**AMES
LABORATORY
IOWA STATE
COLLEGE**

CHEMISTRY. SEMI-ANNUAL SUMMARY RESEARCH REPORT.

JANUARY-JUNE, 1956.

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ISC-757

U N I T E D S T A T E S A T O M I C E N E R G Y C O M M I S S I O N

SEMI-ANNUAL SUMMARY RESEARCH REPORT IN CHEMISTRY

For January - June, 1956

Ames Laboratory Staff

October 12, 1956

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

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Semi-Annual Summary Research Report in Chemistry

For the period January - June, 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 Production of Pure Rare Earths and Yttrium

During the past six months the production of highly purified yttrium and rare earths continued.

A sizable sample of xenotime sand was obtained from Heavy Minerals Company, subsidiary of the Crane Company. This material was subjected to tests to determine its desirability as a source of heavy rare earths and yttrium. The values given in Table I are based on the amounts of each element recovered from two kilograms of finely ground sand which was digested with sulfuric acid. The digestate was diluted, filtered, adsorbed on an ion-exchange column and eluted with EDTA, so that a series of simple binary and ternary rare-earth mixtures was obtained. Each sample was analyzed carefully and the amount of each constituent summed up to obtain the percentage in the original sand.

It appears that this material is an excellent source of yttrium and the heavy rare earths. Since it results from a large scale mining operation and is a by-product which can readily be separated from the main product, it should be a more economical source than gadolinite which we are currently processing.

Table I

Abundance of the Individual Rare Earths in Xenotime
 (As Oxide)

Lu	0.38(?)
Yb	1.96
Tm	0.43
Er	3.42
Ho	1.04
Dy	4.36
Tb	0.54
Gd	1.65
Eu	0.1
Sm	0.70
Nd	1.69
Pr	0.46

*Names indicate group leaders in charge of work.

Table I (continued)

Ce	2.57
La	1.88
Y	35.77
Total	56.95

Twelve 30-inch stainless steel columns, each 10 feet long, have been installed along with the necessary auxiliary equipment to permit the production of five or six pounds of pure rare earth oxide per day using xenotime sand as the source mineral. The first run with this equipment should be under way about August 1 and the first product should be available about November 1.

1.2 Exploratory Work in the Separation of Rare Earths by Ion Exchange

Considerable small column work has been done to determine the elution sequence of common elements and the rare earths with ethylenediaminetetraacetate (EDTA) as the eluant. In these experiments, it was determined that Fe^{+3} , Sc^{+3} , Bi^{+3} , Cr^{+3} and Sn^{+4} were not retained by Cu^{+2} , that Ni^{+2} , Th^{+4} and Pb^{+2} followed Cu^{+2} but preceded Yb^{+3} , that Zn^{+2} , Cd^{+2} , Co^{+2} , Al^{+3} , Fe^{+2} and Mn^{+2} eluted somewhere between Lu and La within the rare earth series, and that Ca^{+2} , Sr^{+2} , Be^{+2} , Mg^{+2} and Ba^{+2} eluted after La. Some minor discrepancies were noted between this work and that of Vickery, but his contention that ions of the same charge eluted in the order of stability of the metal chelate formed with EDTA was substantiated. The main discrepancies were that Ni^{+2} and Cu^{+2} and Zn^{+2} and Cd^{+2} eluted in the opposite order to that stated by Vickery. Th^{+4} , Zn^{+2} , Cd^{+2} and Co^{+2} fall upon the rare earths Lu^{+3} , Yb^{+3} and Tm^{+3} but the actual position has not yet been pinpointed. At an EDTA concentration of 0.0153 M. and a pH of 8.4, the conditions under which this work was performed, Fe^{+2} occurs between Sm and Nd and Mn^{+2} falls between Pr and Ce. This order with respect to the trivalent elements will probably change as conditions are varied. Vickery has reported these elements appearing at several points in the rare earth series depending upon the conditions used.

Further work is being done to pinpoint the elution positions of Pb^{+2} , Th^{+4} , Zn^{+2} , Cd^{+2} , Co^{+2} , Al^{+3} , Fe^{+2} and Mn^{+2} when EDTA is the eluant. Work is also being done to determine the elution sequence of common elements and rare earths when other chelating agents are used.

An interesting separation has been performed, based upon the fact that Sc^{+3} is not retained by Cu^{+2} , whereas all the rare earth elements are. By adsorbing a crude mixture of Sc and the rare earths, obtained from thortveitite, upon a Dowex 50 bed and diluting it

through a second short bed in the Cu^{+2} cycle with EDTA, an excellent separation was obtained. The Sc was recovered from the copper chelate solution and the rare earths were held up on the second resin bed.

It has been established that the heavy rare earths Lu, Yb, Tm and Er can be eluted using citrate at concentrations up to 4 grams of citric acid per liter in the pH range 8.7 to 9.0. Erbium starts to precipitate at pH values below 8.7. The separations between Yb - Tm and Tm - Er mixtures are good (better than is observed with EDTA) but the Lu-Yb separation was poor. It appears that this chelating agent may be useful for isolating Tm from Yb-Tm-Er mixtures following a preliminary separation of this group from the other rare earths using EDTA.

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

2.1 Separation of C^{12} and C^{13}

Preliminary investigations have shown that C^{13} can be enriched in the front portion of an adsorbed CN^- band by eluting cyanide down the hydroxyl form of Dowex 1 with dilute acetic or hydrochloric acid. The separation factor for the carbon isotopes in the reaction

is apparently about 1.01. The constant has not yet been measured with any accuracy, however.

2.2 Separation of N^{14} and N^{15}

An eight-foot long band of adsorbed ammonia was eluted down 320 columns of Dowex 50 resin, 4 1/2 feet long and 4 inches in diameter. Every 40 columns, the depleted front half of the band was discarded and an equivalent amount of ammonia previously enriched to 2% N^{15} was added to the plateau. The N^{15} in the ammonium ion at the rear edge of the band has, at present, reached a concentration of 95 atom percent.

3. Rare Earth Metallurgy

3.1 Production of Rare Earth Metals (F. H. Spedding and A. H. Daane)

3.1.1 General

Tests have shown that the ground calcium metal, used to reduce the rare earth fluorides, adsorbs a large quantity of gas even when it is stored in a protective atmosphere. Much of this gas may be liberated by heating the calcium in a vacuum. Since much of this gas would end up in the rare earth metal in a reduction, it seemed likely that the amounts of impurities in the final metal due to this gas could be reduced by prior outgassing of the calcium. This was verified in an experiment that showed the carbon and nitrogen content of the calcium reduced from 500 and 88 ppm, to 128 and below the detectable limit, respectively.

One of the other impurities that has been detected in the rare earth metals, particularly those with the higher melting points, is the corresponding rare earth oxide, possibly modified by the presence of some fluoride. The platelet form of this impurity indicated a liquid solubility in the metal that decreased to the melting point. By cooling very slowly from the liquid range through the melting point, it is possible to remove some of this impurity by liquation.

In order to prepare rare earth metal samples having the lowest possible neutron cross sections, a metal more suitable than tantalum was sought to serve as a crucible material. Niobium was a metal of choice from the standpoint of cross section, but attempts to melt yttrium metal in niobium crucibles failed, with the yttrium dissolving a large quantity of the crucible. However, melts of lanthanum and neodymium have been made in niobium, indicating a much lower solubility of this metal at the lower temperatures. In the case of lanthanum, the original metal sample contained 1200 ppm carbon, but after melting in the niobium, only 200 ppm was present. The surface of the lanthanum next to the niobium was covered with a hard, silvery, acid-insoluble layer, which X-ray diffraction analysis showed to be niobium carbide.

3.1.2 Semi-Continuous Reduction Apparatus

The need for some of the rare earth metals in larger-than-gram quantities instigated attempts to devise continuous and semi-continuous methods for preparing these metals. As described in the previous report from this laboratory, a continuous reduction of yttrium fluoride and calcium was attempted in a furnace having a hopper on the top from which the charge was dropped into a tantalum reduction chamber; this chamber was equipped with two tapping pipes set at positions in the chamber so that one would

draw off the slag into one water cooled mold, and the other would draw off the metal into another mold. Baffles were placed in the chamber so as to permit complete reaction of the charge before any of it escaped through one of the top holes, but it was not possible to get complete separation of slag and metal, and yields were only fair, so this method has not received further study.

A semi-continuous production method has been devised which has worked with moderate success for the preparation of yttrium. In this process, the charge is added to a tantalum reaction chamber as described above, but the reaction chamber to which the charge is added is provided with a small-diameter pipe which extends from the bottom and far enough out of the induction coil to remain cool. The pipe is closed, for the reduction of the initial charge, by melting a small piece of yttrium and allowing it to solidify in the pipe. After all of the initial charge has reacted in the chamber, the induction coil is lowered around the pipe and the power input is increased so that the metal is melted out of the pipe, and the metal and slag is tapped into a water cooled mold below. Several molds are located in a rotating head so that another mold may be rotated into position below the pipe, another charge added to the reaction chamber, and another reduction carried out. This process, when perfected, should lend itself to scaling-up to make larger quantities of the rare earth metals. As there is little or no erosion of the tantalum chamber, the tantalum consumption is reduced tremendously in comparison to a process in which a separate crucible is used for each reduction, and, inasmuch as tantalum sheet is next to impossible to obtain at the present time, this factor would be very pertinent in any rare earth metal production operation which utilizes tantalum.

3.1.3 Preparation of Europium

With interest increasing in the possible uses of europium, samarium and gadolinium, where their large neutron cross sections make them attractive, work has begun on a study of the preparation and properties of europium. Quantities of samarium and gadolinium salts have been available for some time, the metals have been prepared and some of their properties determined. However, europium has been obtainable only recently in quantities sufficient to make possible a similar study of this element. Previously, fractional-gram quantities of europium metal had been prepared in this laboratory by reducing europium oxide with lanthanum metal, the volatile europium metal being obtained as a condensate on a tantalum condenser. This sample was observed to react with

atmospheric gases much more rapidly than do any of the other rare earth metals, and, when in contact with water, it reacted somewhat like calcium. More recently several grams of europium metal was prepared in this laboratory by this same process, realizing a yield of greater than 90%. It was possible to observe that the metal distilled at an appreciable rate (representing a pressure of 10^{-1} mm or higher) at 1000°C , and melted at below 900°C . Work is under way to prepare about 75 grams of europium metal and to determine some of its physical properties.

Figure 1 shows an apparatus for the reduction of europium oxide. The charge of Eu_2O_3 and 5% excess lanthanum turnings is placed in the tantalum reduction crucible (3) and heated to about 1200°C in a high vacuum. The europium condenses in the delivery tube and, after introducing purified argon into the system to prevent distillation of the metal, it is melted down into the tantalum crucible (6) by lowering the induction coil. A test of this apparatus was made using ytterbium as a stand-in for europium, and excellent results were obtained. Figure 2 is a cobalt-60 radiograph of the system showing the ytterbium metal after it had been melted down into the crucible; further heating of the charge produced sufficient metal to cover the thermocouple well. A measurement of the melting point of ytterbium in this system was in good agreement with the figure of 824°C reported previously from this Laboratory.

3.1.4 Tantalum Recovery

Because of the scarcity of tantalum sheet in recent months, the recovery of scrap tantalum was attempted by arc melting the scrap in a helium atmosphere. Buttons were obtained which were then rolled without annealing. This process works well with clean scrap, but material that had become brittle from reaction in dirty furnace atmospheres was not suitable scrap for this process. It was possible to roll the buttons to a 10-mil sheet in a simple two-high mill.

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

3.2.1 Melting Points

The melting point of terbium was determined on a 300-gram specimen of this metal contained in a tantalum crucible. A cooling curve was run using a Pt/Pt-13% Rh thermocouple which showed the melting point to be $1368^{\circ}\text{C} \pm 10^{\circ}\text{C}$, with a transition at $1317^{\circ}\text{C} \pm 10^{\circ}\text{C}$.

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Fig. 1 - Apparatus for the Reduction of Europium Oxide

Fig. 2 - Cobalt-60 Radiograph Showing Europium Metal
in Thermal Analysis Furnace

A similar determination on yttrium showed it to melt at $1552^{\circ}\text{C} \pm 15^{\circ}\text{C}$, with a transition very near this temperature (within 50°C). Melting points determined with an optical pyrometer were in agreement with these figures.

3.2.2 Vapor Pressures

The vapor pressure of yttrium was measured by the effusion method and was found to be 10^{-2} mm at 1500°C , and 10^{-4} mm at 1360°C , corresponding to a heat of vaporization of about 80 Kcal/mole.

Additional measurements of the vapor pressure of thulium, previously reported (ISC-706), are in good agreement with the values found earlier. The partial pressure of thulium over thulium-neodymium alloys is being measured to determine the ideality of these solutions.

3.2.3 Crystal Structures

Lanthanum metal has been prepared in good yields by reducing lanthanum fluoride by lithium metal in a sealed tantalum bomb. The metal obtained has been found to be face-centered cubic in structure, even after prolonged annealing in what is normally the hexagonal range. After exposure to air for a period of time, followed by a recasting operation, the metal was found to be in the hexagonal form. Whether this phenomenon is a result of the purity of the original lanthanum salt used for this work, or whether the contamination by atmospheric gases was responsible for the change in crystal structure is not known, but the problem is being examined in detail.

For some calorimetric studies, experiments were carried out on samples of lanthanum, cerium, praseodymium and neodymium to observe the effect of quenching from their liquid states to -195°C . In case of praseodymium, only the room temperature form of the metal was observed, but in the case of lanthanum, cerium and neodymium, some evidence was found for the partial quenching of a high temperature form of the metal. But since the samples were predominantly in the room temperature forms of these metals, and since the quench to -195°C is considerably more drastic than the quench to 0°C in the Bunsen calorimeter, it is believed that no great difficulty will be introduced into the calorimetric studies from this effect.

3.2.4. Thermal Properties

Our results for the heat capacity of holmium, reported in ISC-706, have been re-examined. We have changed our estimate of the heat

capacity below the temperature of our lowest measurements. Although this change does not affect the energy appreciably, we now estimate the entropy at 300°K. to be 17.91 e. u. This value more nearly confirms the assumption that the room temperature contribution to the entropy from the 4f electrons is $R \ln(2J + 1)$.

In the course of this work, we have examined carefully how much we are able to say at present about the room temperature contribution to the entropy of the 4f electrons of the rare earth metals. In order to estimate this contribution, we must estimate the lattice and conduction electron contributions to the heat capacity.

The lattice contribution has been evaluated on the assumptions that the lattice heat capacity follows a Debye curve; that the Debye temperature for lanthanum is 132° and for gadolinium is 152°; and that the Debye temperature varies linearly throughout the rare earth series. We have found that none of these assumptions is completely justified; each of the three assumptions may give an error of about one entropy unit at room temperature in the most unfavorable circumstance.

The conduction electron contribution to the heat capacity has been evaluated on the assumption that it is constant throughout the rare earth series and is equal to $1.6 \times 10^{-3}T$, the value found by Simon, Parkinson and Spedding for lanthanum. A reevaluation of their data tends to confirm the coefficient of 2.1×10^{-3} found more recently at Columbia University. Nothing is known about the constancy of this value throughout the rare earth series.

We conclude that the room temperature magnetic entropy of the rare earths is consistent with the value $R \ln(2J + 1)$, but that this value has only been confirmed to about 20%. In order to sharpen this confirmation, it is necessary that more very low temperature heat capacity work be performed on the rare earths.

Measurements have been made of the heat capacity of terbium from 15° to 330°K. The thermodynamic functions have not yet been tabulated, but it is established that there is a λ type anomaly at 227.6°K which has a small shoulder on it at 221°K.

In conjunction with measurements of susceptibility being made by Experimental Physics Group II, we have been studying the effect of dilution on the heat capacity of gadolinium. A sample of gadolinium diluted with 50 atomic percent lanthanum showed no anomalies between 15°K and 300°K. A sample of gadolinium diluted with 49 atomic percent yttrium showed a single anomaly at 271°K. The peak appears to be less narrow than that of pure gadolinium.

4. Calorimetry (F. H. Spedding and A. H. Daane)

In building the Bunsen calorimeter mentioned above, several innovations have been introduced that appear to be improvements on previous designs of such an instrument.

- a. A screen has been placed near the bottom of the external ice bath in the calorimeter thermostat, and ice is introduced under this screen, as well as over it. Any tendency to establish an uneven temperature distribution in the thermostat is effectively defeated, for as water that is warmer than 0°C settles to the bottom of the thermostat, it drifts into the ice retained below the screen, and is cooled.
- b. An improved method has been devised for freezing out the ice mantle in the calorimeter proper. Helium gas is passed through a coil of copper tubing covered with liquid nitrogen; the gas then passes down into a perforated, closed-end copper tube suspended in the finned calorimeter chamber. By adjusting the position of the perforated end of the tube, the ice mantle may be frozen out evenly and rapidly on the finned section.

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

In studying the lanthanum-carbon alloy system, the compounds La_2C_3 and LaC_2 have been observed; La_2C_3 was previously reported to be LaC . Lanthanum sesquicarbide has been found to have a body-centered cubic structure with $A_0 = 8.8169\text{\AA}$; with the space group $I4_3d(\text{Td}^6)$. It has the plutonium carbide type structure, D_{5h} . As previously reported by Stackelberg, LaC_2 was found to have body-centered tetragonal structure with $A = 3.9339\text{\AA}$, $C = 6.5732\text{\AA}$ in the space group $I4\text{ mm}(\text{D}_{4h}^{17})$. Hydrolytic studies of these carbides are being made using a mass spectrometer. These have indicated the presence of C_3 hydrocarbons in the product from samples of La_2C_3 , but no detectable C_3 hydrocarbons from LaC_2 .

In attempts to synthesize lower oxides of samarium, quantities of Sm_2O_3 and samarium metal have been heated together in sealed tantalum bombs. The products of such treatment have been

samarium metal and a transparent phase whose crystals were tinted a light violet shade. The amounts of these two phases observed in the product indicated that the crystalline phase must have a composition near Sm_2O_3 . Single crystal X-ray diffraction studies have shown the material to be the B-form of Sm_2O_3 reported by Douglass and Staritzky¹(1), which they prepared by high temperature ignition of the C(cubic) form of Sm_2O_3 .

In the preparation of ytterbium by the reduction of Yb_2O_3 with lanthanum metal, a dark, crystalline phase was observed in the region of the condensate. Studies indicate that this material is probably an oxide of ytterbium.

6. Fused Salts

6.1 Potassium Chloride-Zinc Chloride System (F. R. Duke)

A paper entitled "Density and Electrical Conductance in the System $\text{KCl} - \text{ZnCl}_2$ " by F. R. Duke and R. A. Fleming (ISC-734) was submitted for publication in J. ELECTROCHEM. SOC.

Abstract

The phase diagram of the system $\text{KCl}-\text{ZnCl}_2$ indicates the presence of the solid state compound $2\text{KCl} \cdot \text{ZnCl}_2$. Density vs. composition isotherms in the range $475-650^\circ\text{C}$ are approximately linear. Isotherms of equivalent conductivity deviate negatively from additivity when plotted against composition, the maximum negative deviation being found near $X_{\text{KCl}} = 0.71$. The heat of activation for ionic migration falls rapidly from that of zinc chloride until X_{KCl} has reached 0.30, then slowly falls to the limiting value for pure KCl .

6.2 Metal-Metal Salt Solubilities (J. D. Corbett)

Additional solubilities determined during this period include:

¹ Douglass, R. M. and Staritzky, E. Anal. Chem. 28, 552 (1956).

System	Solubility, mole % metal	Temperature
Ga-GaBr ₂	9.31	170°C
Zn-ZnI ₂	0.28	500
	1.05	620
	1.64	670
Al-AlCl ₃	«0.01	215
Pb-PbI ₂	0.04	440

The results with these and earlier systems have indicated the probable formation of slightly-stable halides in the post-transition metal-metal halide systems. It appears that the effect of foreign salts on the extent of the interaction can logically be interpreted in terms of the acid-base reactions expected between the added salt and the two oxidation states present in the melt. Added base, i.e. halide ion, would stabilize the more acidic, higher oxidation state and thereby decrease the amount of subhalide formed. Conversely, an acidic salt capable of complexing halide would stabilize the lower state. This was found with Ga(GaCl₄) and Ga(AlCl₄). Use of AlCl₃ in other systems has allowed the isolation of the Cd(I) and Bi(I) oxidation states.

The solubility of metal in CdCl₂ at 750°C amounts to 21% conversion to the subhalide; this amount of solute Cd₂Cl₂ is incapable of existence as pure phase and disproportionates on solidification. In the presence of 2 moles AlCl₃ per mole CdCl₂, the metal solubility at 330°C corresponds to the formation of 71.5% of the stoichiometric amount of Cd(I). Moreover, the solid, light gray in bulk, white when ground to a powder, shows the typical properties of a subhalide, readily disproportionating in the presence of water, dioxane or alcohol.

Similarly, the use of AlI₃ in the Cd-CdI₂ system increases the amount of Cd(I) formed from 8.7% at 600°C to 40.5% at 350°C, giving a yellow solid that also produces metal when contacted with water.

In the Bi-BiCl₃ system, the solubility at 260°C amounts to 45% conversion to BiCl, an asphalt-like mixture is obtained on quenching. With the addition of the stoichiometric amount of AlCl₃, the reaction $\text{BiCl}_3 + 2\text{Bi} + 3\text{AlCl}_3 = 3\text{Bi}(\text{AlCl}_4)$ takes place quantitatively. The reddish-brown product is diamagnetic,

and disproportionates essentially quantitatively on contact with most solvents and with air. Both the Cd(I) and Bi(I) products give characteristic powder pattern diffraction lines.

7. The Chemistry of Gallium (J. D. Corbett)

Dielectric constant measurements on dilute solutions of Ga_2Cl_4 in benzene indicate the presence of a very polar molecule. Accordingly, the correct structure of the compound Ga_2Cl_4 must be $\text{Ga}(\text{GaCl}_4)$ and not $\text{Cl}_2\text{Ga-GaCl}_2$. Although the compound is $\text{Ga}^+\text{GaCl}_4^-$ at infinite dilution, rapid aggregation of the ion pairs takes place with increasing concentration. Analysis of the molecular weight data in terms of the concentrations of the various species indicates an unusual stability for the trimer. Raman spectra measurements on $\text{Ga}(\text{GaCl}_4)$ and $\text{Ag}(\text{GaCl}_4)$ solutions in benzene also support the above structure.

The small solubility of Ga in liquid Ga_2Cl_4 (4 mole %) indicates that GaCl has only a slight stability unless the halide is coordinated to the acidic GaCl_3 , as in $\text{Ga}(\text{GaCl}_4)$. Use of the strong acid AlCl_3 to accomplish this stabilization allows complete reductions of the Ga(III), according to the reaction $\text{Ga}_2\text{Cl}_4 + 2\text{Ga} + 4\text{AlCl}_3 = 4\text{Ga}(\text{AlCl}_4)$. The product is, as expected, physically very similar to $\text{Ga}(\text{GaCl}_4)$.

"The Use of Thermistors in Cryoscopic Measurements", by R. K. McMullan and J. D. Corbett, appeared in J. CHEM. ED., 33, 313 (1956).

8. Equations for a Lattice Gas (F. R. Duke)

A paper entitled "Equations for a Lattice Gas. II. Multi-component Systems" by Howard B. Levine was submitted to J. CHEM. PHYS. for publication.

Abstract

An expression is developed for P/kT for a multicomponent lattice gas with an arbitrary lattice as a multiple power series in a set of k -th nearest neighbor interaction parameters, λ_{ab}^k , where a and b index the components, with the coefficients functions of the activity set z . By straightforward differentiation, corresponding expressions are obtained for other thermodynamic variables, and also for the probability of finding a pair of particles of specified components on a pair of specified sites. A

transformation is outlined which permits the substitution of the number density set ρ for the activity set as independent variables.

9. Reaction Kinetics

9.1 Calcium-Water Vapor (H. J. Svec)

A report (ISC-777) entitled "Kinetics of the Reaction Between Calcium and Water Vapor" by Charles T. Apel and H. J. Svec is being distributed.

Abstract

Calcium metal underwent reaction with water vapor at temperatures of 20, 25, 30, 35, 40, 45, 50, 55, 60 and 70 C and at water vapor pressures of 18, 32, 55, 72 and 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,

$$W = K \log(1 + 0.45t),$$

where W is the weight of water in milligrams consumed per square centimeter of calcium surface, t is the time in hours and K is a constant at a given temperature and water vapor pressure. The rate constant K was observed to be linearly dependent on water vapor pressure below 70°C and to decrease with increasing temperature below 50°C. At 70°C. it was found to be independent of water vapor pressure. The activation energy was determined to be -7.52 kcal./mole. Temperature and water vapor pressure were related to the rate constant K in its pressure dependent ranges and the following expression fits the data for all water vapor pressures greater than 10 mm. Hg:

$$K = 2.57 \times 10^{-6} (P-10) e^{3785^\circ/T},$$

where P is the water vapor pressure in millimeters of mercury and T is the absolute temperature. The value -10 is due to a probable limiting water vapor pressure.

9.2 Magnesium-Water Vapor (H. Svec)

A report (ISC-779) entitled "Kinetics of the Reaction Between Magnesium and Water Vapor" by Dale Gibbs and H. J. Svec is being distributed.

Abstract

Reactions of magnesium and water vapor were studied at temperatures of 425, 450, 475, 500, 525, 550 and 575°C and at water vapor pressures of 31, 55, 92, 153 and 208 mm. Hg. The products of the reactions were magnesium oxide and hydrogen exclusively, and the reactions took place according to the equation

A manometric method was used to determine the rates of reaction. The reactions were found to proceed according to the linear rate law,

$$y = kt + C,$$

where y is the weight of water reacted in milligrams per square centimeter of magnesium surface, t is the time in hours, k is the rate constant and C is a constant. The rate constants k were found to be linearly dependent on the water vapor pressure. The activation energy was determined by an Arrhenius plot and was found to be dependent upon both temperature and water vapor pressure. Two straight lines were obtained at each water vapor pressure. One straight line covered the temperature range between 425 and 500°C and the other the range between 525 and 575°C. There was a large increase in the activation energy in the higher temperature range. Also, there was a gradual increase in the activation energy with decrease in the water vapor pressure in the lower temperature range. The increase in the activation energy as the temperature increased and the water vapor pressure decreased is explained on the basis of a change from a surface to a vapor phase reaction. The vapor phase reaction appeared at the higher temperatures and lower water vapor pressures. This is presumably due to the very large increase in the vapor pressure of the magnesium metal between 500 and 600°C.

10. Pyrolysis of Toluene (L. D. Jennings)

A report (ISC-746) entitled "The (C-H) Bond Dissociation Energy in the Methyl Group of Toluene" by Joseph I. Genco, M. Griffel and F. R. Duke is being distributed.

Abstract

A kinetic study of the pyrolysis of toluene by a flow technique has been made, and assuming Szwarc's mechanism two activation energies (78.3 and 84 kcal/mole depending on the temperature range used) have been derived for the dissociation of the (C-H) bond in the methyl group of toluene. The lower value agrees quite well with Szwarc's, and the higher value turns out to be approximately the average of 77.5 and 89.9. The results of this research suggest 84 kcal/mole as the upper limit for the activation energy.

The ultraviolet spectra of the solid decomposition product indicated that the solid was not pure dibenzyl but probably contained small amounts of a compound possessing a diphenyl nucleus. The rate of formation of hydrogen and methane was found to be inhibited by small amounts of air, and the percentage of hydrogen was found to increase slightly with temperature. A detailed description and operation of the apparatus have been given.

The concept of group potential has been introduced to predict bond dissociation energies of carbon-hetero atom and carbon-carbon bonds.

11. Magnetic Properties of Chromic Halides (L. D. Jennings)

We have further developed our method for measuring the susceptibility of anhydrous chromic halides in the temperature region where this susceptibility is field dependent. The method depends on cancelling the magnetic moment of the sample with the field of a solenoid which closely surrounds it. We have found that it is easy to measure a magnetic moment of one c.g.s. unit with a precision of 0.1%. This magnetic moment is of the order of that of one cubic centimeter of a paramagnetic salt at room temperature. This value of precision was checked using several paramagnetic salts packed in two different containers. In all cases the results substantiated measurements by the Gouy method to the accuracy of the latter (about 2%).

For a powder sample 1.3 centimeters long and one centimeter in diameter, we found that chromic fluoride and chromic iodide display hysteresis. For the fluoride the remanence is .036 Bohr magnetons per molecule, and the coercive force is 200 oersteds. For the iodide the remanence is .34 Bohr magnetons per molecule after applying a magnetizing field of 15,850 oersteds, and the coercive force is 1300 oersteds under the same conditions. The results make it clear that 15,850 oersteds are insufficient to saturate this material.

In order to examine the behavior of the fluoride near 45°K, where there is an anomaly in the heat capacity, we measured the value of the magnetic moment in a negative field of 80 oersteds as the temperature was raised. There was no striking effect near 45°K. The remanence disappeared near 69°K, the temperature of another anomaly in the heat capacity.

12. Adsorption Studies (R. S. Hansen)

12.1 Adsorption From Binary Solutions

The theory of van der Waal's adsorption from regular binary solutions was developed and adsorption behavior for such a model was investigated over the entire concentration range for various values of the parameter governing liquid component interactions. Salient adsorption characteristics of this model are the following:

1. One of the two components is preferentially adsorbed over the entire concentration range; i.e., there is no adsorption inversion.

2. For sufficiently low concentrations, adsorption is proportional to $\left[\ln \frac{1}{x}\right]^{-1/3}$, where x is the mole fraction of the component preferentially adsorbed.

3. For slightly soluble liquid pairs adsorption is, to good approximation, proportional to $\left[\log x^1\right]^{-1/3}$ over the entire concentration range. (x^1 = saturation mole fraction)

4. The proportionality factor in (2) and (3) is itself inversely proportional to the molar volume of the preferentially adsorbed species, and directly proportional to the difference between cube roots of the polarizabilities of the preferentially adsorbed component and the second component in the binary solution.

12.2 Liquid-Solid Adsorption

A theoretical paper "The Structures of Adsorbed Monolayers. I. Normal Aliphatic Alcohols and Carboxylic Acids Adsorbed From Aqueous Solution of Graphon" was written in collaboration with Dr. Donald Graham, E. I. du Pont de Nemours and Company and has been submitted for publication in J. PHYS. CHEM.

Abstract

Adsorption data indicate that normal aliphatic alcohols are adsorbed from aqueous solutions by Graphon without hydration and with only part of the carbon chains in contact with the adsorbent. The higher members show evidence of a transition at about 90% coverage in which the area occupied by a single molecule on the adsorbent surface is reduced by an amount approximately equal to that covered by one - CH_2 - group. The normal aliphatic carboxylic acids, on the other hand, appear to be adsorbed as monohydrates. At low coverage (at least in the cases of acetic and propionic acids) they tend to lie flat on the Graphon surface. At higher coverage only part of the carbon chain is directly bound to the solid.

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12.3 Liquid-Gas Adsorption

A paper entitled "A Study of Mixed Gas Adsorption on Mercury" by R. S. Hansen and D. V. Stage was submitted for publication in the IOWA STATE COLLEGE JOURNAL OF SCIENCE.

Abstract

A pendent drop apparatus for the measurement of the surface tension of mercury and similar substances in high vacuum under conditions of maximum purity was designed, built, and demonstrated to be suitable for experimental operation. Provisions for the admission of one or more vapors of high purity to desired partial pressures were incorporated.

The dependence of mercury boundary tension on partial pressures of ethanol and heptane in gaseous mixture was investigated at 30°C, the investigation including also the pure ethanol and pure heptane gases. The surface tension of mercury was observed to be 461 ± 2 dynes/cm. at 30°C. The highly accurate work of Kemball almost certainly establishes the surface tension of pure mercury at this temperature within the range 483 ± 1 dyne/cm., and from this it must be inferred that, despite tedious purification of the mercury used, its purity was not entirely satisfactory.

Adsorption of both ethanol and heptane from the gaseous mixtures was calculated using the Gibbs adsorption equation. Observed adsorption of pure heptane was in good agreement with that found by Kemball, while observed adsorption of pure ethanol was significantly less than Kemball's values.

The theory of mobile monolayers of one component is generalized to permit calculation of surface pressure dependence on partial pressures of a number of components in a mixture, given the dependence of surface pressure on pressure of pure components. Predicted surface pressures are in agreement with experiment for low to moderate total adsorption, and are significantly higher than those found experimentally at high total adsorption. The discrepancy is ascribed to multilayer adsorption.

12.4 Inference of Adsorption from Double-Layer Capacitance Measurements

A paper entitled "The Inference of Adsorption from Differential Double-Layer Capacitance Measurements" by R. S. Hansen, R. W. Minturn and D. A. Hickson was submitted to J. PHYS. CHEM. for publication.

Abstract

Frumkin's theory of the dependence of surface tension on polarization and solute activity is modified and extended to establish the dependence of differential capacitance on polarization and adsorption. The resulting equation is applied to experimental capacitances in the system mercury-0.1M perchloric acid-pentanoic acid. Variations of both actual and apparent adsorption with polarization are emphasized, and the relevance of these variations to the capacitance determination of adsorption is discussed.

Pyrometallurgy

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

In the pyrometallurgical separations program we have considered a number of the aspects of the separations in some detail. Work has been in progress on the extraction of uranium with silver and lanthanum and the treatment of these extractants to remove the material which they have extracted.

Groups of experiments were run with silver and lanthanum extractants in which the volume ratios of extractant to uranium were varied over the range of 1/9 to 8/2. In general these changes in ratio did not seem to make marked changes in either the fraction removed or the distribution coefficient.

It has become apparent in a number of the different extraction experiments that some unknown factors were causing a high lack of reproducibility, particularly in the case of the rare earth fission products. Consequently, some effort has been made to understand in detail what is happening in these extractions.

Cerium metal with a larger than usual amount of tracer Ce^{144} was made by reducing active CeF_4 . Uranium-cerium alloy with cerium concentration in the range of 0.1% was made up using this labelled cerium. Silver extractions of this metal made in tantalum crucibles were studied by radioautographic techniques. By machining off a portion of the crucible it was possible to expose the U-Ta, U-Ag and Ag-Ta interfaces. Photographic film was

wrapped around the cylinder and developed after a short exposure. The resulting pictures were highly illuminating. Concentrated spots of activity appeared along the U-Ta interface and at the U-Ag interface. No similar spots existed at the Ag-Ta interface. The Ag phase had much more activity than the bulk of the U phase. It was apparent that the analyses of the U phases in these melts had been including more or less of these spots of high concentration and that this had caused the observed lack of reproducibility.

The casting was machined to remove all of these active spots and sectioned to give samples of both phases apart from the U-Ag interface. Analysis of these samples showed the distribution coefficient for cerium between silver and uranium to be approximately 50.

Further work will now be done to find a crucible material which will not give such high concentration spots. The nature of these spots and the reasons for their formation in the particular areas in which they were found will be studied.

Work on the second step treatment of the extractant phase has been continued. Previous work with silver chloride indicated that this salt, either pure or in a mixture with sodium chloride, would quantitatively oxidize and extract the fission products out of the silver. However, a silver chloride system has considerable disadvantages due to the low solubility of silver chloride in water and the corrosive nature of chloride. Consequently, other salt systems have been investigated which could replace chloride in such an extraction process. Unfortunately, nitrates decompose at temperatures below the melting point of silver and most other salts of silver are unsatisfactory for other reasons. Chloride still seems to be the only possibility for such treatment.

2. Alloy Studies (A. H. Daane)

Attempts to determine the crystal structure of the intermetallic compound UBi_2 have not been successful because of the extremely reactive nature of this material. Partial oxidation sufficient to destroy the crystalline nature of the compound occurred in atmospheres that had been scavenged quite carefully. It is apparent that extreme precautions will be required to preserve this compound in handling operations.

The intermetallic compound U_5Sb_3 has been found to have a hexagonal structure and is isomorphous with Mn_5Si_3 .

3. Corrosion Studies (A. H. Daane)

In the "hot-loop" experiments in which the Engineering Group has circulated liquid metals through a tantalum loop encased in an inconel protective jacket, localized reaction between inconel and tantalum was observed in several spots. This reaction appeared to be sufficiently severe to warrant further investigation. X-ray diffraction studies of the areas evidencing the reaction indicated the presence of a face-centered cubic material with a lattice constant of 4.44Å. This appeared to be related to the face-centered cubic compound TaC with a lattice constant of 4.45Å, but must melt at a considerably lower temperature than does TaC to have formed in macroscopic quantities below 1000°C. Compacts of tantalum, nickel and carbon powders corresponding to the compositions TaNiC and TaNiC₂ were prepared and were found to have melting points considerably lower than that of TaC. Also, a face-centered cubic phase was observed in each specimen, with lattice constants of 4.43Å and 4.45Å. This would indicate that reaction between inconel and tantalum was caused by the presence of carbon, perhaps from a welding operation or from carbonaceous material that may have gained entry into the system during evacuating and flushing operations.

In another "hot-loop" a reaction layer was observed between the thorium-magnesium eutectic liquid phase and the tantalum pipe. X-ray diffraction analysis indicated this to be hexagonal tantalum nitride, probably formed as a result of the tantalum scavenging the eutectic of any nitrogen impurity it contained.

The resistance of several boride coatings to attack by molten uranium-thorium-aluminum eutectic is being studied. Screening experiments have indicated little promise for zirconium coated with zirconium boride. Tantalum boride on tantalum and niobium boride on niobium appear more promising. At 800°C, tantalum boride coats retained their integrity and appeared intact, but had been penetrated by the alloy in one week. Niobium did not appear to be as promising as tantalum. The tantalum boride coatings appeared to fail because of a porosity in the original boride coat as it was formed; in the regions where a continuous coat had been formed, there appeared to be little attack.

Analytical Chemistry

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

1.1 Gallium (C. V. Banks)

A method was developed for the determination of gallium in very dilute gallium chloride solutions. The method involved the spectrophotometric measurement of the yellow gallium-8-quinolinol complex in chloroform solution.

1.2 Ruthenium (C. V. Banks)

A procedure was developed for the separation and subsequent determination of trace amounts of ruthenium in uranium and uranium-chromium alloys. Mixed perchloric and sulfuric acids are used to oxidize the ruthenium to the volatile tetroxide which was distilled, separating the ruthenium from uranium and chromium. The ruthenium tetroxide evolved was absorbed in a dilute hydrochloric acid solution containing hydroxylamine. The ruthenium was determined by a new spectrophotometric method based on the color developed when ruthenium is heated with 1,10-phenanthroline in the presence of a reducing agent.

1.3 Selenium (C. V. Banks)

A method was found for the complete removal of selenium from solutions containing copper and selenium, on which copper was to be determined. The removal was necessary because of the interference by selenium in the determination of copper by electrolysis. The most satisfactory method proved to be the reduction of selenium to the metal by sulfur dioxide from a 30 per cent hydrochloric acid solution.

1.4 Determination of Cerium and Chromium (C. V. Banks)

A paper entitled "Determination of Cerium and Chromium in Cerium-Chromium-Uranium Mixtures" by C. V. Banks and J. W. O'Laughlin was submitted to ANAL. CHEM. for publication.

Abstract

A procedure is described for the determination of cerium and chromium in cerium-uranium-chromium alloys. Chromium is determined (on an aliquot of the sample) titrimetrically after preferentially oxidizing it to chromium(VI) with fuming perchloric acid. Cerium is not oxidized by fuming perchloric acid under the conditions used. The total milliequivalents of cerium and chromium are determined on another aliquot of the sample by titrating with iron(II) after complete oxidation of both cerium and chromium with peroxodisulfuric acid in the presence of silver(I).

A reason for the low results often obtained for chromium following the perchloric acid oxidation is postulated, and the necessary conditions are described for the quantitative oxidation of chromium with perchloric acid.

1.5 Determination of Sulfate (J. S. Fritz)

Oxidation with sodium peroxide in a bomb constitutes a convenient and rapid method for destroying organic sulfur compounds and converting the sulfur to sulfate. Unfortunately, the large excess of alkali salts used makes the subsequent sulfate determination more difficult. In a method recently developed, the organic sample is decomposed in a peroxide bomb, and the sulfate is then separated from most of the salts by being preferentially adsorbed onto an alumina column. The sulfate is eluted with dilute ammonia and passed through a cation exchanger in the hydrogen form. The sulfate is then titrated in 80% alcohol with 0.01 M. barium perchlorate according to the method of Fritz and Yamamura. A wide variety of compounds have been analyzed for sulfur with an error of 1% or less.

A paper entitled "Titration of Sulfate Following Separation with Alumina" by J. S. Fritz, M. Johnson and S. S. Yamamura has been accepted by ANAL. CHEM. for publication.

Abstract

In acid solution a column of activated alumina will retain sulfate more readily than most other anions. It is therefore possible to separate small amounts of sulfate from large quantities of chloride, nitrate, perchlorate and from most metal ions. The sulfate is then eluted from the column with dilute ammonia, passed through a small cation exchange column, and titrated with 0.01 M. barium perchlorate using Thorin (2-(2-hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic acid) as the indicator. This method has been used to determine sulfate in samples containing as little as 0.5 ppm of sulfate. Small amounts of sulfate in metal salts can be determined except in those cases where the metal ion forms a slow-reacting sulfate complex. A simple modification of the procedure permits separation of sulfate from Zr (IV) or Cr (III). The alumina column is also used in conjunction with a peroxide bomb combustion for determination of sulfur in organic compounds. A wide variety of organic compounds have been analyzed for sulfur with an error of 1% or less.

1.6 Extraction of Cupferron Complexes (J. S. Fritz)

The extraction of the cupferron complexes of some tri- and tetra-valent metal ions has been studied. The purpose of this study is to remove these interfering ions so as to permit titration of divalent metal ions with Enta (ethylenediaminetetraacetate). It was found that reasonably large amounts of Fe(III), Th(IV), Zr(IV) and Bi(III) can be removed completely by a single extraction into a 1:1 mixture of isoamyl alcohol and benzene. The remaining aqueous solution containing Mg^{++} , Ca^{++} , Mn^{++} , Zn^{++} , Cd^{++} , Co^{++} , or Ni^{++} can then be analyzed by titration with Enta.

1.7 Rare Earth Mixtures (C. V. Banks)

A paper entitled "Spectrophotometric Determination of Rare Earth Mixtures" by C. V. Banks and Donn W. Klingman was submitted to ANAL. CHIM. ACTA for publication.

Abstract

The molar absorptivities for most of the rare earths have been determined at the wavelengths of the various analytically significant absorption bands. These molar absorptivities have been determined on the Beckman Model DU spectrophotometer with and without a photomultiplier attachment as well as on a Cary Model 14 recording spectrophotometer.

The techniques and instrumentation necessary for the satisfactory analysis of rare earth mixtures are discussed. A general procedure is presented which has been found most useful for the routine analysis of a wide variety of rare earth mixtures.

1.8 Neodymium-Yttrium Mixtures (C. V. Banks)

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

Abstract

A differential spectrophotometric method for the determination of macro amounts of neodymium in neodymium-yttrium mixtures is described. The method permits the determination of neodymium in the presence of yttrium with errors in concentration of only two to three parts per thousand. A theoretical treatment of corrections made necessary by differences in the lengths and absorbances of the cells is given.

1.9 Determination of Zinc (C. V. Banks)

A paper entitled "Spectrophotometric Determination of Zinc and Other Metals with α , β , γ , δ -Tetraphenylporphine" by C. V. Banks and R. E. Bisque was submitted to ANAL. CHEM. for publication. A more detailed report (ISC-781) is being distributed.

Abstract

The lack of adequate spectrophotometric methods for the determination of trace amounts of zinc in certain metals brought about this investigation. Procedures were developed for the determination of trace amounts of zinc utilizing the spectrophotometric properties of the zinc complex of α , β , γ , δ -tetraphenylporphine (TPP) in glacial acetic acid. Procedures deserving of special mention are those for the determination of trace amounts of zinc in cadmium, magnesium, rare earth, beryllium, iron, yttrium and the alkali metals.

A method for the indirect determination of several other metals in certain compounds was also developed.

1.10 Separation of Uranium(VI) from Copper(II) and Zinc(II) (J. S. Fritz)

A rapid ion exchange separation of U(VI) from Cu(II) and Zn(II) has been achieved. Sulfosalicylate is added to form a negatively charged complex with the U(VI) and ethylenediamine is added to form a positively charged complex with the Zn(II) or Cu(II). The uranium is then removed on a column of Dowex 1-X2 and the copper or zinc in the effluent titrated with Enta. This method should also separate uranium from Co, Ni, Cd, Ag and Hg. It should also be possible to separate Fe, Th, rare earths, Al, Pb, etc. from the divalent metal ions listed earlier. These possibilities will be explored.

1.11 Separation of Lithium from Alkali Metal Ions (G. S. Hammond)

A paper entitled "The Separation of Lithium from Alkali Metal Ions" by G. A. Guter and G. S. Hammond was submitted to J. AM. CHEM. SOC. for publication.

Abstract

It has been found that dipivaloylmethane, DPM, binds lithium ions selectively and firmly under alkaline conditions. By use of an ether solution of the reagent as an extractant, it is possible to determine lithium in the presence of the other alkali metals. A small correction is necessary if large amounts of sodium are present.

Despite the increasing use of organic chelating agents in the separation and determination of metal ions, no reagents have heretofore been found which permit the separation of lithium from other metals except by tedious procedures which involve the stepwise removal of other ions from lithium. We have found that a new chelating agent, dipivaloylmethane, DPM (I), is applicable to the separation of lithium from sodium and potassium.

This compound, which is found to exist almost entirely in the form of the symmetrical enolic modification II in the pure liquid and in organic solvents, binds lithium firmly in the form of a lithium chelate which is soluble in ether and other organic solvents but is sparingly soluble in water. It is very probable that the chelate has structure III and that the specificity for the lithium ion is due to the small radius of that ion (0.60Å) as compared with the sodium and potassium ions. In keeping with this view is the fact that sodium gives a minor interference in extraction experiments whereas potassium gives none.

III

We have found that ether is the best of the common organic solvents for use in extraction procedures. As is indicated by the data presented in the experimental section,

it is possible to extract substantially all of the lithium from alkaline aqueous solutions under conditions which lead to the removal of only minor amounts of sodium. Because only limited amounts of DPM were available at the outset of these studies, a large number of orienting experiments were carried out (and are reported) under conditions which were recognized not to be ideal for quantitative procedures.

2. Analytical Reagents (C. V. Banks and J. S. Fritz)

2.1 Alkyl-1,2-Cyclohexanedionedioxime (C. V. Banks)

A paper entitled "Preparation and Properties of Some Alkyl-1,2-Cyclohexanedionedioximes" by C. V. Banks, D. T. Hooker and J. J. Richard was published in J. ORG. CHEM., 21, 547 (1956).

Abstract

It has been known for some time that certain alicyclic vic-dioximes possessed properties making them useful as analytical reagents for nickel and palladium. In this connection it became advisable to synthesize a series of alkyl-1,2-cyclohexanedionedioximes (alkylnioximes). The present paper is concerned with the preparation and properties of the following alkyl-1,2-cyclohexanedionedioximes: 4-methyl-, 4-isopropyl-, 4-tert-amyl-, 4-(1,1,3,3-tetramethylbutyl)-, 3-methyl-, 3-ethyl-, and 3,6-dimethyl-1,2-cyclohexanedionedioxime. The higher molecular weight, 156 to 254, alkyl-1,2-cyclohexanedionedioximes consistently melt at a significantly lower temperature (160 to 205°C) than do straight chain aliphatic vic-dioximes such as 2,3-butanedionedioxime. This is not unexpected, however, since the alicyclic ring would greatly restrict the rotation about the carbon-carbon bond between the adjacent oxime groups and thus seriously interfere with the formation of hydrogen-bonded chains, which are known to be present in crystals of 2,3-butanedione-dioxime. The aqueous solubilities of the vic-dioximes likewise indicate that both rotation about the carbon-carbon bond between the adjacent oxime groups and substitution in the 3-position of the alicyclic ring markedly affect the constitutive properties of the crystalline state of these compounds.

2.2 3,4-Bis(2-furyl)-1,2,5-oxadiazole (C. V. Banks)

A paper entitled "The Preparation of 3,4-Bis(2-furyl)-1,2,5-oxadiazole" by C. V. Banks and C. I. Adams was submitted for publication as a Note in J. ORG. CHEM.

2.3 1,10-Phenanthroline (C. V. Banks)

A paper entitled "Kinetics of 1,10-Phenanthroline Chelation. I. Mono(1,10-phenanthroline)Nickel(II)" by D. W. Margerum, R. I. Bystroff and C. V. Banks was submitted to J. AM. CHEM. SOC. for publication.

Abstract

The effect of hydrogen ion concentration on the kinetics of formation and dissociation of the mono(1,10-phenanthroline)-nickel(II) complex is examined. Two mechanisms are proposed as possible reaction paths. One mechanism is the acid catalyzed reaction of an unstable intermediate formed between the ligand and nickel(II); the other mechanism is the reaction of the 1,10-phenanthroline ion with nickel(II) to form an intermediate. Both mechanisms fit the general expression $k_{lf} = (H^+ + 0.0043)/(2.62 H^+ 0.258) 10^5 \text{ l. mole}^{-1} \text{ sec}^{-1}$. The equilibrium constants of the mono-, bis-, and tris(1,10-phenanthroline)nickel(II) complexes are $K_1 = 2.5 \times 10^{-9}$, $K_2 = 8 \times 10^{-9}$, $K_3 = 2.8 \times 10^{-8}$, respectively.

2.4 α -Furildioxime (C. V. Banks)

A report (ISC-699) entitled "Annotated Bibliography of α -Furildioxime" by C. V. Banks and J. P. LaPlante was distributed.

Abstract

This annotated bibliography of the preparation and use of α -furildioxime has been prepared as a reference for analytical research. The authors of this bibliography hope that it will be of service to those engaged in analytical research and that further work on the uses of the α -dioximes in analytical chemistry may be stimulated by the availability of this reference.

The references contained herein deal for the most part with the preparation and use of α -furildioxime. In addition, the preparations of furoin and furil have been included. The references have been listed chronologically and are numbered consecutively.

2.5 2,2'-Bipyridine and 1,10-Phenanthroline (C. V. Banks)

A report (ISC-782) entitled "Reaction of Some Anions with 2,2'-Bipyridine, 1,10-Phenanthroline and the Iron(II) Complexes of These Reagents" by Patrick Grimes and C. V. Banks is being distributed.

Abstract

The distribution curve for 1,10-phenanthroline into chloroform has been determined. The deviation of this curve from simple theory can be explained by considering the formation and extraction of ion pairs of monoprotonated-, and diprotonated-1,10-phenanthroline, and formation of an alkali metal complex of 1,10-phenanthroline. The formation constants of monoprotonated- and diprotonated-1,10-phenanthroline perchlorates and the sodium complex are 1.0, 1.4, and approximately 1, respectively. The distribution coefficients of monoprotonated and diprotonated-1,10-phenanthroline perchlorates between chloroform and water are 0.3 and 0.11, respectively.

The effect of various anions on the extractability of ferroin into several solvents was investigated. Perchlorate, metaperiodate, and iodide ions were effective in promoting the extraction of ferroin into chloroform, n-hexanol, and nitrobenzene.

Cyanide and thiocyanate ions react with ferroin to produce the bis(1,10-phenanthroline)dicyanoiron(II) and bis(1,10-phenanthroline)dithiocyanatoiron(II) which are extractable into organic solvents.

The magnetic studies of the solid bis(1,10-phenanthroline)dicyanoiron(II) and bis(1,10-phenanthroline)dithiocyanatoiron(II) indicated zero and four unpaired electrons, respectively.

2.6 Preparation of Indicators (J. S. Fritz)

A series of compounds has been prepared which can be used as indicators in the complexometric titration of metal ions. The compounds successfully prepared are 7-phenylazo---, 7-naphthylazo---, 7-p-chlorophenylazo---, and 7-p-nitrophenylazo---, 5-sulfo-8-hydroxyquinoline. Apparently the 8-hydroxyquinoline part of the molecule is responsible for the chelating properties, the azo part gives color to the molecule and to the metal chelates,

and the sulfonic acid group makes everything water soluble. The naphthyl derivative is the most promising because it gives the most color contrast between the free dye and the metal ion complexes. This indicator has been used successfully for the titration of several metal ions.

2.7 Survey of Masking Agents (J. S. Fritz and C. V. Banks)

A literature survey (SC-663) entitled "Survey of Masking Agents Used in Quantitative Analysis" by members of the Analytical Chemistry Staff was distributed.

2.8 Properties of Masking Agents (C. V. Banks)

A report (ISC-780) entitled "Some Properties of Sulfoacetic Acid and 3-Sulfopropionic Acid and Their Use as Analytical Masking Agents" by Joseph Zimmerman and C. V. Banks is being distributed.

About 300

1. The values of K_{a1} for sulfoacetic and 3-sulfopropionic acids were determined potentiometrically. The values are $(8.6 \pm 0.2) \times 10^{-5}$ and $(3.0 \pm 0.1) \times 10^{-5}$, respectively. These values of K_{a1} were much lower than those predicted by the Branch and Calvin equation for the calculation of values of pK_a of derivatives of acetic acid.

2. The presence of inter-molecular hydrogen bonds in sulfoacetate and 3-sulfopropionate accounted for some of the discrepancy between the calculated and observed values of K_{a2} for sulfoacetate and 3-sulfopropionate.

3. A proposition was made that the assumption of single bond character for the sulfur-oxygen bond in the Branch and Calvin treatment yields high results for the values of K_{a2} of acids with substituted sulfonate groups. It was suggested that the sulfonate group be classified as a resonating group for the Branch and Calvin treatment, and that it be given an inductive constant as a unit.

4. The water solubility of acetate at pH 5.0 was found to be much greater than sulfoacetate or 3-sulfopropionate at this pH.

5. At any given concentration, acetate was found to be a more effective masking agent for thorium than either sulfoacetate or 3-sulfopropionate. The three masking agents in the order of their decreasing masking

efficiencies are, acetate > 3-sulfopropionate > sulfoacetate.

6. A method for the determination of trace amounts of aluminum in thorium was set up using Enta and 3-sulfopropionate to mask the thorium. Aluminum was extracted from aqueous thorium solutions with a 0.5 per cent solution of 8-quinolinol in chloroform. The aluminum was determined spectrophotometrically as the tris(8-quinolinolo) aluminum (III) complex.

2.9 Determination of K_{a2} Values (C. V. Banks)

A paper entitled "The K_{a2} Values of Sulfoacetic and 3-Sulfopropionic Acids" by C. V. Banks and Joseph Zimmerman was submitted to J. ORG. CHEM. for publication.

Abstract

The K_{a2} values for sulfoacetic and 3-sulfopropionic acids were determined potentiometrically. The values obtained were much lower than those predicted by the Branch and Calvin treatment. It is shown that intramolecular hydrogen bonding can account for some of this discrepancy. It is proposed that the assumption of single bond character for the sulfur-oxygen bond in the Branch and Calvin treatment yields high results for K_a values of acids with substituted sulfonate groups. It is suggested that the sulfonate group be classified as a resonating group for the Branch and Calvin treatment and that it be given an inductive constant as a unit.

3. Calorimetry (C. V. Banks)

A paper entitled "Cell Corrections in Precision Colorimetry" by C. V. Banks, P. G. Grimes and R. I. Bystroff was submitted to ANAL. CHIM. ACTA for publication.

Abstract

Errors introduced by the non-uniformity of cells limit the practical application of precision colorimetric theory. The methods of correcting for these errors are not readily evident from the theoretical discussions in recent literature. Three methods of correction for variations in cell length and absorbance which apply to precision colorimetry are presented.

4. Service Analyses (C. V. Banks)

A total of 4,834 service analyses were made during the period of this report.

Spectrochemistry

1. Development of Spectrographic Analytical Methods (V. A. Fassel)

The following methods were developed in order to provide analytical data for various investigations being conducted by the Ames Laboratory and the AEC.

1.1 Determination of Major Amounts of Terbium in Complex Rare Earth Mixtures

The method is an extension of the procedure previously reported.¹ A 9:1 dilution with CeO_2 spectroscopic buffer-internal standard is used to overcome reversal effects on the terbium analysis lines.

1.2 Determination of Thorium in Pure Cerium

CeO_2 is mixed with powdered flake graphite and formed into conducting briquets in a briquetting press. Overdamped condenser discharges are used for excitation.

Analysis of commercial primary standard grades $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ shows a ThO_2 content based on CeO_2 of 0.6%. The inability of previous investigators to detect thorium in cerium was apparently caused by line misidentifications in the spectra of cerium. The reported wavelengths of spectral lines of cerium were apparently measured in spectra obtained from cerium compounds which contained appreciable amounts of thorium. Thus, the stronger lines of thorium appearing in these spectra were all identified as cerium lines. Subsequent investigators therefore assumed that all of the stronger thorium lines were subject to cerium interference, and on the basis of the absence of the weaker spectral lines of thorium in cerium preparations, believed that thorium was not detected.

¹ J. Opt. Soc. Am., 39, 187 (1949).

1.3 Quantitative Separation of Traces of Rare Earths From Thorium by Ion Exchange Techniques

Quantitative separation of micro amounts of rare earths from thorium has been achieved. A ten-gram sample of thorium, as ThO_2 , in 4N HCl solution is adsorbed onto a 5 cm dia. x 45 cm bed of Dowex-50 (12% DVB) cation exchange resin. The rare earths are quantitatively eluted with 4N HCl; the thorium is quantitatively retained by the resin. The method simultaneously separates from the rare earths most common elements present as impurities in the thorium; e.g., alkalis, Al, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Zn, and U. This procedure can be conveniently used to prepare very pure thorium compounds.

2. Spectroscopic Research (V. A. Fassel)

2.1 Emission Spectrometric Determination of Oxygen in Metals

A brief discussion of the spectrographic determination of oxygen in plain carbon steel and lanthanum metal was presented in ISC-706.

Because of the great interest in the possibility of determining oxygen in titanium and yttrium metals, efforts have been directed towards determining the experimental conditions necessary for removing the oxygen from these metals. A platinum bath technique appears to hold greatest promise. This bath is provided as follows: a wafer of platinum, approximately 1.5 mm thick and 5 mm in diameter is formed from 80-gauge platinum wire in a high-pressure briquetting press. The metal sample, weighing about 0.1 gram, is pressed into this wafer to form a cohesive cylindrical pellet. An analytical curve for the determination of oxygen in titanium metal and alloys has been established. The standard samples for these experiments were supplied by the titanium industry Panel on Analytical Methods. The lack of similar standard samples of yttrium metal has prevented us from establishing analytical curves. The synthesis of reliable standard samples is now receiving primary attention.

2.2 Infrared and Molecular Spectroscopy

A paper entitled "The Infrared Spectra of Aromatic Compounds. IV. The Nitro Valence Vibrations in p-Disubstituted Nitrobenzenes" by R. D. Kross and V. A. Fassel was submitted to J. AM. CHEM. SOC. for publication.

Abstract

The characteristic nitro asymmetric and symmetric frequencies of para-substituted nitrobenzenes are correlated with structure related parameters which are sensitive to the electronic effect of the para-substituent on the nitrobenzene nucleus. It is shown that molecular dipole moments, as well as Hammett's sigma constants for the para groups, yield straight line curves when plotted against the corresponding nitro asymmetric frequency. A plot of nitro asymmetric vs. symmetric frequency yields a discontinuous curve, the reasons for which are discussed. Evidence is also presented which places the C-NO₂ stretching frequency in aromatic nitro compounds in the 1300 cm.⁻¹ region.

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

During the period of this report, 4523 samples were analyzed or examined by emission, fluorescence and infrared spectroscopic techniques.

Radiochemistry

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

A study of the production of nuclear isomers by photoactivation is being pursued using the bremsstrahlung spectrum of the 70 Mev. synchrotron as the source of radiation. The object is to determine the relative yields of metastable and ground states in various isomeric pairs as a function of the maximum energy of the bremsstrahlung beam. Data are available for the 4.4 hr. Br^{80m}-18 min. Br⁸⁰ pair at 24 Mev. from work by Katz and coworkers. Our results agree with their values at this energy but the ratio changes at other values of the maximum energy.

2. Multiple Photo-Neutron Reactions (A. F. Voigt)

At the higher energies available in the synchrotron (> 50 Mev.) the breakup of the compound nucleus to liberate several neutrons (γ, xn) competes with the customary single neutron release (γ, n). A study has been started on the relative yields of such reactions particularly comparing the $\gamma, 3n$ and γ, n reactions. Elements for which such a study is feasible are not as numerous as might be imagined due to competing reactions and half-lives which do not permit analysis. Thus far, work has been done on the Ga⁶⁹($\gamma, 3n$) Ga⁶⁶ and Ga⁶⁹(γ, n) Ga⁶⁸ ratio. Other work has been done on this at 320 Mev. with which the present work at 68 Mev. was compared. Results are in fair agreement.

In this research, it would be of considerable value to use Szilard-Chalmers enrichment of the isotopes produced. Compounds suitable for such enrichment are being sought. Complexes of metals with cyclopentadiene, with phthalocyanines, with disalicylal-ethylenediamine and other reagents are being studied to determine whether or not they are usable for Szilard-Chalmers enrichment.

3. Other Photonuclear Reactions (D. S. Martin)

The program for the determination of the differential cross sections of photonuclear reactions with thresholds above 20-30 Mev. has been continued. With the new integrator energy indicator and control for the electron beam of the synchrotron, a complete activation curve was obtained for the $\text{Ca}^{40}(\gamma, 3p3n) \text{Cl}^{34}$ photonuclear reaction. The activation was determined relative to the ionization recorded by a Victoreen ionization chamber in the center of a 12-inch paraffin cube and also relative to the $\text{Cu}^{63}(\gamma, n) \text{Cu}^{62}$ process induced simultaneously in a disc mounted behind the counter. As a part of this program, the efficiency of the experimental counting arrangement has been calibrated by comparison of the Cl^{34} counting rates with the disintegration rate measured in a 4π counter. The computation of the cross section curve has not been completed but the preliminary estimates have indicated a peak with a maximum at about 45-50 Mev. and, at most, a very low tail at high energies above 65 Mev.

Preliminary experiments have been undertaken in the determination of the $\text{Mg}^{24}(\gamma, 3p3n) \text{F}^{18}$ activation curve. Some attention has been directed toward the standardization of the fluoride recovery process so that reproducible recoveries can be achieved.

The determination of the yields of chlorine activities Cl^{38} (37 min.) Cl^{39} (55 min.) produced by the $\text{A}^{40}(\gamma, p, pn)$ as a function of the maximum bremsstrahlung energy has also been initiated. It has been impossible to resolve the two activities by counting methods, so the combined activation is being measured.

4. Thorium Fission Yield (A. F. Voigt)

Work is continuing on the study of the yields of certain products of the fast neutron fission of thorium. The purpose is to study the discontinuities in the fission yield curve using absolute β counting as the method of study. Preliminary work in developing methods of counting and of analysis is essentially finished and work on irradiated material will begin soon.

5. Mercurous Ion Reactions (A. F. Voigt)

In very dilute solution the dimeric mercurous ion may undergo two different reactions, a dismutation into free mercury and mercuric ion or a dissociation into monomeric mercurous ions.

A literature report that the latter reaction occurred at a concentration of about 10^{-7} molar mercurous ions has been checked by tracer technique. It appears very likely that the reaction actually observed was the first one. Closely related to these reactions is the solubility of free mercury in water which is about 10^{-7} moles per liter. Since the tracer method has sufficient sensitivity for the study of reactions at concentrations of the order of 10^{-6} to 10^{-8} molar, it has been applied to a study of the interrelations between these various reactions. The data now available are consistent with the hypothesis that the reaction which occurs when solutions of mercurous ion are diluted to these concentrations is the dismutation of Hg_2^{++} into dissolved mercury and mercuric ion. The equilibrium constant obtained for this reaction, the known constant for the dismutation at higher concentrations into liquid mercury and mercuric ion, and the measured solubility of free mercury make a consistent set of constants, giving us confidence in the method and its interpretation.

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

For the studies of Szilard-Chalmers type reactions for the photonuclear process, $\text{Co}^{59}(\gamma, n) \text{Co}^{58m}$, the activated cobalt must be electroplated on an inert metal backing if it is to be satisfactorily counted. Since it has been difficult to obtain good quality plates, attention has been given to improving the procedure. A procedure utilizing an ammoniacal sulfamate plating solution has produced plates of high quality. Preliminary self-absorption measurements have given a consistent counting rate function of thickness, which is a severe test of the plating procedure.

The Szilard-Chalmers process in tetraphenylarsonium chloride, $(\text{As} \phi_4) \text{Cl}$, for the process $\text{As}^{75}(n, \gamma) \text{As}^{76}$ - 27 hr. has been compared with results from the photonuclear reaction $\text{As}^{75}(\gamma, n) \text{As}^{74}$ - 17.5 d. Dry crystals, which were irradiated, were subsequently dissolved in water. The AsO_4^{--} fraction was first

removed by precipitation of carrier as $\text{Mg}(\text{NH}_4)\text{AsO}_4$. H_3AsO_3 was then oxidized to AsO_4^{3-} and precipitated as $\text{Mg}(\text{NH}_4)\text{AsO}_4$. Finally, the activity retained in the $(\text{AsO}_4)^+$ ion was determined by repeated recrystallizations. The amount of retention indicated by this method was equivalent to the activity which passed through a column of strong base anion-exchange resins. Results are given in Table I. The fraction of activity measured with the H_3AsO_3 carrier was consistent with that collected when AsCl_3 was distilled from a hydrochloric acid solution of the target compound. A portion of the activity was not recovered in one of the three forms and probably corresponds to the formation of additional chemical entities, probably organo-arsenic compounds. The fraction not collected was especially large for the photonuclear process which involves much higher recoil energies.

Table I

As-Activity Recovered in Different Fractions From Irradiations of $(\text{AsO}_4)\text{Cl}$

	Fraction of Total Activity (γ, n)	(Percent) (n, γ)
As AsO_4^{3-}	23	8
As H_3AsO_3	39	67
As $(\text{AsO}_4)^+ \text{ (Retention)}$	<5	9, 11

Irradiated crystals were also aged at 105-110°C. In the case of the photonuclear activation, no difference in the retention of activity was apparent over a period of several days. For the neutron capture activation the retention had fallen from the original 10% to 4% in 26 hours, a value comparable with photonuclear activation. This behavior is different from the case of some cobalt complexes in which healing of the crystals re-forms the target compound. The difference in the results of neutron capture and photoactivation may reflect effects of the radiation field or may result from the difference in recoil energies of the two processes.

7. Exchange Reactions (D. S. Martin)7.1 Chlorine

The chemical system formed when $K[Pt(NH_3)Cl_3]$ is dissolved in water has been studied further. The results have been interpreted in terms of the reversible reaction:

The formation of a titratable acid has been demonstrated, and the formation of this acid has been correlated with the change in the visible and ultraviolet spectra. Values of the measured equilibrium constants and of the rate constants are given in Table II, as a function of temperature. The values obtained from 15°C to 40°C gave a reasonably constant ΔH° for the aquation. The values at 0°C and 5.5°C were made at the freezing points of H₂O and benzene. The constants for these two low temperatures are badly out of line with the results at higher temperatures; however, the experiments have been repeated several times. A low temperature thermostat with a refrigerating unit has been set up so that the system can be studied in the range 0 - 15°C. Isotopic exchange of chlorine between the complex and chloride

Table II

Equilibrium Constant, K , and First Order Rate Constant, k_1 , For The Aquation of $[Pt(NH_3)Cl_3]^-$.

Temperature, °C	K moles/liter	k_1 hr ⁻¹
30	0.0160	0.215
25	0.0131	0.135
20	0.0114	0.0796
15	0.0089	0.0409
5.5	0.011	0.0119
0	0.011	0.0075

ion has been studied by introducing Cl^{36} , contained in small quantities of KCl, into steady-state systems. Addition of tetraphenylarsonium nitrate precipitated only $(AsO_4)[Pt(NH_3)Cl_3]$. From the activity found in the precipitates the rates of exchange have been computed. It was found that the aquation reaction did

not account for all the exchange, but that an exchange process, first order in $[\text{Pt}(\text{NH}_3)\text{Cl}_2]$ - and independent of chloride, occurred. It is interesting that both cis- and trans- chloride in the complex exchange with comparable rates; i.e., there is no "trans-effect" for the exchange which normally exists for the substitution reactions of this complex. It is possible that the chloride trans to NH_3 alone undergoes the exchange process; however, the present rate data can not distinguish between such a case and the case in which all three chlorides undergo equivalent substitution and exchange.

7.2 Silver

Some exploratory experiments were conducted in which the exchange of Ag^+ between an aqueous phase and solid AgIO_3 was followed. Tracer Ag^+ in a nitrate solution was placed in contact with AgIO_3 for at least two weeks. The solution phase was then transferred to a vessel containing a weighed amount of solid inactive AgIO_3 . At intervals, an aliquot of the solution phase was forced by pressure through a sintered filter and the activity remaining in the solution phase was determined by an electroplating assay. The solution phase was carefully analyzed. The silver content of the solution was an order of magnitude greater after equilibration at 70°C with AgIO_3 than was indicated by an extrapolation of the solubilities which had been determined up to 50°C . Despite the large excess of silver in the solution phase, a large decrease in the specific activity of the solution fraction was observed during the contact of the solution with solid AgIO_3 . Although the behavior of the system must be carefully checked, the results would be consistent with the formation in the aqueous phase of a polymeric silver species which did not undergo rapid exchange with either Ag^+ or solid AgIO_3 . In any event the solid AgIO_3 , unlike the silver halides, undergoes only very slow exchange with Ag^+ (aqueous).

X-Ray Chemistry

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

1.1 Iron Tetracarbonyl

This compound forms a trimer, $[\text{Fe}(\text{CO})_4]_3$. By use of X-RAC at Pennsylvania State College it is now reasonably certain that in the trimer the iron atoms form a triangle,

It has, however, been very difficult to find the CO positions due to a disorder in the structure. It appears, however, that none of the postulated structures, based on directed theory of valence or analysis of vibrational spectra, are correct. Work on this compound is being continued.

1.2 Manganese and Rhenium Pentacarbonyls

The pentacarbonyls of manganese and rhenium are dimers, $\text{Mn}_2(\text{CO})_{10}$. By X-ray investigation they are found to be monoclinic and isomorphous.

$$a = 14.15, \quad b = 7.11, \quad c = 14.67 \text{ \AA}, \quad \beta = 105^\circ$$

$$a = 14.70, \quad b = 7.15, \quad c = 14.91 \text{ \AA}, \quad \beta = 106^\circ$$

Space Group = $I 2/a$ or Ia

$Z = (\text{no. of dimers}) \quad 4$

Metal positions have been found in both, and intensity data have been obtained for Fourier projections. Metal-metal distances in the dimer are 3.02 Å in the Re compound, 2.95 Å in the Mn compound. Whether the metal atoms are bridged by carbonyls or not is as yet unknown, but fairly rapid solution of the complete structure seems likely.

Structures of polynuclear carbonyls are, as yet, mostly unknown. There have been, in recent years, many interesting suggestions without, however, adequate experimental backing. It appears that careful X-ray analysis will be necessary to clear up this whole field.

2. Structure of Tetraphenylarsonium Tetrachloroferrate(III) (R. E. Rundle)

A paper entitled "The Crystal Structure of Tetraphenylarsonium Tetrachloroferrate(III)" by Bertram Zaslow and R. E. Rundle was submitted for publication in J. AM. CHEM. SOC.

Abstract

The crystal structure of $(C_6H_5)_4AsFeCl_4$ is tetragonal, $a = 13.16 \text{ \AA}$ and $c = 7.15 \text{ \AA}$, with space group $I4$, and two formula units per unit cell. The $FeCl_4^-$ ion is a tetrahedron, flattened along z , with an Fe-Cl bond distance of $2.19 \pm .02 \text{ \AA}$ and Cl-Fe-Cl bond angles of 114.5° and 107.0° .

In contrast with the iodide salt, where the tetraphenylarsonium ion has at least very nearly D_{2d} symmetry with the phenyl planes normal to the mirror planes, the cation mirror planes are destroyed in the tetrachloroferrate(III) compound by a 28° rotation of the planes of the phenyl groups about the As-C bonds.

Although the $FeCl_4^-$ ion is tetrahedral with five unpaired electrons, both the short Fe-Cl distance and an MO treatment suggests that iron 3d-orbitals are involved in bonding to chlorine.

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

Trimethylindium is tetragonal, space group $P 4_2/n$, $Z = 8$ (monomers).

Lattice constants are:

$$a = b = 13.1 \text{ \AA}, c = 6.5 \text{ \AA}.$$

A Patterson projection onto (001) yielded indium metal positions which are, approximately, $x = 0.214$, $y = 0.005$; $Z = 0.415$, from $h0l$ data. The approximate nearest In - In distances are $4.44 \text{ \AA}$, and the eight indium atoms are arranged into two tetrahedral groups, flattened along c , the 4 axis of the group. It is pretty clear that trimethylindium is a tetramer with some sort of weak bridging of indium atoms through methyls. Refinement of very crude carbon positions is in progress.

This result is very interesting when compared with the structure of the trimethylaluminum dimer. In trimethylaluminum there are bridging methyl groups, with the geometry in the bridge shown below:

It was predicted, at the time the structure of trimethylaluminum was investigated, that trimethylindium would be unable to form such sharp bridge angles because of metal repulsion within the bridge. It appears now that this is true, and the nature of the delocalized bonds in trimethylindium may indicate what sort of bridge-methyls are to be expected in heavy metal alkyls.

A paper entitled "Electron Deficient Compounds" by R. E. Rundle was submitted for publication in J. PHYS. CHEM.

Abstract

There are a number of compounds for which the number of chemical bonds exceed the number of valence electron pairs, presenting a serious problem for classical valence theory. Historically, the boron hydrides provided the first example, but the problem is general to chemistry. Indeed, the first "electron deficient compound" to be given adequate structural study was the tetramethylplatinum tetramer, in which a quarter of the methyl groups are bonded equally to three platinioms.

The "cause" of electron deficient bonding is easily stated. When atoms, inevitably metallic, with fewer valence electrons than low energy bonding orbitals, form compounds with atoms or groups containing no unshared electron pairs, bonding is delocalized to make use of all of the low energy metallic orbitals. This arises from the same quantum mechanical principles that lead to chemical bonding, and has perhaps been best treated for the H_3^+ ion, which serves as a prototype for electron deficient compounds.

It has been possible to predict where new electron deficient compounds are to be sought, but understanding of structure and compositions, both in the boron hydrides and generally, has come from structural work. The geometry of methyl bridges is singled out for special discussion.

Delocalization of bonding arising from "excess" orbitals, always from metal atoms, provides an interesting correlation running from organic compounds, through organometallic compounds and interstitial compounds, to metals themselves, delocalization increasing with fraction of "excess" orbitals. Certain special features of the generalization giving rise to weak metal-metal bonds in dsp^2 -square transition metal complexes will be noted. One might term this latter bonding to be "configuration interaction bonding".

4. Neutron Diffraction Studies (R. E. Rundle)

In cooperation with Dr. S. Sidhu's group at Argonne National Laboratory the structures of the layer-like simple hydroxides, $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Li}(\text{OH})$ and the corresponding deuterated hydroxides have been examined by neutron diffraction powder methods. These are interesting since infrared data had indicated that the hydrogen positions might be complex, though the X-ray structures are simple.

Neutron diffraction data definitely disclose that in all cases the hydrogen positions are as simple as deduced from X-ray results but that there are interesting thermal motions of the hydrogens involved. These motions are being given further study.

APPENDIX I: LIST OF REPORTS FROM THE AMES LABORATORY

1. Reports for Cooperating Laboratories

- ISC-288 D. R. Wilder. Sintering Mechanism as Applied to Refractory (Suppl.) Oxides.
- ISC-638 Hobart Cammack and G. L. Bridger. Recovery of Uranium from Slag from the Electric Furnace Production of Phosphorus.
- ISC-644 Ames Laboratory Staff. Metallurgy. Quarterly Summary Research Report. April, May, June, 1955.
- ISC-647 Loren R. McMurray and D. J. Zaffarano. A Possible Method for Beam Extraction from an Alternating Gradient Synchrotron.
- ISC-648 Lawrence S. Ring, Jr., and D. J. Zaffarano. Beta Spectra of Some Short-Lived Nuclides.
- ISC-652 J. W. Murdock and Glenn Miller. Secondary Electron Emission Due to Positive Ion Bombardment.
- ISC-654 R. W. Laity and F. R. Duke. Measurements and Significance of Transport Number in Fused Salts.
- ISC-655 R. A. Lowry and G. H. Miller. Measurement of the Ionization Yield of Low Energy Atomic Particles in Gases.
- ISC-659 George Pulliam and E. S. Fitzsimmons. Reaction of Lanthanum and Cerium with Ceramic Oxides.
- ISC-662 Martin Welt and Morton Smutz. Thorium and Uranium from Monozite.
- ISC-663 C. Adams, D. W. Barnum, R. Bisque, R. I. Bystroff, F. Debbrecht, J. S. Fritz, D. E. German, P. G. Grimes, M. Johnson, W. Lane, A. Moye, J. W. O'Laughlin, J. L. Spooner, S. Sutton, W. Trask, G. Umbreit, E. Wadsworth, S. S. Yamamura, R. E. Yerick and J. Zimmerman. Survey of Masking Agents Used in Quantitative Analysis.
- ISC-666 R. C. Strittmater and G. C. Danielson. Measurement of Specific Heats by a Pulse Method.
- ISC-667 Max Q. Freeland and J. S. Fritz. I. Direct Titration of Sulfate. II. High Precision Spectrophotometric Analysis.
- ISC-668 J. J. Renier and D. S. Martin. Iodato-Silver Complexing Equilibria.
- ISC-671 F. R. Parchen and F. R. Duke. Kinetics of the Exchange Reaction Between Two Oxidation States of Cerium.

- ISC-672 Richard Hedges and Harrison Shull. The Absolute Infrared Absorption Band Intensities of the Methylene Group Vibrations of Some Methylene Halides.
- ISC-678 W. W. Davis and Morton Smutz. Effect of Phosphate Rock Particle Size on Recovery of Uranium from Superphosphate.
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- ISC-682 R. P. Cox and G. H. Beyer. Separation of Hafnium from Zirconium Using Tributyl Phosphate.
- ISC-685 R. D. Redin and G. C. Danielson. Measurement of Magnetic Field Gradient by the Hall Effect.
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- ISC-688 O. N. Carlson, F. A. Schmidt and H. A. Wilhelm. Preparation of Zirconium and Hafnium Metals by Bomb Reduction of their Fluorides.
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APPENDIX II: LIST OF SHIPMENTS

<u>Destination</u>	<u>Item</u>
University of California Los Alamos Scientific Laboratory Los Alamos, New Mexico	20 gm erbium metal 20 gm yttrium metal 20 gm lanthanum metal 66 gm neodymium metal 69 gm samarium metal 72 gm gadolinium metal 77 gm erbium metal
Mr. H. A. Boorse Pupin Physics Bldg. New York, New York	1 cylinder lanthanum metal
Atomics International North Am. Aviation, Inc. Downey, California	250 gm thorium metal
General Electric Company General Engineering Laboratory Schenectady, New York	100 mg dysprosium oxide 100 mg terbium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide 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
Dr. Franz R. Metzger Bartol Research Foundation Swarthmore, Pennsylvania	10 gm special N ¹⁴
Carbide & Carbon Chemical Company Union Carbide & Carbon Corp. Oak Ridge, Tennessee	50 gm pure cerium metal
Dr. Richard A. Ogg, Jr. Stanford University Stanford, California	1 gm N ¹⁵

<u>Destination</u>	<u>Item</u>
General Electric Company ANP Department Cincinnati, Ohio	1 gm cerium oxide 1 gm lanthanum 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
General Electric Company Richland, Washington	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
Dow Chemical Company Midland, Michigan	20 lbs. anhydrous thorium
Dr. J. F. McClendon Albert Einstein Medical Center Philadelphia, Pennsylvania	1 gm special hafnium oxide
Brookhaven National Laboratory Upton, Long Island, New York	20 mg holmium oxide
Dr. Thomas C. Hoering Department of Chemistry University of Arkansas Fayetteville, Arkansas	2 samples N ¹⁵
Battelle Memorial Institute Columbus, Ohio	2 gm terbium metal 2 gm erbium metal 2 gm ytterbium metal 2 gm holmium metal 2 gm praseodymium metal

<u>Destination</u>	<u>Item</u>
Research Laboratories of Colorado, Inc. Newtown, 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 lutetium oxide
Dr. T. J. Bond Department of Chemistry Baylor University Waco, Texas	1 gm neodymium oxide 1 gm dysprosium oxide 1 gm yttrium oxide 1 gm erbium oxide
Dr. Sumner Davis Massachusetts Institute of Technology Cambridge, Massachusetts	1 gm terbium oxide 1 gm holmium oxide 1 gm dysprosium oxide
Yale University New Haven, Connecticut	40 gm gadolinium oxide 10 gm terbium oxide 20 gm holmium oxide 5 gm thulium oxide 20 gm dysprosium oxide 20 gm erbium oxide
The Eagle-Picher Research Laboratories Joplin, Missouri	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 California Scripps Institution of Oceanography La Jolla, California	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 gm dysprosium oxide 100 mg holmium oxide 100 mg erbium oxide 100 mg ytterbium oxide 100 mg thulium oxide 100 mg lutetium oxide
Florida State University Tallahassee, Florida	10 gm praseodymium oxide 10 gm neodymium oxide
Professor Tarhen Huus Institute for Teoretisk Fysik Copenhagen, Denmark	100 mg terbium oxide
Dr. Allen J. VanderWeyden, U.S.A.E.C. Liaison Officer Atomic Energy of Canada, Ltd. Chalk River, Ontario, Canada	2 gm yttrium oxide 2 gm dysprosium oxide 2 gm ytterbium oxide
Dr. Jagdish Shanker Chemistry Division Department of Atomic Energy Government of India Bombay, India	1 gm gadolinium oxide 1 gm dysprosium oxide
U.S.A.E.C. c/o Mallinckrodt Chem. Works Uranium Division St. Louis, Missouri	100 mg holmium oxide 100 mg terbium oxide 100 mg dysprosium oxide 100 mg erbium oxide 100 mg thulium oxide
Argonne National Laboratory Lemont, Illinois	1 sample gadolinium metal 1 sample erbium metal
University of Saskatchewan Betatron Department Saskatoon, Saskatchewan, Canada	25.6394 gm yttrium oxide 50 gm lutetium oxide 50 gm thulium oxide 50 gm terbium oxide 50 gm yttrium oxide 50 gm holmium oxide

<u>Destination</u>	<u>Item</u>
Dr. Fisher c/o Air France Cargo Department New York International Airport Jamaica, Long Island, New York	25 gm neodymium oxide
Anaconda Aluminum Company Columbia Falls, Montana	1 gm hafnium oxide