3. Automatic Titrator (J. S. Fritz)

An instrument has been built that will automatically titrate and plot the entire potentiometric curve for a titration. We have obtained good curves for redox titrations, acid-base titrations in aqueous and nonaqueous solution, and for EDTA titrations using a mercury indicator electrode.

4. Ion Exchange Separations (J. S. Fritz)

4.1 Zirconium(IV) and Cerium(III)

Zr(IV) and Ce(III) were successfully separated by a rapid ion exchange method. Excess EDTA is added to the sample mixture and the pH is adjusted to a point (pH 2.0) where the Ce(III) will be taken up by a cation exchange column, but the Zr(IV) will remain complexed by the EDTA and will pass quantitatively through a short column. The separation is complete in just one pass through a short column. We are studying the conditions necessary for separation of zirconium from other rare earths.

4.2 Separation of Copper(II)

Copper(II) has been quickly and quantitatively separated from uranium(VI), iron(III), thorium(IV) and Al(III) by an ion exchange method. Ethylenediamine is added to form a cationic complex with the copper(II), and sulfosalicylate is added to form an anionic

complex with the uranium, iron, thorium or aluminum. The separation is effected by a single pass through a short column containing cation exchange resin in the ammonium form. The copper is eluted from the column with hydrochloric acid and titrated with EDTA using the naphthyl azoxine indicator previously described.

5. Service Analyses (C. V. Banks)

A total of 4,229 service analyses were made during this period.

Spectrochemistry

1. Spectroscopic Research (V. A. Fassel)

1.1 Determination of Oxygen in Metals

An emission spectrometric method for the determination of oxygen in titanium and titanium alloys has been developed. The procedure is based on the d.c. carbon arc excitation of a special electrode assembly which provides a molten platinum bath after the arc is initiated. The oxygen content of the titanium samples is rapidly liberated from this bath into an argon atmosphere which supports the arc discharge. The intensity ratio of the line pair O 7771A is related to the oxygen content of the titanium sample. A 7891A

This procedure provides oxygen determinations with a precision comparable to vacuum-fusion or bromination-reduction techniques, but with greatly reduced time requirements. Preliminary results show that this technique can also be used for the determination of oxygen in yttrium and niobium metals.

A paper entitled "The Spectrographic Determination of Oxygen in Metals. I. Plain Carbon Steels" by V. A. Fassel and R. W. Tabeling was submitted for publication in SPECTROCHIM. ACTA.

Abstract

The presence of oxygen in metals may greatly influence the physical properties of the metal. Although progress has been made in applying chemical methods to the determination of oxygen in metals, the performance of the analysis is a singularly difficult task. The problems encountered in

extending conventional spectrographic techniques to this determination are surveyed and techniques for surmounting some of the problems are presented. A d.c. carbon-arc excitation method for the determination of oxygen in plain-carbon steels in the concentration range 20 to 2000 parts per million is discussed in detail. The method is based on the liberation of the oxygen as carbon monoxide into an argon atmosphere which supports a conventional arc discharge between a counter electrode and the sample supported in a carbon electrode. The intensity ratio of the line pair 0-7771.93 A-7891.07 is related to the oxygen concentration in the usual manner. The precision is comparable to results obtained by most vacuum fusion methods, whereas considerably less time is required per determination.

1.2 Preliminary Experiments on the Determination of Nitrogen in Metals

The simultaneous spectrographic determination of nitrogen in metals is a desirable extension of the spectrographic method for the determination of oxygen in metals. It has been demonstrated that molecular nitrogen is evolved from the samples under the excitation conditions employed for the determination of oxygen. However, the excitation energy available in a d.c. arc discharge is not able to dissociate N_2 and excite the atomic emission spectrum with sufficient sensitivity. Cyanogen is readily formed in the arc column and the band head at 3871.4 Å can be detected down to about 20 ppm. It has been found that the CN band intensity is enhanced by the presence of metallic vapors in the arc column; this produces fluctuations in CN band emission which introduce errors in the analytical method. For the determination of nitrogen in steel, a standard deviation of $\pm 15\%$ of the amount present has been obtained.

1.3 Preliminary Experiments on the Determination of Oxygen in Organic Compounds

The determination of oxygen in organic compounds is also a difficult task. In principle, it should be possible to determine the oxygen content of these materials by modifying the basic method for determining oxygen in metals. If solid organic compounds are vaporized slowly through an orifice of a carbon-supporting electrode which forms the anode of a d.c. carbon arc discharge in

argon, pyrolysis and complete reduction should occur. The CO so formed is then dissociated and the oxygen excited in the arc column. A straight line analytical curve has been obtained from a series of 10 organic compounds containing from 6 to 70 per cent oxygen.

1.4 Determination of Yttrium in Rare Earth Mixtures

The chemical and physical properties of yttrium and the true rare earths are so similar that these elements occur together in classical chemical separations. The determination of the yttrium content of rare earth ores and rare earth mixtures therefore cannot be achieved by chemical methods. An X-ray fluorescent spectrometric method for performing these analyses has been completed. For the determination of yttrium in ores, a preliminary rare earth group separation is required. The samples are analyzed in solution form, using added strontium as an internal standard. The use of strontium as an internal standard provides internal compensation for gross and mutual absorption and enhancement effects of thorium present in the sample. At 50% yttrium oxide content, the coefficient of variation of the measured intensity ratios is 0.74. About 10 minutes are required per determination.

1.5 Separation of Rare Earths from Thorium, Uranium and Zirconium

A report (ISC-851) entitled "Quantitative Separation of Small Amounts of Rare Earths from Thorium, Uranium and Zirconium by Ion Exchange" by H. J. Hettel and V. A. Fassel is being distributed.

Abstract

A successful method has been developed for the determination of certain rare earths in thorium in the fractional p.p.m. range. The procedure is based on the ion exchange chromatographic separation of the rare earths plus added yttrium carrier from the thorium followed by emission spectrometric determination of the rare earth impurities in the yttrium carrier. A simultaneous separation from the rare earths of the common element impurities present in the thorium has been accomplished. A high degree of compensation for procedural errors is achieved by the use of a pure rare earth as both the carrier in the separation and purification procedure and the matrix material in the spectrographic determination.

The method fulfills the requirements of accuracy, sensitivity, and speed necessary for use in the routine analysis of reactor-grade thorium metal. It can find application, in its present form, also for the simultaneous determination of part-per-billion amounts of common element impurities in thorium.

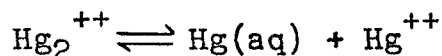
2. Spectroscopic Service Analyses

During the period of this report, 5422 samples were analyzed or examined by emission, fluorescence, or infrared spectroscopic techniques.

Radiochemistry

1. Behavior of Mercury and the Mercurous Ion (A. F. Voigt)

The study of the dismutation of the mercurous ion in dilute aqueous solution by tracer techniques has been completed. By making use of the greater solubility of mercury metal in organic solvents than in water a method was developed by which the constant for the dismutation reaction



could be estimated. This constant was found to be 5.5×10^{-9} . It was also possible to show that the mercurous dimer does not undergo dissociation to monomeric Hg^+ ions under these conditions and to place an upper limit of 10^{-7} to 10^{-8} for the dissociation constant.

If free mercury is equilibrated with a solution of mercuric ion, the two species react to form mercurous ion with a constant equal to about 100. This constant can be combined with the solubility of mercury metal in water to obtain an independent estimate of the dismutation constant. In order to do this the solubility of mercury was measured by tracer techniques. Radiolysis of the water by the radiation from the Hg^{203} used made it necessary to have a reducing agent present at low concentration in order to prevent the oxidation of mercury. Hypophosphorous acid was used for this purpose and the solubility was found to be 3.0×10^{-7} moles per liter, independent of the concentration of hypophosphorous acid over the range 10^{-3} to 10^{-1} molar. If this solubility is coupled with the constant for the

formation of Hg_2^{++} from $\text{Hg}(1)$ and Hg^{++} , a value of about 3×10^{-9} is obtained for the dismutation constant. With the uncertainties involved in this calculation, this can be considered good agreement with the value of 5.5×10^{-9} obtained by the direct measurement.

The solubility of mercury in a number of organic solvents was also determined (see Table IV). In these solvents its solubility is greater than it is in water by factors of 20 to 40. Correlation with solubility theory was attempted but the measured solubility was less than that predicted by the Hildebrand-Scott theory by factors of 2 to 15 for all except the least polar solvents. Thus, good agreement was obtained for n-hexane but increasingly poor agreement for the other solvents as their nature varied from that of aliphatic hydrocarbons. This lack of agreement is not surprising since the theory is not expected to be more than an approximation.

Table IV. Solubility of Mercury in Various Solvents at 25°C

Solvent	Observed, g atoms/liter	Calculated, g atoms/liter
n-hexane	$(6.4 \pm 0.3) \times 10^{-6}$	6.2×10^{-6}
cyclohexane	$(11 \pm 0.2) \times 10^{-6}$	21×10^{-6}
carbon tetrachloride	$(7.5 \pm 0.3) \times 10^{-6}$	37×10^{-6}
toluene	$(12.5 \pm 0.5) \times 10^{-6}$	48×10^{-6}
benzene	$(12.0 \pm 0.6) \times 10^{-6}$	72×10^{-6}
nitrobenzene	$(9.3 \pm 0.1) \times 10^{-6}$	157×10^{-6}
water	$(3.0 \pm 0.1) \times 10^{-7}$	

A paper entitled "Dismutation of the Mercurous Dimer in Dilute Solutions" by Herbert C. Moser and A. F. Voigt was submitted for publication in J. AM. CHEM. SOC.

2. Formation and Extraction of Thallium Chloride (A. F. Voigt)

A paper entitled "The Formation of Thallium Chloride Complexes and Their Extraction into Ether" by Donald Horrocks and A. F. Voigt was submitted for publication in J. AM. CHEM. SOC.

Abstract

The extraction of thallium(III) chloride into isopropyl ether has been studied using tracer techniques with Tl^{204} . Appreciable extraction occurs under conditions of high acidity,

and the extraction is markedly dependent upon the ionic strength of the solution. In order to study the effect of varying acidity and chloride concentration over a wide range, the study was run at rather high ionic strength. The temperature coefficient and heat of extraction were determined in the range of 20-30°C. The empirical formula of the extracted species was found to be HTlCl_4 and a higher complex, H_2TlCl_5 , was found not to be extractable. At low chloride concentrations and low acidity the extraction cannot be explained completely by this mechanism and it is postulated either that TlCl_3 extracts or that HTlCl_4 ionizes in ether under these conditions.

3. Thorium Hazards (A. F. Voigt)

A paper by A. F. Voigt entitled "Hazards Associated with Thorium Metallurgy" will be published in the Transactions of the American Society for Metals.

Abstract

A consideration of the hazards which confront personnel who handle thorium through metallurgical operations must include several different sources of potential danger: chemical toxicity, radiological toxicity and fire and explosion hazards. Since the seriousness of the hazard depends on the chemical and physical form of thorium which is being handled, the problem becomes one of considerable complexity if all of the commonly used forms of thorium are considered.

Thorium health hazards have not received as much consideration in the atomic energy program as have those due to some of the other materials of interest in that program, and operating limits are not well established. In this paper we have attempted to show the reasoning behind the establishment of limits in order to help the investigator understand the nature of the hazard which he needs to guard against.

4. Photonuclear Reactions (A. F. Voigt and D. S. Martin)

4.1 Relative Yields of Nuclear Isomers (A. F. Voigt)

Research was completed on the study of the yield ratio of the bromine 80 isomers produced by the reactions $\text{Br}^{81}(\gamma, n)\text{Br}^{80m}$

and $\text{Br}^{81}(\gamma, n)\text{Br}^{80}$ using bremsstrahlung from the Iowa State College 70 Mev. Synchrotron. A value of 2.4 ± 0.1 was obtained for the ratio $\text{Br}^{80}/\text{Br}^{80m}$. It was shown to be independent of the energy over the range studied, 15-70 Mev. for the maximum energy of the bremsstrahlung beam.

A paper entitled "Relative Yields of Photoneutron-Produced Nuclear Isomers of Br^{80} Produced by a (γ, n) Reaction" by A. M. King and A. F. Voigt was submitted for publication in PHYS. REV.

4.2 Photonuclear Reactions in the Propyl Bromides (A. F. Voigt)

A report entitled "Chemical Effects of Photonuclear Reactions in the Propyl Bromides" by A. E. Richardson and A. F. Voigt is being distributed as ISC-855.

Abstract

When nuclear reactions occur in atoms in molecules, chemical changes follow as a result of the recoil of the product atoms. The nature of these chemical changes has been studied intensively for a number of systems but in most cases the magnitude of the recoil energy has been about the same. In the present studies, use was made of a much greater recoil energy than that normally used. The reaction $\text{Br}(\gamma, n)\text{Br}^*$ gives a recoil bromine atom with an energy of the order of 10^5 ev, compared to 10^2 ev for the product of the $\text{Br}(n, \gamma)\text{Br}^*$ reaction which is usually used.

The chemical nature of the products resulting when the propyl bromides were irradiated with neutrons and 70-Mev. gamma rays was studied by established techniques. It is possible to differentiate between the reactions which occur while the recoiling bromine atom still is highly energetic, or "hot", and those which occur after it has been slowed down to thermal energies. The products of the hot reactions show little dependence on the initial recoil energy. In the case of the thermal reactions, the higher energy recoil produces a greater number of products which are different from the original molecules. This can be attributed to the presence of a higher concentration of free radical fragments which are produced in slowing down the higher energy recoiling atom. These fragments combine with the radioactive bromine after it has reached thermal energies to form a greater variety and amount of new products.

4.3 Other Photonuclear Reactions (D. S. Martin)

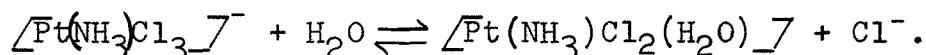
The cross section function for the photonuclear process, $\text{Ca}^{40}(\gamma, 3p3n)\text{Cl}^{34}$, was determined. For this investigation the X-ray flux of the Iowa State College Synchrotron was evaluated by three methods: (1) the simultaneous activation of $\text{Cu}^{63}(\gamma, n)\text{Cu}^{62}$ for which the cross section function is reported in the literature, (2) the calculated response of an air ionization chamber with thick paraffin walls and (3) the calorimetric calibration of an ionization chamber having 1/8-inch lead walls. The cross section function peaks sharply with a maximum of 0.3 millibarns at 50 Mev. The width at half-height of the peak is 6 Mev. and the integrated cross section for the process is 2.7 Mev. mb. or 4% of the integrated cross section for $\text{Ca}^{40}(\gamma, n)\text{Ca}^{39}$.

Activation of A^{40} to give Cl^{39} by the (γ, p) process and Cl^{38} by the (γ, pn) reaction was carried out as a function of the maximum bremsstrahlung energy. A procedure was set up to resolve the Cl^{38} and Cl^{40} contributions by a computer least-squares treatment of the sample decay curves.

5. Exchange Reactions (D. S. Martin)

5.1 Aquation of $\text{[Pt(NH}_3\text{)Cl}_3\text{]}^-$

Further studies were made of the kinetics and equilibrium for the aquation of the ion, $\text{[Pt(NH}_3\text{)Cl}_3\text{]}^-$ as indicated in the following equation:



Some earlier results were modified when careful analysis of solid samples $\text{K[Pt(NH}_3\text{)Cl}_3\text{]}$ indicated the presence of water of crystallization, not in the coordination sphere, for which corrections were necessary. The kinetics and equilibrium results are summarized in Table V. The aquation process provides a path for isotopic exchange in which Cl^* , introduced as Cl^- , may enter the coordination complexes. Experiments have indicated that isotopic exchange occurs so rapidly that alternative processes besides this reaction must also provide exchange. A procedure has been discovered by which it is possible to evaluate the independent exchange rates with chloride for each of the species $\text{[Pt(NH}_3\text{)Cl}_3\text{]}^-$ and $\text{[Pt(NH}_3\text{)Cl}_2\text{(H}_2\text{O)]}$. Each process is first order in complex and independent of chloride ion. Rate constants of 0.059 hr^{-1} and 0.21 hr^{-1} , respectively, for the two species were indicated by the experiments.

Table V

Specific Rate Constant and Equilibrium Constant

for the Aquation of $\text{[Pt(NH}_3\text{)Cl}_3\text{]}^-$

Temp °C	Equilibrium Constant moles/l.	k_1 hr ⁻¹
0.0	0.0115	0.0077
5.5	0.0122	.013
10.0	0.0128	-
15.0	0.0134	.047
20.0	0.0142	.085
25.0	0.0148	.134
30.0	0.0154	.21
35.0	0.0162	-

5.2 Exchange in Silver

In isotopic exchange experiments of silver between aqueous Ag^+ and crystalline AgIO_3 , inconsistencies in the exchange fractions and the chemical composition of the phases were noted. Since several authors have reported very rapid exchange between Ag^+ and AgCl , it was proposed to use AgCl as a scavenger for Ag^+ . However, it was found that only a small fraction of the aged AgCl samples utilized underwent rapid exchange. A large fraction of the exchange required a period of several hours. Additional exchange experiments have been carried out with solid adherent plates of AgCl prepared by anodic electrolysis. Exchange of the aqueous silver ion, with a major part of these samples is relatively slow, requiring a period of several hours.

5.3 Exchange in $\text{[Pt(en)Br}_3\text{]}^-$

A study has been undertaken to utilize radioactive tracers in the investigation of the compound, $\text{[Pt(en)Br}_3\text{]}^-$, where en = ethylenediamine. In this compound platinum is believed to exist as Pt(II) and Pt(IV) . However, the intense green color of its crystals, metallic luster and the degree of dichroism indicate a strong interaction between the two oxidation states. By means of tracer and exchange techniques it may be possible to determine if the Pt atoms become equivalent. Therefore, the experiments have dealt with solutions of the compound in dimethylformamide, in which $\text{[Pt(en)Br}_3\text{]}^-$ appears to dissociate into $\text{[Pt(en)Br}_2\text{]}^-$

and $\text{[Pt(en)Br}_4\text{]}$ and γ -butyrolactone, the only other known satisfactory solvent. For an initial investigation, the exchange between $\text{[Pt(en)Br}_2\text{]}$ and $\text{[Pt(en)Br}_4\text{]}$ in solution was chosen.

These solutions are relatively stable; however, over a period of several days, reduction of the Pt(en)Br_4 has been noted. Radioactive platinum, primarily Pt^{195} , was prepared by irradiation of the metal in the Argonne CP-5 reactor. Chemical separations were carried out to remove Au and Ir activities. Repeated separations were necessary to eliminate the Ir^{194} which was especially troublesome because of its long half-life and high cross section of formation from Ir impurities. A NaI crystal scintillation spectrometer has been very valuable for the analyses of the combined radioactivity for the Ir component. In the exchange experiments which have been performed, it appears that some separation-induced exchange may occur. However, chemical reduction of Pt(en)Br_4 by the solvent and possibly the Ir impurity may account for a major part of this feature. Exchange times between the $\text{[Pt(en)Br}_2\text{]}$ and $\text{[Pt(en)Br}_4\text{]}$ have been very short; however, the lack of consistency in carefully executed experiments has indicated that catalysis by an uncontrolled trace constituent may play a dominant role in effecting the exchange.

X-Ray Chemistry

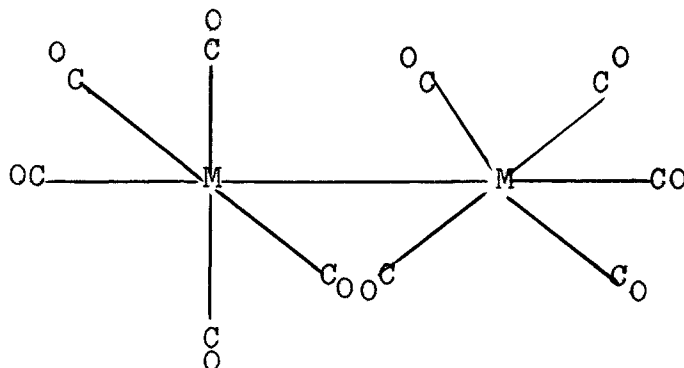
1. Polynuclear Metal Carbonyls (R. E. Rundle)

The structure of $\text{Re}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_{10}$ has been essentially completed. The isomorphous compounds are monoclinic with probable space group $I 2/a$ and four molecules per unit. (There is still a possibility that slight tipping of the molecules leads to the space group Ia .)

$$\text{Mn}_2(\text{CO})_{10} \quad a = 14.15, b = 7.11, c = 14.67\text{\AA}, \beta = 105^\circ$$

$$\text{Re}_2(\text{CO})_{10} \quad a = 14.70, b = 7.15, c = 14.91\text{\AA}, \beta = 106^\circ$$

The molecular structure is shown below. All bonds angles are



$\sim 90^\circ$, so that there are six bonds to each metal, nearly octahedrally directed. CO's about each metal are rotated $\sim 45^\circ$ to give a staggered configuration. The M-M bonds are notably long: Mn-Mn = 2.97 Å, Re-Re = 3.0 Å. This long distance probably results from steric interaction of CO's and quite probably from the relatively high negative formal charge on the metals which leads to some real negative charge and tends to increase the size of the metals.

The M-M bond is exactly normal to the monoclinic axis in I 2/a, and this arrangement is at least approximately correct.

This is the first known example of a dimer whose dimerization is due wholly to metal-metal bonds of transition metals. As such it is not in accord with many of the recent ideas concerning metal carbonyls. There are no bridge CO's, and correspondingly, there is no CO frequency near 1800 cm^{-1} where bridge CO frequencies are presumed to occur.

2. Magnus Pink and Green Salts (R. E. Rundle)

The slightly soluble Magnus salts, $\text{Pt}(\text{NH}_3)_4\text{PtCl}_4$, result promptly from mixing of solutions of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ and K_2PtCl_4 . The reaction is capricious; sometimes the green salt, and sometimes the pink salt results, and no control is as yet possible. The type of isomerism presents an interesting chemical problem.

The crystal structure of the green salt has been determined with high accuracy from single crystal data. It is tetragonal, $a = 9.0\text{Å}$, $c = 6.5\text{Å}$, $z = 2$, with space group I $4/m\text{nc}$. PtCl_4 and $\text{Pt}(\text{NH}_3)_3^{++}$ ions alternate along c in planes $c/2$ apart. Within planes there are equal numbers of positive and negative ions. Pt-Pt-Pt chains run along c with Pt-Pt = 3.25Å . K_2PtCl_4 is colorless, while $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ is red (pink when finely divided). The green color quite apparently results from weak metal-metal bonding of a type described before for nickel dimethylglyoxime. [Godycki and Rundle, Acta Cryst., 6, 487 (1953); see also Rundle, J. Am. Chem. Soc., 76, 3101 (1954)] 7.

The pink salt is unavailable as single crystals of sufficient size for diffraction work. A radial distribution curve has, however, been run, using X-ray powder data collected with a Geiger counter diffractometer, and it has been found that in the pink salt,

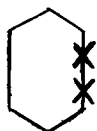
the closest Pt-Pt distance is 5.6Å. Hence, without the close Pt-Pt bonding the color apparently results from $\text{Pt}(\text{NH}_3)_4^{++}$ ions.

It seems likely that isomerism results from accidents of nucleation. The green salt is the stable form, due to metal-metal bonding. There may be an activation energy for forming the metal-metal bond, and packing considerations alone probably favor the pink salt.

3. Benzene-Positive Ion Complexes (R. E. Rundle)

Benzene-positive ion complexes are excellent examples of charge-transfer complexes generally, and may have some added interest in that most aromatic substitution results from the attack on benzene of a positive ion, or at least an electron accepting group. The best studied example to date has been the $\text{AgClO}_4 \cdot \text{benzene}$ complex, which can be obtained in crystalline form. Here it has been found that there is π -complexing of Ag^+ to the benzene in such a manner that the Ag^+ ion sits over the ring between two carbon atoms.

Recently we have been refining this structure and we now find that the Ag^+ ion does not sit half-way between the two carbons, but is displaced toward one or the other, at points marked X



on the hexagon. In the crystal there is, then, some randomness in the structure.

Mulliken first pointed out that in a charge transfer complex of this sort, symmetry arguments above preclude the Ag^+ ion from sitting on the hexagonal axis of the benzene ring. His argument is essentially as follows: The highest energy orbitals of the benzene ring belong to e_1 , while an s-orbital or g-orbital in a system of C_{6v} symmetry would belong to a_1 . Hence there can be no electron transfer from the highest benzene level to the lowest silver level for a system with C_{6v} symmetry because the appropriate levels belong to different irreducible representations and are orthogonal. The interaction is permitted for lower symmetry, as observed.

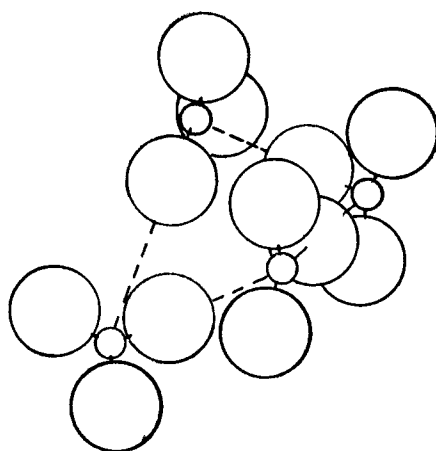
Recently Dr. Corbett of this Laboratory prepared a $\text{GaGaCl}_4 \cdot \text{benzene}$ complex, and it is then clear that this is an altogether different case. For C_{6v} symmetry, the lowest unoccupied levels of Ga(I) are the p-levels, and p_x and p_y belong to e_1 and can accept electrons from benzene. We are now studying to see if Ga(I) lies on the

benzene axis. At least we know that $\text{Ga} \cdot \text{GaCl}_4 \cdot \text{benzene}$ is not isomorphous with $\text{AgClO}_4 \cdot \text{benzene}$. The gallium complex is at least pseudo-hexagonal which does not discourage the view that Ga may lie on the 6-fold axis of the benzene ring.

A paper entitled "Concerning the Symmetry of Benzene Positive Ion Complexes; Unipositive Third Group Ions" by R. E. Rundle and J. D. Corbett has been submitted to J. AM. CHEM. SOC. for publication as a Communication to the Editor.

4. Electron Deficient Compounds (R. E. Rundle)

Considerable progress has been made in finding the carbon positions in the trimethylindium tetramer. It now appears that nearly trigonal monomer molecules are tied together by very weak, unsymmetrical bridges, and that quite probably there is also weak association of the tetramers. About any one indium the geometry appears to be about as follows:



LARGE CIRCLE = METHYL
SMALL CIRCLE = In

5. Transition Metal Complexes (R. E. Rundle)

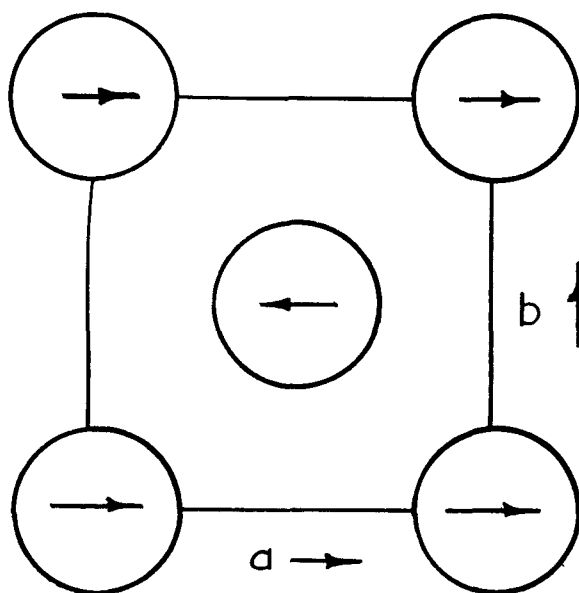
Knowledge of the exact proton positions in the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ crystals, obtained by the neutron diffraction work of Levy and Peterson, Oak Ridge National Laboratory, led us to re-examine our conclusions derived from the nuclear magnetic resonance data of Poulis and Hardeman [W. J. Poulis and G. E. Hardeman, *Physica*, **18**, 201 (1952); *J. de chim. Phys.*, **50**, C110 (1953)]. Some new and interesting results were observed; however, these results are quite compatible with our conclusions reached earlier.

The protons in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ are used as probes for the crystalline magnetic field in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in both the para- and antiferromagnetic ranges. This can be determined by proton magnetic resonance since the energy difference between the parallel and the antiparallel orientation of the proton moment depends upon the absolute magnitude of the field at the proton:

$$\Delta E = K |H|.$$

ΔE is measured in the resonance experiment and H depends upon the external and the crystalline field. From Poulis and Hardeman's data the following can be shown:

- (1) The magnetic alignment of the magnetic electron moments is:



where the moments are shown on the molecules of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at 000 , and $\frac{1}{2} \frac{1}{2} 0$. In alternate planes along c , the moments are antiparallel.

- (2) The magnetic electron wave function is not localized upon copper but is distributed as follows:

$$\begin{array}{ccc} 0.25 & 0.50 & 0.25 \\ \text{Cl} & \text{Cu} & \text{Cl} \end{array}.$$

(3) From the paramagnetic resonance it can be shown that the magnetic electron is less than 1% on the water oxygen.

(4) This is compatible with an MO treatment, but not with crystal field or valence bond treatments of transition metal complexes.

A detailed report entitled "A Theoretical Study of the Electronic Structures of Transition Metal Complexes" by J. W. Richardson and R. E. Rundle is being distributed.

6. Tin Whiskers (R. E. Rundle)

A paper entitled "X-Ray Investigation of Tin Whiskers" by H. G. Smith and R. E. Rundle was submitted for publication in J. APPL. PHYS.

Abstract

Intensities were measured for several whiskers varying in diameter from 2μ to 11μ . Some of the data were obtained by means of a Geiger counter with $\text{CuK}\alpha$ radiation and some by photographic methods with $\text{MoK}\alpha$ radiation. The observed structure factors were corrected for extinction according to the dynamical theory of X-ray diffraction with the crystallite size as a parameter and then compared to the calculated structure factors. The agreement is very good for a crystallite size of 1.5μ for a 5.5μ whisker and 2.7μ for whiskers of about 10μ in diameter. The whiskers were observed growing in several crystallographic directions.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-673 G. A. Guter and G. S. Hammond. Steric Effects on the Formation Constants of Metal Chelates of β -Diketones.
- ISC-695 R. A. Foos and H. A. Wilhelm. Separation of Yttrium and Some Rare Earths by Liquid-Liquid Extraction.
- ISC-703 D. L. Horrocks and A. F. Voigt. The Formation of Thallium Chloride Complexes and Their Extraction into Ether.
- ISC-708 Ames Laboratory Staff. Metallurgy. Semi-Annual Summary Research Report. July-December, 1955.
- ISC-720 Charles Baroch and G. H. Beyer. Preparation of Zirconium from Zirconium Tetrafluoride.
- ISC-737 Charles V. Banks and Howard B. Nicholas. Annotated Bibliography of 1,2-Cycloheptanedionedioxime.
- ISC-738 Charles V. Banks, Howard B. Nicholas and James L. Pflasterer. Annotated Bibliography of 1,2-cyclohexanedionedioxime.
- ISC-743 O. N. Carlson, N. Ida, D. Peterson, F. Tate and H. A. Wilhelm. Preparation of Ingots of Uranium-Niobium Alloy.
- ISC-744 O. N. Carlson, F. A. Schmidt and F. H. Spedding. Preparation of Yttrium Metal by Reduction of Yttrium Trifluoride with Calcium.
- ISC-760 Ames Laboratory Staff. Engineering. Semi-Annual Summary Research Report. January-June, 1956.
- ISC-761 Compiled by P. Chiotti. Hanford Slug Program. Semi-Annual Summary Research Report. January-June, 1956.
- ISC-793 E. L. Koerner and M. Smutz. Separation of Niobium and Tantalum - A Literature Survey.
- ISC-794 Charles V. Banks and Richard Fullerton. Annotated Bibliography of Diaminoethanedionedioxime.
- ISC-795 S. G. Epstein, D. M. Bailey, R. L. Smythe, G. R. Kilp and J. F. Smith. Tabulation, Bibliography, and Structure of Binary Intermetallic Compounds. I. Compounds of Lithium, Sodium, Potassium, and Rubidium.

2. Publications

- Banks, C. V. and C. I. Adams
The Preparation of 3,4-Bis(2-Furyl)-1,2,5-Oxadiazole.
J. Org. Chem. 21, 815 (1956).
- Banks, C. V., P. G. Grimes and R. I. Bystroff
Cell Corrections in Precision Colorimetry. Anal.
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- Banks, C. V. and Donn W. Klingman
Spectrophotometric Determination of Rare Earth Mixtures.
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- Banks, C. V. and J. W. O'Laughlin
Determination of Cerium and Chromium in Cerium-Chromium-Uranium Mixtures. Anal. Chem. 28, 1338-1340 (1956).
- Banks, C. V., John L. Spooner and Jerome W. O'Laughlin
Differential Spectrophotometric Determination of Neodymium in Neodymium-Yttrium Mixtures. Anal. Chem. 28, 1894-1897 (1956).
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The K_a Values of Sulfoacetic and 3-Sulfopropionic Acids. J. Org. Chem. 21, 1439-1440 (1956).
- Beyer, G. H. and F. M. Jacobsen
Operating Characteristics of a Centrifugal Extractor.
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The Fe(II)-Tl(III) Reaction at High Chloride Concentration.
J. Phys. Chem. 60, 1015 (1956).
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Infrared Dichroism Studies of Some Molecular Complexes. *Spectrochim. Acta* 8, 142-151 (1956).
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A Correlation of Bond Length with Stretching Frequency for C-O and C-N Systems. *J. Chem. Phys.* 25, 135-138 (1956).
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APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
Prof. K. Jargensen Copenhagen, Denmark	5 gm gadolinium oxide 2 gm dysprosium oxide 1 gm ytterbium oxide 1/2 gm holmium oxide 1 gm erbium oxide
Prof. Dr. H. Hopperman Heidelberg, Germany	10 gm yttrium metal
Nuclear Metals, Inc. Cambridge, Massachusetts	200 gm cerium metal
Atomics International Canoga Park, California	15 gm gadolinium metal 15 gm samarium metal
H. M. Wingard Westinghouse Electric Corp. Research Laboratories Pittsburgh, Pennsylvania	110 gm thorium
Colorado School of Mines Research Foundation, Inc. Golden, Colorado	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Colorado School of Mines Geology Department Golden, Colorado	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide

<u>Destination</u>	<u>Item</u>
University of Minnesota Minneapolis, Minnesota	1/4 gm terbium metal 1/4 gm thulium metal 1/4 gm lutetium metal 1/4 gm holmium metal 2/10 gm europium metal
State University of Iowa Chemistry Department Iowa City, Iowa	10 gm samarium metal 10 gm lanthanum metal 5 gm ytterbium metal 5 gm cerium metal 5 gm neodymium metal
Jet Propulsion Laboratory Pasadena, California	300 gm cerium metal
Knolls Atomic Power Laboratory Schenectady, New York	2 gm thulium metal
University of Southern California Los Angeles, California	10 gm ytterbium metal 200 gm cerium metal
Massachusetts Institute of Technology Cambridge, Massachusetts	1/2 gm samarium metal
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	100 gm holmium oxide 20 gm holmium metal 100 gm yttrium metal
National Spectrographic Laboratory 6300 Euclid Avenue Cleveland, Ohio	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Argonne National Laboratory Lemont, Illinois	5 gm ytterbium metal
University of Illinois Urbana, Illinois	100 mg terbium oxide 100 mg terbium metal

<u>Destination</u>	<u>Item</u>
University of Wyoming Laramie, Wyoming	1 gm lanthanum oxide 1 gm cerium oxide 1 gm praseodymium oxide 1 gm neodymium oxide 1 gm samarium oxide 1 gm gadolinium oxide 1 gm yttrium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Purdue University Lafayette, Indiana	10 gm cerium metal
Dr. Frank A. Kanda University of Syracuse Syracuse, New York	113 gm pure calcium
Dr. W. C. Koehler Oak Ridge National Laboratory Oak Ridge, Tennessee	1 bar polycrystalline neodymium
University of Kentucky Chemistry Department Lexington, Kentucky	15 gm cerium metal
Stephen M. Shelton Oregon Metallurgical Corp. Albany, Oregon	1 lb. yttrium fluoride
Dr. R. S. Milliken University of Chicago Chicago, Illinois	3 gm N ¹⁵
Dr. Joseph G. Graca Iowa State College Ames, Iowa	273 cc 5% NH ₄ Nd versinate 273 cc NH ₄ EDTA (ethylenediamine- tetraacetate) 200 cc each of 5.0% aqueous solutions of cerium, lanthanum praseodymium, and neodymium chloride. 200 cc each of cerium chloride versinate and lanthanum chloride versinate.
University of Wisconsin Madison, Wisconsin	66 gm neodymium metal 66 gm samarium metal 77 gm erbium metal

<u>Destination</u>	<u>Item</u>
Tufts University	3 gm lanthanum metal
Chemistry Department	3 gm gadolinium metal
Medford, Massachusetts	
Walter Reed Army Medical Center	10 gm cerium oxide
Washington, D. C.	