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PHYSICAL AND INORGANIC CHEMISTRY GROUPS

1. Separation of Rare Earths by Ion Exchange

- 1.1 The Separation of Rare Earths by Ion Exchange. VI. Conditions for Effecting Separations with Nalcite HCR and One-Tenth per cent Citric Acid - Ammonium Citrate Solutions. F. H. Spedding, E. I. Fulmer, J. E. Powell T. A. Butler and I. S. Yaffe. (ISC-123) (Accepted for publication in J. Am. Chem. Soc.).

Abstract

Ion-exchange procedures were developed for the successful separation of the rare earths using a high capacity resin, Nalcite HCR; 0.1% citrate solution was used as the eluant. A detailed study was made of the factors important to the production of spectrographically pure neodymium and praseodymium oxides on a large scale. The factors investigated were as follows:

1. The effect of varying column length with a fixed weight of sample.
2. The effect of varying sample weight of columns of fixed length.
3. The effect of varying column length and sample weight proportionately.
4. The effect of varying pH of the eluant.

It was shown that 33 kilograms of Nd_2O_3 or 16 kilograms of Pr_6O_{11} may be produced >99.9% pure per year using twenty 6-inch, i.d., columns.

Although the heavy rare earths are, in general, more difficult to separate than are the lighter rare earths, conditions were determined by which gram quantities of highly pure erbium, holmium and dysprosium were obtained.

Quantities of pure rare earths prepared by the ion-exchange method have been supplied to a number of investigators who are studying their chemical and physical properties.

1.2 An Efficient Separation of Dysprosium and Yttrium.

F. H. Spedding and J. L. Dye, J. Am. Chem. Soc. 72 5350 (1950). (Since this paper is a communication to the Editor and is brief, it is presented here in its entirety.)

A rapid and efficient separation of the difficultly separable rare earth pair, dysprosium and yttrium, has been accomplished by elution with 5% ammonium citrate solution at room temperatures on Nalcite HCR resin. This is achieved because of a shift in the order of elution of yttrium relative to the other rare earths. With 0.1% citrate solution, the order of elution is Dy-Y-Tb,¹ while the order observed with 5% citrate is Dy-Tb-Y. Previously, it had been reported that elution at 100° of tracer amounts of rare earths with 5% citrate showed yttrium eluting ahead of dysprosium.

When eluting with 5% citrate at pH values greater than 2.8, the rare earth band immediately precedes the hydrogen band on the column, and results in a square-type band front. At lower pH values, the ammonium ions pass the rare earth ions and consequently the rare earths are on an ammonium bed. The resultant band front at these lower pH values is sloping and the elution curves resemble those previously obtained with other rare earths using similar conditions.³ At all pH values when 5% ammonium citrate is used as eluant, the observed order of elution is Dy-Tb-Y.

A load of 7.6 g of oxides was placed on a column containing 450 g of resin and eluted with 5% citrate. The resin bed length was 60 cm and the diameter was 4 cm. These oxides, obtained by column fractionation of R_2O_3 from gadolinite ore, had the composition 10% Dy_2O_3 , 89% Y_2O_3 , 0.5% Ho_2O_3 , 0.5% Tb_4O_7 . Analyses were made by spectrophotometric and spectrographic methods. At a pH value of 2.80, 85% of the available Y_2O_3 was obtained spectrophotometrically pure (>99%). Previous work using 0.1% citrate at pH values of 5.5-6.0, eluted less than 10% of the available Y_2O_3 with comparable purity. The total time of a run using 5% citrate at a pH of 2.80 is only one-third that required with 0.1% citrate. The concentration of rare earths in the eluate using 5% citrate is correspondingly higher.

It appears that the most efficient way to obtain pure Y_2O_3 and pure Dy_2O_3 from an ore concentrate involves two ion exchange procedures: (1) first a preliminary elution using 0.1% citrate with pH values between 5.8 and 6.1, which separates dysprosium

and yttrium from the other rare earths; (2) elute the yttrium-dysprosium fractions so obtained with 5% citrate using a pH value of 2.8, to obtain the pure salts.

1.3 Methods of Preparing Spectrographically Pure Praseodymium Salts. F. H. Spedding and T. A. Butler. (ISC-148).

Abstract

An ion-exchange process was developed for the separation of spectrographically pure praseodymium salts in kilogram amounts from commercially available concentrates. The application of either 0.5% or 0.1% citrate solutions as eluting agents was shown to result in excellent separations of praseodymium from samarium, neodymium, and lanthanum when the mixed rare earths were eluted from Amberlite IR-100 or Nalcite HCR cation-exchange resins.

A number of variables were investigated which were shown to be important in the ion-exchange method for preparing pure praseodymium salts. It is desirable to approach equilibrium conditions as closely as possible during the elution process in order that the small differences between the equilibrium constants of the individual elements may be fully utilized. Sufficient time must be allowed for the cations to diffuse into and out of the resin so that an equilibrium may be established between the rare earths in the resin phase and those complexed by the citrate ions in the surrounding solution phase. Experimental evidence is given to show that a reduction in the flow-rate of the eluting solution and a decrease in resin particle size, which decreases the length of the diffusion path in the resin, resulted in a closer approach to equilibrium conditions and increased the separation of adjacent rare earths.

Small differences in the pH of the citrate solutions, used to elute the rare-earth band from the resin bed, resulted in both a qualitative and quantitative change in the shape of the elution curves. The variation in the shape of the curves was interpreted as being related to a change in the relative importance of different rare-earth citrate complexes in the eluting solution. The existence of at least five such complexes have been reported by Spedding and co-workers. In general, lower pH values of the citrate solutions, in the applicable pH range, resulted in better separations. However, in large-scale production, a compromise must

be made between the increased time necessary to complete the elution, with somewhat better separation, at lower pH values, and labor cost.

There is little choice between the use of 0.5% or 0.1% citrate solutions for separating small amounts of pure praseodymium. However, 0.1% citrate is to be preferred for large-scale production since the cost of the operation is reduced.

Nalcite HCR resin was shown to be superior to Amberlite IR-100 for large-scale praseodymium separations. Nalcite HCR not only has a higher capacity but the spherical form of the particles permits better packing in a column, thus reducing the tendency of the rare-earth band to form streamers or to channel during the elution. Direct observation showed that irregularity of the band-fronts of the individual rare earths may account for a large percentage of the overlapping of adjacent rare earths. In other words, the region of mixed rare earths in an elution may be attributed in part to the mechanical difficulties of maintaining a horizontal rare-earth band-front during the elution.

Preliminary experiments showed that a greater percentage yield of the available praseodymium resulted from increasing the sample weight of the praseodymium concentrate with a proportionate increase in the column length. This increase in yield occurs because the region of overlapping rare-earth bands remains essentially constant if a minimum resin bed-length is provided for allowing full development of the component rare earths into bands. Further increase in resin bed height above the minimum length for a given column load does not result in further separation between adjacent rare earths.

A complete investigation of the relation between column load and column length was prevented by the formation of a slightly soluble rare-earth citrate compound which precipitated in the resin bed as the sample weight was increased. The rare-earth citrate precipitation in the resin bed was prevented by adding excess hydrochloric acid or ammonium chloride to the mixed rare-earth chlorides before the sample was adsorbed on the resin bed.

The conditions of elution were successfully scaled up from small column experiments to pilot-plant operation which was demonstrated to have a capacity for producing 15 kilograms of spectrographically pure praseodymium oxide per year. In the spectrographically pure material, the emission lines of any possible rare-earth impurity were absent which showed that less than 0.1% of such contaminants were present.

During the course of these investigations, seven kilograms of spectrographically pure praseodymium oxide were prepared and made available to a number of investigators conducting theoretical researches on the properties of the rare earths.

1.4 Pilot Plant Operations

The pilot-plant for the ion-exchange separation of the rare earths comprises a cascade system of 20 Pyrex pipe columns five feet long and six inches in diameter. These columns were mounted on an angle-iron framework in bands of 10 columns. The ends were closed with monel metal plates. The make-up and storage tanks were of stainless steel as was the constant head tank. The columns were mounted about three feet from the floor in order that 45-liter carboys could be placed on carts and run under the columns for collection of the effluent solutions. Two views of this pilot-plant are shown in Figure 1 and 2.

Special note should be made of the efforts to obtain a uniform flow of the eluting solution through the columns. The rare-earth mixture forms into bands of individual rare earths on the resin during the elution process and it is important to the separation that these bands be maintained distinct and horizontal throughout the elution. A serious channeling in the bed would result if the solution were withdrawn from a limited area at the bottom of the column. In the case of 22-mm diameter columns, a bulb of about 20 ml capacity was left between the porous glass disc and the point of outlet. This volume was sufficient to allow the pressure to equalize over the entire surface of the glass disc and resulted in fairly even flow through all parts of the resin bed.

The bottom plate for each of the 6-inch diameter columns was fitted with seven symmetrically-arranged outlets which withdrew solution from a reservoir one inch in depth below the resin bed. The seven outlets joined a common glass bulb which then had a single outlet for discharge of the solution. In this manner, the flow was rendered more uniform throughout the resin bed.

Operation of the cascade system resulted in the production of many fractions in enrichments capable of yielding pure components, after one or two more column processes, of every rare earth. Enough terbium concentrate is now on hand to make a column load;

Fig. 1. Pilot Plant for separating Rare Earths

Fig. 2. Pilot Plant for separating Rare Earths

it is hoped that this column run, scheduled for the near future, will yield very nearly pure terbium.

Several samples of ytterbium rich oxide obtained from the cascade were combined and the ytterbium extracted with sodium amalgam.

Preliminary experiments have been performed which indicate that the separation of mixtures of ytterbium, thulium and erbium by ion-exchange is feasible. Several grams of >99.9% thulium have been prepared, using small scale columns.

2. Conductances, Transference Numbers and Activity Coefficients

The conductances, transference numbers and activity coefficients of chlorides of some low atomic number rare earths in aqueous solution are given in detail in ISC-142, by F. H. Spedding and Paul E. Porter. The conductances, transference numbers and activity coefficients of chlorides of some high atomic number rare earths in aqueous solution are given in detail in ISC-143, by F. H. Spedding and James M. Wright. For the sake of brevity, abstracts of the two reports have been combined as follows:

The conductances, transference numbers, and activity coefficients of aqueous solutions of the chlorides of lanthanum, cerium, praseodymium, neodymium, samarium, europium, and ytterbium have been determined for concentrations up to 0.1 normal. The transference numbers were determined by the moving-boundary method as developed by Longworth and MacInnes;⁴ the activity coefficients were measured by using concentration cells with transference; and the conductances were obtained with a conventional apparatus of the type recommended by Jones and Josephs.⁵ The accuracy of all measurements was within 0.1 per cent.

The data for all rare earths agree with the Onsager limiting law for conductance up to about 0.002 normal. There is a regular decrease in the conductances of the rare earth chlorides with increasing atomic number beginning at about neodymium. The chlorides of lanthanum, cerium and praseodymium have about the same conductances, while that of neodymium chloride is slightly higher.

The behavior of the first four rare earths is thus anomalous in that the rare earths would be expected to show a regular change in properties over the whole series. A possible explanation of the observed data is that a second coordination number may become possible as the ions become larger with decreasing atomic number, so that an equilibrium may be set up between two kinds of hydrated ions having different coordination numbers. Such an alteration in the coordination numbers should produce substantial changes in the effective radii of the hydrated ions which would greatly influence their conductances. The importance of the degree of hydration of the ions in determining the conductance of the solution is indicated by the fact that, in the latter part of the rare earth series, the conductances decrease with decreasing ionic radius as measured crystallographically. The greater mobility which should result from the smaller ion is more than compensated by the effects of hydration. At the present time insufficient data are available for any definite conclusions to be made; measurements of conductances should be extended to all members of the rare earth series including not only chlorides but also other salts of different anion valence types. In addition, more crystallographic data on hydrated salts would be useful, in order to study the coordination numbers of the hydrated ions and to correlate them with the conductive behavior.

The transference numbers do not merge with the theoretical Onsager limiting slope. This is somewhat surprising in that the conductances merge with the limiting slope at concentrations as high as 0.002 normal. The transference data indicate that the same effect which causes a non-uniform behavior in the case of the conductances, also produces an analogous effect in the case of transference numbers. Little change in transference numbers is observed for the first five rare earths; however, a regular decrease seems to occur for higher members of the series.

The activity coefficients for all salts agree well with the Debye-Hückel theory. The values obtained for $\bar{a}$, the average effective ionic diameter, show no regular behavior. The first three earths are about the same, neodymium is slightly higher, and the remaining three earths are slightly lower. The magnitudes of the $\bar{a}$ values for all the earths exceed the sum of the ionic radii of the rare earth and chloride ions by approximately the diameter of one water molecule. If the $\bar{a}$ values have physical significance, the above fact indicates that the first sheath of water molecules adheres tightly to the rare earth ion. The diameter of this sheath would undoubtedly depend largely upon the coordination number of the central ion; hence, if an

equilibrium were established between two coordination forms in solution, the magnitude of α , which is an average property, would depend upon the point of the equilibrium. The observed variation of the values of α is thus a further indication of the effect noted in the conductances.

3. Preparation and Properties of the Rare Earth Metals

3.1 Preparation of Rare Earth Metals. F. H. Spedding and William J. McGinnis. (ISC-149).

Abstract

The techniques described in the present study have been successfully employed in the preparation of gadolinium metal, gadolinium powder and yttrium metal. The method possesses the following advantages:

1. The magnitude of the charge is limited only by the size of the tantalum reaction vessels which can be fabricated. Reductions were carried out on a 50-gram scale, a 140-gram scale, a 225-gram scale, and a 300-gram scale.
2. The quantity of reaction mixture in the one and one-sixteenth-inch inside diameter crucibles can be increased by compacting the charge into one-inch pellets; increases of up to 50% have been effected.
3. Under optimum conditions resulting yields approached the theoretical quantity of gadolinium present in the chloride.
4. Experimental reductions which proved unsuccessful did not present the recovery difficulties which had been encountered in the previous reduction method. The reaction mixture does not fuse to a porous magnesium oxide liner thereby introducing large quantities of magnesium and complicating the recovery of the rare earths present.
5. The presence of helium in the reduction tube minimizes the possibility of formation of rare earth oxides or of rare earth nitrides in the metals.

6. Separations of samarium from gadolinium have been effected by the reduction of gadolinium to the metal.
7. Yttrium metal was produced by this method but the percentage yield was not as high as that of the rare earth metal investigated.
8. The method of preparing rare earth metals yields a product of very high purity because the reaction was carried out in containers which were not attacked by the metal produced and the presence of an inert atmosphere minimized the possibility of contamination due to oxide or nitride formation.

The method presented in this thesis can undoubtedly be extended to the preparation of the heavier rare earth metals but the process will be complicated by the melting-point of the metal which increases with increase in atomic weight. The slag resulting from the production of the heavy rare earths would boil at a temperature below that required to cause the metal to agglomerate; it may be necessary to employ the rare earth fluorides with calcium in the reduction process in order to obtain calcium fluoride as the calcium reaction product. Calcium fluoride has a boiling-point substantially above the temperature required to cause agglomeration of the metal.

3.2 The Vapor Pressures of Lanthanum and Praseodymium. Adrian H. Daane (ISC-121).

A technique for preparing rare earth metals was devised in which their chlorides were reduced by calcium in tantalum vessels; the resulting metal was cast in tantalum molds to remove volatile impurities. Lanthanum and praseodymium were prepared in 20 gram batches with yields of $100 \pm 1\%$; a $90 \pm 5\%$ yield of lanthanum was obtained on a 250 milligram scale. It was not possible to prepare samarium metal by reducing samaric chloride with calcium under the same conditions which were successful with lanthanum and praseodymium.

Gadolinium chloride, containing 1.7% samaric chloride and 0.23% europic chloride, was reduced with calcium to produce a 96% yield of metal; samarium and europium were not detected in the product. This separation of samarium and europium from gadolinium is more convenient than are the ordinary chemical methods.

A technique for measuring vapor pressures of materials of low volatility was devised; this consisted of modifying Knudsen's effusion method by placing a quartz fiber balance inside of the vacuum apparatus to measure weight losses from the effusion vessel. To test this technique, the vapor pressures of copper and silver were measured; the results are in reasonable agreement with the accepted values in the literature.

The vapor pressures of lanthanum and praseodymium were determined over the range 10^{-2} to 10^{-4} mm Hg using the above technique. For lanthanum, the vapor pressure equation is

$$\log P = \frac{-17753 \pm 308}{T} + 6.816 \pm 0.166;$$

the heat of vaporization and extrapolated normal boiling point of lanthanum may be obtained from this equation, and are respectively, -81.0 ± 1.4 Kcal. mole $^{-1}$ and $4515^{\circ} \pm 150^{\circ}\text{K}$. For praseodymium, the vapor pressure equation is

$$\log P = \frac{-17188 \pm 243}{T} + 8.098 \pm 0.156;$$

the heat of vaporization and extrapolated normal boiling point are, respectively, -79.5 ± 1.1 Kcal. mole $^{-1}$ and $3290^{\circ} \pm 90^{\circ}\text{K}$.

4. Hydrogen Determination by Decomposition

The possibility of developing a specific method of determining hydrogen content of small quantities of organic compounds by decomposition with active uranium at temperatures above the decomposition temperature of uranium hydride is being investigated. It was thought the uranium would combine with the other elements forming stable compounds, and the hydrogen could be determined in the gaseous state by a pressure measurement of a given volume. First tests with benzoic acid gave results which were much too low. It was observed that the compound reacted slowly and a considerable amount sublimed out of the active uranium without decomposition. However, by using larger amounts of uranium and heating slowly the yields of hydrogen approach the theoretical value closely. The study is being continued.

5. The Adsorption Separation of Zr and Hf. Robert S. Hansen, Keith Gunnar, Alfred Jacobs and C. Robert Simmons. (J. Am. Chem. Soc. 72, 5043 (1950)).

Abstract

An adsorption purification of zirconium from hafnium has been discovered. Most satisfactory results have been obtained from the preferential adsorption of hafnium from a methanol solution of zirconium and hafnium tetrachlorides by silica gel. Other solvents have been investigated, as well as effects of concentration, flow rate and gel properties. Concentration of adsorbed hafnium to 30-60% products in good yields has been achieved by differential stripping.

6. Ion Exchange Separation

Considerable work has been done on development and modification of an ion-exchange separation of zirconium and hafnium suggested by E. Gluekauf of Harwell Laboratory. This separation is based on the differential elution with sulphuric and oxalic acids, of hafnium and zirconium adsorbed from oxychloride solution. Results, which have been only moderately encouraging, are being analyzed. The ion-exchange study has had as its objective development of a recovery method for hafnium as by-product of the silica gel adsorption purification of zirconium.

7. Slurry Studies

A program aimed at the development of stable uranium slurries suitable for reactor fuels was initiated. A method has been developed for preparing very fine uranium oxide particles (surface area 14 square meters per gram checked by gas adsorption and electron microscopy, with average particle diameters of 75 millimicrons). These particles have been prepared by the ignition of atomized solutions of uranium nitrate in acetone. It is believed that even smaller particles can be made if necessary. A colloid mill was purchased and installed, and will be used to study the dispersal of aggregates of particles obtained in various solvents.

8. Basic Concepts in Surface Thermodynamics. Robert S. Hansen
(Accepted for publication in J. Phys. and Colloid Chem.) (AECU-880).

Abstract

It has been shown that, in the case of inert, nonswelling solid adsorbents, measured gas or liquid solution adsorption quantities are related to Gibbsian surface excesses by multiplicative, experimentally determinable constants. The discussion is based on actual experimental procedures. In the case of gas adsorption, measured quantities are most directly related to surface excesses referred to a mathematical surface located by setting the surface excess of the solid component equal to zero ("l" convention). In the liquid solution case, measured quantities are most directly related to the "V" convention surface excesses of Guggenheim and Adam, but in general, these may be expected to be substantially equal to those defined by the "l" convention.

9. Adsorption Studies

Approximately half of the results in a program investigating the adsorption of fatty acids and aliphatic alcohols from aqueous solutions by non-porous adsorbents have been obtained and are being analyzed.

Apparatus for the study of adsorption of rare gases by non-porous adsorbents has been completed and the study is under way; insufficient results have been obtained to date to justify analysis.

10. Reaction Mechanisms

a. A new program on liquid-liquid extraction kinetics was undertaken. Thus far, the research has consisted of development of methods and procedure, and testing of analytical procedures adaptable to kinetics work; zirconium nitrate extraction from aqueous solution is the subject under study.

b. Tests were run on zirconium nitride to see whether or not the nitride would react explosively with iodine. The nitride was heated to approximately 800°C, and iodine vapors passed over

the nitride. After ten minutes, no change in the nitride could be detected. It is concluded that zirconium nitride will not react; explosively or otherwise, with iodine under conditions where Zr metal reacts rapidly.

c. The reactions between cationic oxidants and anionic reductants have been studied much more thoroughly than those between cationic reducing agents and oxidizing anions. In order to find out whether or not the latter reactions involve complexes, the reaction between perchlorate and titanous with perchlorate is under investigation. The preliminary data indicate that complexes are indeed involved. The evidence upon which this is based depends upon the effect of anions with which perchlorate might have to compete in coordination; such anions slow the reaction. It is still necessary to eliminate a number of possibilities until only one is left.

The program on the mechanism of precipitation has been studied further, and the mechanism, $\text{MnO}_4^- + (\phi)_4\text{As}^+ \rightarrow \phi_4\text{AsMnO}_4$ (Ion Pairs), the ion pairs acting as nuclei for crystals, has been substantiated. A study of the effect of ionic strength has shown that the crystals get larger, as one would predict, as the ionic strength increases. Also, a study of the effect of temperature has indicated a ΔH of -15 kcal for the first reaction above.

The hypothesis that cationic oxidants coordinate anionic reducing agents prior to the oxidation-reduction reaction was given a severe test by the study made of the reaction

The hexammine cobaltic ion is recognized as one of the more stable complexes, and therefore any other group such as HSnO_2^- should find it difficult to coordinate with the cobalt by displacing ammonia. Thermodynamically, the reaction should proceed if a mechanism for the process is provided.

During the past few months a study of the above reaction has shown that a mechanism involving the hexammine cobaltic ion cannot be kinetically considered, because the slow reaction turned out to be a rearrangement or ionization of the HSnO_2^- ion. No detectable reaction between Co(III) and Sn(II) could be found, except for the "activated" Sn(II) in which a possible mode of rearrangement is:

Or it may be that stannite ion always exists as HSnO_2^- and the slow reaction is the removal of the remaining hydrogen by ionization. This view is supported by the fact that the kinetically slow reactants are HSnO_2^- and OH^- .

d. The reaction between ferric and sulfite ions was studied to determine the effect of the ferric-sulfite complexes in the reaction. It was found that in the presence of excess sulfite and sulfate, the reaction was second order in ferric and zero order in sulfite. In the absence of added sulfate, the reaction slowed down as the sulfate was formed as a reaction product. This indicates that sulfate participates in the complexing. The kinetically slow reaction is $2 \text{Fe}(\text{SO}_3)^{++} + \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{++} + \text{H}_2\text{SO}_3 + \text{H}_2\text{SO}_4$. The complex $\text{Fe}(\text{SO}_3)^{++}$ was established by a continuous variation method.

e. A study of the reaction between $\text{Ce}(\text{IV})$ and Cl^- was continued and considerable new data added. Although we are certain that complexes involving cerium and chloride are involved, the data have not yet been quantitatively analyzed.

One of the possible generalizations which have emerged from studies of electron-transfer is that coordination complexes are, under certain conditions, reaction intermediates. This appears to be especially applicable to oxidation reduction reactions involving cationic oxidants and anionic reductants. Systems of this type which have been studied include the $\text{Mn}(\text{III})$ -oxalate, $\text{Fe}(\text{III})$ - I^- , $\text{Ce}(\text{IV})$ -glycol, $\text{Fe}(\text{III})$ -sulfite, $\text{Ce}(\text{IV})$ -oxalate.

11. Calculation of Transition Probabilities Using the Dipole Velocity Operator

The calculations upon hydrogen have been completed. The results of these calculations show that this new method of calculation is a very promising one for molecular problems. Excellent agreement is obtained between the dipole length and the dipole velocity methods using both the molecular orbital (LCAO) and atomic orbital approaches with reasonable assumptions for the form of the atomic orbitals. In particular, good agreement is obtained by adjusting the effective Z value for the bonding orbital upwards to 1.2 and using a Rydberg form for the excited orbital. It is interesting to note that the value 1.2 is that required by the variation treatment of Coulson. Agreement is also good with the best experimental data available.

The calculations on C_2 and N_2^+ using a similar method have proceeded rapidly during this period, and the computations are now completed. Final evaluation of the data is, however, not yet finished. In general the important features of these computations are the sensitivity of the dipole velocity results (in contrast to the dipole length studies) to changing ratio of Z excited to Z normal, and the insensitivity to the absolute magnitudes of the Z's. The results seem to indicate that previous estimates of the degree of hybridization in C_2 and N_2^+ are about right, perhaps a little low and that previous choices for the effective Z in the present case are essentially correct. The method promises to be applicable to the problem of degree of hybridization under certain restricted conditions. Further possible applications of the method are planned for future study.

12. Theoretical Calculations on Benzene

Previous rough computations in the same approximation as that used by Mayer and Sklar⁶ showed the possibility that a variation in the effective Z value downwards by a reasonable extent might invert the theoretically predicted positions of the B_{1u} and B_{2u} levels in benzene. These computations have been extended carefully with inclusion of all three-center and four-center integrals (suitably approximated) with the result that it has been shown definite⁷ that such inversion does not occur. This strengthens the previous assignments for both the lowest singlet and triplet states of the molecule. In the process of obtaining the approximations to three and four-center integrals it was noted that, generally, of the methods of approximation suggested by Sklar⁷ on the one hand and by Mulliken⁸ on the other, each tended to become much too high in the case of appropriate two-center integrals which could be evaluated exactly. If one took the lower of the two methods, one obtained consistently good results, and essentially this method was adopted in the present calculations. Further calculations were undertaken to attempt the elucidation of the nature of W_{2g} which arises in this method, but these resulted in no findings of significance.

13. Experimental Progress

A high pressure mercury arc source AH6 was received from General Electric and has now been set in operating condition. After initial experimental tests, T-T' absorptions in aromatic

systems will be determined along with related spectral properties if these are not available from other sources.

Previously obtained spectra in the Werner complexes of cobalt with various groups have been examined in sufficient detail to show that the purity and nature of the compounds available were not sufficiently well known to justify a complete theoretical treatment of these spectra. A program of systematic preparation and identification of these compounds is underway preparatory to obtaining infrared and Raman spectra and to pursuing a complete theoretical analysis of the problem.

14. Low Temperature Calorimetry

During the past six months the hydrogen calorimeter was put in working order. This involved completion of the measuring circuitry, installation of galvanometers, completion of the calorimeter parts and their assembly, manufacture and calibration of thermocouples and finally wiring the calorimeter for complete test runs which are now in progress.

The circuit details are now drawn up and an assembly drawing for the calorimeter has been completed. Some difficulty in thermal contact between the calorimeter can and the platinum resistance thermometer may require more careful machine work on the former.

The helium temperature calorimeter has been designed and is ready for manufacture. Some thought has been given to the thermometry involved. A helium gas thermometer to be used in calibration of secondary thermometers has been designed and is now being built. Various types of carbon resistors have been accumulated and it is planned to test them for their temperature characteristics to determine their suitability. We are also attempting to get leaded phosphor-bronze wire for this purpose.

All the materials for a 4" electromagnet have been assembled and are ready for the shops to begin construction.

Further work has been done in designing a crystallizing apparatus for use with extremely corrosive liquids.

It is planned to measure first the heat capacity of metallic thorium, at hydrogen temperatures.

15. Miscellaneous Research

Apparatus for measuring activity coefficients in binary solutions of non-polar liquids has been completed, but work in this field is awaiting the delivery of a large constant temperature bath. Several compounds for the study have been purified.

Equilibrium pressures of hydrogen and deuterium over active uranium at several temperatures are being measured.

RADIOCHEMISTRY GROUPS

1. Ruthenium Thiourea Complexes

Ruthenium is a polyvalent transition element with chemistry which, because of its difficulty and little interest, had received little study until a few years ago. In the development of processes for the separation of plutonium from fission products, it was found that in many processes ruthenium resembled and followed plutonium to a greater extent than did any other fission product. Coupled with the long life, 1.0 year, and high energy of the radiation from the $\text{Ru}^{106}\text{-Rh}^{106}$ pair, this posed a considerable problem in the development of separation processes. Consequently all aspects of the chemistry of ruthenium became of great interest in the overall AEC program.

This part of that program has been concerned with the complexes which ruthenium forms in its lower valence states. In preliminary work using tracer ruthenium the attempt was made to find a complex which would be extractable into an organic solvent. No reagents with any promise were uncovered. Literature references to intense color production with certain thio compounds led to the investigation of these and the use of the spectrophotometer as the method of study. The interest here has been in the fundamental chemistry of these complex compounds, their formulae and formation constants, and incidentally in their absorption spectra. The first of these compounds to be studied was thiourea and it is with this system that this report is concerned.

The blue color formed between ruthenium and thiourea has been reported previously^{9,10,11} in connection with its use as an analytical reagent. During the course of this work an additional paper appeared which dealt with this aspect.¹² The approach in these papers has been empirical and designed for analytical application. Our own approach dealt more with the fundamental chemistry involved.

Tetravalent ruthenium has been the material studied thus far. Since it is highly hydrolyzed in anything other than fairly acidic solutions the study had to be made in strong acid. Perchloric acid was chosen because of its well-known low complexing tendencies. Studies were made from the range 2.2 to 0.25 molar perchloric acid. The ionic strength was maintained at a constant value by replacing the perchloric acid with lithium perchlorate at the lower acidities.

The ruthenium solutions were prepared by fusing the metal in a mixture of potassium nitrite and hydroxide. The ruthenate so formed was dissolved in water and distilled from permanganate-sulfuric acid. The tetroxide was collected and reduced to the tetravalent form in perchloric acid containing hydrogen peroxide. Spectrographically the samples showed traces of the alkali metals but no other platinum or iron group metals. The $\text{Ru}(\text{ClO}_4)_4$ gave a spectrum (see Figure 3) which agreed with those recently published.¹³ It was standardized by distillation from perchlorate, reduction to RuO_2 from solution followed by hydrogen reduction to the metal. The thiourea solutions were prepared fresh each time they were used in order to avoid oxidation by perchlorate. Since thiourea absorbs strongly in the ultraviolet (see Figure 4) but not in the visible, measurements were confined to the latter region. The Cary Model 12 spectrophotometer was used.

Preliminary studies demonstrated the presence of two complexes of rather low stability. The method of continuous variation and the slope ratio method were not of great utility. An additional quite serious complication was presented by the reduction of the ruthenium to the trivalent state by thiourea with consequent loss of thiourea. Mixtures with an excess of ruthenium could not be studied since the exact thiourea concentration was unknown. The approach to the complexes was therefore made from the high thiourea side, up to several thousand fold excess.

The treatment of spectrophotometric data was based on the mathematical discussion which follows. Taking the reaction

and considering C to be the total ruthenium concentration in both forms and Y that in the first complex, the (non-thermodynamic) equilibrium constant expression for the reaction becomes

$$K_2 = \frac{C-Y}{Y} \frac{[\text{H}^+]^n}{[\text{HTh}]^n}$$

At constant hydrogen ion concentration

$$\frac{K_2}{[\text{H}^+]^n} = K'_2 = \frac{C-Y}{Y} \cdot \frac{1}{[\text{HTh}]^n}$$

Fig. 3 Absorption spectra of ruthenium IV perchlorate in 2.285 N HClO₄ at ionic strength 3.0.
 A. $1.117 \times 10^{-3} \text{M}$ C. $2.235 \times 10^{-4} \text{M}$
 B. $5.585 \times 10^{-4} \text{M}$ D. $1.117 \times 10^{-4} \text{M}$

Fig. 4 Absorption spectra of thiourea in 2.285 N HClO₄ at ionic strength 3.0.
 A. $2.235 \times 10^{-1} \text{M}$ C. $1.117 \times 10^{-3} \text{M}$
 B. $2.235 \times 10^{-2} \text{M}$ D. $1.117 \times 10^{-4} \text{M}$

$$Y = \frac{C}{1 + K_2' [\text{HTh}]^n}$$

$$C - Y = \frac{K_2' [\text{HTh}]^n}{1 + K_2' [\text{HTh}]^n}$$

$$\text{and } D = d_1 \frac{Y}{C} + d_2 \frac{C - Y}{C}$$

In the last expression D is the observed optical density while d_1 and d_2 are the optical densities which the first and second complexes would have if present at concentration C . These expressions can be combined to give

$$D + (D - d_2) K_2' [\text{HTh}]^n = d_1$$

By plotting D vs $(D - d_2) [\text{HTh}]^n$ we can obtain K_2' as slope and d_1 as intercept. The optical density of the second complex, d_2 , (see Figure 5) is asymptotically approached at high thiourea excess, (see Figure 6) so that d_1 , K_2' and n are the three unknowns. Out of various values chosen for n , 1.5 and 2 were the only reasonable numbers which gave any agreement. Of these $n=2$ was much the better and we consider that 2 is correct. The equilibrium constant and d_1 were calculated at 10 mμ intervals throughout the wavelength region from 400-600 mμ (see Figure 7). An average value of 4.6 ± 0.2 was obtained for K_2 using data at the lowest acidity, 0.254M, at which acidity the most reliable results were obtained. Data at higher acidity, 0.508M, gave a constant in agreement with this if n was assumed to be 2 giving additional evidence that this is the case. This also shows that thiourea is behaving as an acid, liberating a hydrogen ion for each thiourea molecule which goes into the complex.

The constant for the first reaction was determined using points to the left of the maximum (see Figure 6). Since d_1 is now known, d_0 and K_1 become the unknowns. The data gave a consistent picture if the second complex is written $\text{Ru}(\text{Th})_3$ and the first RuTh . The first reaction is therefore written

with $K_1 = 20 \pm 5$. The calculated value of d_0 differs from the adsorption curve of $\text{Ru}(\text{ClO}_4)_4$ as is to be expected if the ruthenium has been reduced in the process. The calculated curve agrees with the published curves¹⁴ for RuIII within reasonable limits.

Fig.5 Absorption spectra of Ru(Th)_3 in 0.254 N HClO_4 at ionic strength 3.0.

A. $3.351 \times 10^{-4}\text{ M}$
B. $2.235 \times 10^{-4}\text{ M}$
C. $1.117 \times 10^{-4}\text{ M}$

Fig. 6 Variation in optical density of $3.351 \times 10^{-4} \text{ M Ru(ClO}_4)_4$ in 0.254 N HClO_4 at ionic strength 3.0 with increasing thiourea concentration.

Fig. 7 Calculated absorption spectra of $3.351 \times 10^{-4} M Ru(Th)_2^{+2}$ in $0.254 N HClO_4$ at ionic strength 3.0.

Other types of measurements used in this problem included magnetic susceptibility and electrical migration studies. The magnetic susceptibility measurements demonstrated that the second (3 to 1) complex was paramagnetic. The measured values of the gram susceptibility of Ru IV was -0.3 and of thiourea -0.60. A solution with a large excess of thiourea, in order to put a large part of the ruthenium in the complex, was measured. After subtracting the large contributions to the total given by the thiourea and other components of the solution, the net value for the gram susceptibility of the complex was $+3 \pm 1.5$. This is sufficiently positive to indicate the undoubted paramagnetic nature of the complex, and if multiplied by the molecular weight (331) gives a molar susceptibility of 1000 ± 500 . Since the contribution of one unshared electron would be about 1300 and since Ru^{III} has one unshared electron, within the experimental error this shows that Ru is in the III state.

The ion migration studies were less definite. Under some circumstances no migration to either electrode occurred. Under other conditions the cathode compartment very slowly acquired a color characteristic of ruthenium but not the blue color of the complex. The blue color grew more faint on the anode side and more intense on the cathode side of the center compartment. It appeared that the complex was dissociating in the electric field, the ruthenium being pulled toward the cathode. The dissociation constants are large enough so that one might expect an appreciable fraction of the ruthenium ions to be free so that they could migrate in the electrical field.

Considering all the evidence available the best, consistent picture is obtained if the second complex is considered to be neutral $\text{Ru}(\text{NHCSNH}_2)_3$ and the first complex $\text{Ru}(\text{NHCSNH}_2)^{++}$.

2. Studies on the Radiochemistry of Phosphorus

Recent work in the physics section of this Laboratory and in other laboratories has demonstrated that radio-phosphorus obtained by the reaction $\text{S}(n,p)\text{P}$ contains a radioactive nuclide in addition to the expected P^{32} . This nuclide has a half-life of 25 days and a maximum beta ray energy of 0.25 Mev (See ISC-135).

In order to demonstrate the chemical nature of this nuclide a study has been begun on the separation of phosphorus from other elements by ion exchange columns. Various anion exchange resins were studied for this ability to purify phosphate, particularly

to separate phosphate and sulfate. None of the resins gave more than minor enrichment factors. Correspondence with the manufacturers indicated that no successful studies on this subject were known to them.

After some exploratory experiments a tailor made adsorption column was developed which appears to give an excellent separation of these two anions at carrier-free concentration and to separate carrier-free phosphate from large amounts of sulfate. This column is prepared by adsorbing ferric ion onto a cation resin such as Nalcite HCR from an acid solution. The iron adsorbs strongly and remains quite tightly fixed. If a slightly basic solution of phosphate is passed through the bed so prepared the phosphate is quantitatively adsorbed. Sulfate is adsorbed only slightly, if at all, even if present in macro concentrations. The phosphate can be eluted with slightly acid solutions. Exact conditions, pH, flow rate, etc. need to be developed since the experiments to date have not established optimum values. Conditions for successful operation do not appear to be critical.

Samples of radiophosphate containing the low energy component mentioned above were carried through the Nalcite-Fe^{III} column and early, middle and late fractions were measured on a Geiger counter. The ratio of high energy beta to low energy beta radiation was determined using absorbers. No difference was detected in any samples from the first to the last fraction. Similar experiments with the anion resin Amberlite 410 gave the same results. It is our conclusion that the low energy component is chemically phosphorus.

Studies are continuing on this system using tracer sulfate (³⁵S), to determine the purification which can be obtained for sulfate as well as phosphate and to establish optimum conditions.

3. Service Separations

The radiochemistry group has given a large amount of time and effort toward research in experimental physics. This assistance has ranged from the preparation of many samples for the beta-ray spectrometer and other instruments, through the performing of separations of irradiated samples, to the conducting of minor research projects designed to improve the separations or to devise new methods of performing them.

One problem of this type was the separation of radiophosphorus in carrier-free form from cyclotron irradiated sulfur. The technique used at Oak Ridge for this separation was followed with some modifications caused by the presence of copper from the target in the sulfur sample. Because of the interest in this problem the research on radiophosphorus described in the above section was started.

Another problem which involved some original experimentation was the separation of tellurium from antimony. This separation has previously been done by the reduction of tellurium using sulfur dioxide, a procedure which has a number of drawbacks. The substitution of hydrazine, as the chloride, for the sulfur dioxide gave a more rapid and complete reduction of the tellurium and appears to be a much more satisfactory procedure.

In the separation of strontium and yttrium as in the $\text{Sr}^{90}\text{-Y}^{90}$ chain, the use of 8-hydroxy quinoline to precipitate the yttrium on lanthanum carrier gave consistently better results than did the lanthanum hydroxide precipitation used previously.

One general problem of considerable interest is the development of Szilard-Chalmers type processes for synchrotron-irradiated samples. The yield of active isotopes from the synchrotron is considerably less than that obtainable using other types of irradiation due to the low cross sections of nuclei for gamma radiation. Consequently any study on nuclides isotopic with the targets must be done with very low specific activities unless recoil separation processes can be developed for the particular target element.

Several studies in this direction have been started. The 33 minute isotope of chlorine, Cl^{34} , was concentrated from CCl_4 targets by extracting the irradiated CCl_4 with dilute aqueous ammonia and evaporating to dryness. Care had to be exercised to prevent the volatilization of the product ammonium chloride. This was accomplished by gentle heating; the deposit of NH_4Cl was almost invisible and quite active.

Studies were also made on the concentration of P^{30} (2.55 min) from irradiated organic phosphate esters. Triphenylphosphate was used in benzene solution, the concentration method being extraction with water and precipitation as ammonium phospho-molybdate. No great success was obtained due to the short half life of the product and the difficulty of getting a clean separation of phases in the extraction step.

Other recoil processes have been considered and are being investigated as interest in particular elements demands.

4. Abstracts of Published Reports and Papers

- 4.1 The Spectrophotometric Determination of Overlapping Dissociation Constants of Dibasic Acids. The Acid Constants of Isophthalic, Terephthalic and Chloranilic Acids. B. J. Thamer and A. F. Voigt. (AECU-1127).

Abstract

A new method was developed for using spectrophotometric data to determine the dissociation constants of dibasic acids when the two constants do not differ by more than a factor of fifty.

Using this method the acid constants of isophthalic and terephthalic acids were determined at low ionic strength and extrapolated to zero ionic strength to give the thermodynamic constants. Agreement within the experimental error was obtained with published values. The acid constants of chloranilic acid were determined under conditions of high ionic strength. Agreement with previous values was not good nor did agreement seem to be obtainable by making allowance for ionic strength differences. The reliability of the present values and also of the method appear to be quite good.

Such properties as optical rotation, fluorescence, or magnetic susceptibility are suggested as alternatives to optical density for the determination of the acid constants for acids which demonstrate these properties.

- 4.2 Zirconium Chloranilate Complexes. B. J. Thamer and A. F. Voigt. (AECU-1266).

Abstract

Spectrophotometric measurements at 25°C in 1 to 2 M perchloric acid solutions of ionic strength 2 have shown the following equilibria in the zirconium-chloranilic acid system.

and

For these equilibria $K_1 = (5.69 \pm 0.08) \times 10^5$ and $K_2 \approx 6000$. $Zr(IV)$ represents the zirconium monomer and H_2OCh undissociated chloranilic acid and the constants are in terms of concentrations. A precipitate that forms in these solutions with concentrations of the reactants of roughly 5×10^{-4} molar was shown to have 1.2 ± 0.1 molecules of chloranilic acid per zirconium atom.

A spectrophotometric method was developed for determining zirconium at formalities of 2×10^{-6} to 5×10^{-5} using chloranilic acid and measuring the optical density at 3400Å. The color reaction proceeds rapidly and yields a true solution that is stable indefinitely. Chloranilic acid appears to be an acceptable colorimetric reagent for zirconium as compared with other such reagents.

- 4.3 Magnetically Controlled Quartz Fiber Microbalance.
 Frank C. Edwards and Robert R. Baldwin, Anal. Chem.
23 357-361, (1951). (AECD-2576).

Abstract

During World War II, micro equipment of various forms was developed at Iowa State College. One of these developments, a quartz fiber microbalance, which is controlled by an external variable electromagnetic field, has been further improved and its use broadened by various modifications. Its design and technique of construction are described in sufficient detail to allow its construction by others. The balance is capable of weighing directly an unbalanced load as large as 1.2 mg., of carrying a counterbalanced load of 100 to 150 mg., and giving a sensitivity of 0.1 microgram per 6 minutes of arc. The balance unit is all quartz except for the sealed-in permanent magnet and fits into a tube 2.5 cm in diameter and 12 cm long. With modifications it may be used under wide conditions of temperature and pressure. It is resistive to almost all atmospheres other than hydrogen fluoride. One of its principal advantages is its usability in completely closed systems for the study of gas-solid reactions of various kinds.

4.4 Zirconium Ions in Aqueous Solution. Edgar H. Dewell.
(ISC-146)

Abstract

In work done in this Laboratory in 1945 and 1946, Dr. John Ayres found that zirconium solutions at concentrations greater than 10^{-4} molar and approximately at a pH of 2 did not exchange with cation resin such as Amberlite IR-100. This property appeared to be a measure of the ionic zirconium as contrasted to the polymeric or colloidal hydrolyzed zirconium in the solution.

Studies to investigate this point were initiated using solutions of zirconyl chloride at a concentration of 1.4×10^{-3} molar in the pH range 1.8 to 2.5. Naicite HCR was used as the resin in the ammonium form, the ammonium ion concentration of the solutions being 0.5 M. The resin studies showed that the content of exchangeable (cationic) zirconium was reduced from 99 to 55% as the pH was increased over the above range. These figures are upper limits since the exchangeability decreased as the solutions stood.

Since this time dependence indicated that a slow change was occurring in the nature of the zirconium in solution, a method of study was sought which would allow measurements at frequent intervals. The process of hydrolysis and polymerization undoubtedly results in the release of hydrogen ions to the solution. At these low concentrations the total change in pH was not large so that rate measurements based on pH would not be highly accurate. The conductivity is a sensitive measure of the change in the concentration of a highly conducting species like the hydrogen ion, so it was chosen as the method of observation.

Solutions containing 10^{-4} molar zirconium were prepared by dissolving zirconyl chloride in water. The conductivity and pH were measured immediately, the conductivity was followed as a function of time and at the end an additional pH measurement was made. Experiments were run at 25° and 35°C. At 35° the measurements gave reasonable conductance values for the zirconium species, but at 25° the conductances were too high by a factor of two to be reasonable assuming that the species present were $\text{Zr}(\text{OH})_2^{++}$ and $\text{Zr}(\text{OH})_3^+$. A possibility exists that the first of these ionizes to some extent to give more highly charged ions which would be better conductors.

The problems presented by this research are by no means solved and work on the system will be continued. The goal is the determination of the species present in aqueous solutions of zirconium under a wide variety of acid concentrations.

5. Study of Radioactivity

5.1 Decay Scheme Measurements

The radiations of Yb^{169} were studied by means of absorption-coincidence techniques and the results were reported in collaboration with the Experimental Physics Group operating the beta-ray spectrometer ¹⁵. The half-life of the Yb^{169} was found to be 33 ± 1.5 days and the half-life of the metastable state of the Tm^{169} daughter was measured as 0.67μ seconds. Decay schemes were considered on the basis of the eleven gamma-rays observed in the photoelectron and internal conversion spectra. The coincidence data indicated that two very highly converted gamma-rays with energies of 177.9 and 198.3 Kev occurred in cascade following the metastable state. The relatively high rate of coincidences between preceding photons and delayed electrons indicates that only a small fraction of disintegrations could lead to the ground state of Tm^{169} and suggested that some gamma ray transitions preceded the metastable state. Intensities estimated from the coincidence and the spectrometer counts were not consistent; hence, estimated intensities and internal conversion coefficients of two alternative decay schemes were presented.

5.2 Decay Scheme of Se^{75}

Some old coincidence-absorption data for Se^{75} have been further processed with the aid of intensities and energies of ten gamma transitions recently obtained by the beta-ray spectrometer. The analysis is not complete but indicates that all but one of the gamma-rays have conversion coefficients of only a few per cent. One line at 98.3 Kev is highly internally converted and appears to occur with an intensity of about 5% in an alternative decay branch. The data also indicate that transitions with energies of 138.4 and 268.8 Kev occur in cascade. This conclusion results from photon coincidences with heavy absorbers before each counter and the fact that the energies add accurately to give the energy of the 405.0 Kev transition.

5.3 Preparation of Tantalum Isotopes by Photon Irradiations of Tungsten in the Synchrotron

Samples of sodium tungstate were irradiated by 68 Mev X-rays from the synchrotron. After the target material was dissolved in water, tantalum activities were separated by adsorption on sodium tantalate with a chemical separation efficiency demonstrated to be 100%. Activities with half-lives of 48 min., 8 hr. and 6 d. were obtained. The 48 min. and 6 day activities have been made by Bateman¹⁶ by 30 Mev X-rays. The 48 min. activity has been shown by Duffield, Helao and Sloth¹⁷ to be due to Ta^{185} by the use of separated isotopes. By absorption methods the radiation of the 6 day activity was found to contain β^- with 0.5 - 0.6 Mev. Similar techniques showed the 8.0 hour activity to have a β^- of 0.6 - 0.7 Mev and considerable photon component. These properties were similar to those reported for Ta^{180} and this identification was confirmed by the use of a separate stable isotope, W^{180} , target. The Ta^{185} activity was sufficiently intense for a "feather analysis" of the absorption curve. An energy of 1.6 Mev was obtained for the β^- . However there was a soft component of nearly equal intensity. Coincidence counting experiments showed that these two groups did not occur within a 5 μ sec. delay so that the low energy electron was probably not a conversion electron following the β^- transition. It has been assumed to be a softer β^- component. Irradiations with a 30 Mev maximum energy beam gave nearly the same yield ratio for the 6 day activity and Ta^{185} . However the relative yield of Ta^{180} , which cannot form by a (γ, p) process, was much lower. The 6 day activity can apparently also be formed by a (γ, p) reaction, and its most probable assignment is Ta^{183} . Relative yields for these isotopes compared to Cl are given in Table I.

Table I
Relative Yield of Tantalum Isotopes

Energy	68 Mev
Atoms Ta^{185} / atoms Cl Mole W / Mole C	0.37
Atoms Ta^{183} / atoms Cl Mole W / Mole C	0.64
Atoms Ta^{180} / atoms Cl Mole W / Mole C	0.80

The relatively high yield of Fe^{180} which must be formed by a (γ, pn) , (γ, d) or higher reaction is noteworthy.

5.4 Preparation of High Specific Activities from (γ, n) Reactions

By the irradiation of a complex compound, $\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ in the synchrotron, high specific activities of Co^{58m} have been obtained from the target material following the (γ, n) process.¹⁸ The complex was decomposed by the recoil from the photoneuclear reaction; and when the crystals were dissolved, the radioactive atoms appeared in solution as Co^{II} . Some decomposition occurred which was about equivalent to the ionization to be expected by the synchrotron beams and amounted to about 1-4% of the total compound. The Co^{II} was separated by an ion exchange process and the metal films prepared by electrodeposition on platinum. A half life of 9.2 hr. was obtained for Co^{58m} . A tentative value for the relative yield is $4.0 \frac{\text{atoms Co}^{58m}}{\text{mole Co}} / \frac{\text{atoms ClI}}{\text{mole Cl}}$. A complete

self absorption curve was obtained in these measurements and back scattering of low energy electrons in windowless counters is currently being studied to permit a more accurate evaluation of this quantity. The radioactive cobalt was again made into the oxalate complex and its solution allowed to stand for one day. The long-lived activity formed during this period could be separated and measured by recovery of the Co^{II} as previously. This experiment gave a value of the yield ratio of 0.6 atoms Co^{58} / atoms Co^{58m} for the synchrotron irradiations which is very close to the results obtained by Strauch¹⁹ from cyclotron bombardments. Work has been started for the application of similar techniques to the preparation of platinum and chromium activities.

5.5 Self-Diffusion of Nickel

Preliminary studies have been carried out to determine the migration of radioactive Ni^{63} through thin layers of nickel metal. A thin sandwich of radioactive nickel was laid down in an electroplated deposit. These deposits were heated in vacuo. The increased counting rates arising from active nickel which had migrated toward the surface of the sample were then measured. The very low penetration of the Ni^{63} β -rays (range = 7 $\mu\text{g}/\text{cm}^2$) makes possible the use of exceedingly thin layers. Radioautographs

of the samples showed that there was a negligible migration along the surfaces in these experiments. The migration in several satisfactory samples has been measured for various heating periods but not enough results have been accumulated to demonstrate the reproducibility of the methods or for the reliable estimates of the diffusion constants. The electrolytic deposits by microscopic examination appeared to have no grain structure or large holes. However such deposits are reputed to be fairly porous so the results are to be continued with deposits laid down by the thermal decomposition of nickel carbonyl.

5.6 Activation Analysis for Oxygen in Metals

A program has been initiated to study the possibility of analyzing metals for oxygen by detection of the O^{15} activity with a 2 min. half-life in synchrotron irradiations. These experiments are being carried out in cooperation with one of the Experimental Physics Groups. Preliminary work with zirconium has been carried out, but it is not yet certain whether the desired 0.1% sensitivity can be obtained. The O^{15} is a positron emitter and there is also formed in the irradiations of zirconium metal the isotope Zr^{90m} which has a half-life of 4.5 minutes and has been reported to emit conversion electrons with an energy of 0.56 Mev.²⁰ Our work has shown that the Zr^{90m} also emits positrons with an energy of about 1.6 Mev, hence, any analysis will require the relative positron to electron disintegration rates. A magnetic analyzer has been set up to split the positron and electron components of the samples with two G-M counters so that each component can be counted simultaneously. The magnetic field is produced by a large coil with an 8-inch inside diameter. It is provided with water-cooling and manual control and can operate up to 31 amperes. Preliminary experiments have been concerned with dead time of counters, the counting rate dependence on the field current and various improvements in design. When samples are available some analyses will be attempted.

5.7 Precipitation Equilibria

The methods of radioactivity analysis used in determining solubilities, as described elsewhere²¹ have been applied to chloride solutions of silver. The presence of the complex ion AgI_2^- has been indicated by the increasing solubility at high chloride activities. In addition, the concentration of the

un-ionized species AgCl in saturated solutions would appear to be of the order of 10^{-5} molar. Consequently AgCl would be a weak electrolyte with an ionization constant of about 10^{-5} . At low chloride ion concentration silver activities approached the value indicated by the solubility product determined from electromotive force measurements. The purpose of these experiments has been to test the radioactive techniques for a system which can be studied by emf's. However the region in which the solubility is described by a solubility product has appeared to be very limited because of the importance of the un-ionized species.

5.8 Study of Phosphorous Activities Prepared by Photonuclear Reactions on Sulfur

A sample of sulfur which had been purified by fractional crystallization from CS_2 was irradiated for 12 hours by a 68 Mev beam from the synchrotron. The sample was processed by the method described by Kenny and Spragg²² for the preparation of P^{32} from pile neutron irradiations. A decay curve for the phosphorous fraction was followed with and without a 75 mg/cm^2 aluminum absorber. The decay with the absorber gave a simple curve with a 14.3 day half-life. Without the absorber the decay was resolved into a 20% fraction with a 25-30 day half-life and a 80% fraction with a 14 day half-life. If this longer component corresponds to the one observed by Jensen and Nichols²³ then it was present at high intensity in this sample and consistent with an assignment to P^{33} . The experiment is to be repeated with a procedure which should prove more effective for removing possible other trace impurities.

5.9 Thorium Photofission Yields

Relative fission yield analyses have been carried out on samples of Th metal irradiated for 4-5 hour periods by the 68 Mev X-ray beam of the synchrotron. Satisfactory results have been obtained for the chains 89-91 from Sr samples and for the masses 111, 112 and 113 from Ag samples. Attempts to apply standard fission yield analyses for chain 140 with Ba samples have carried contamination by Ra and its daughter products. A satisfactory method has not been found for taking Zr samples from the thorium solutions which would give chains 95 and 97. The results obtained are listed in Table II.

Since mass 113 lies very near a symmetric fission point it would appear from these results that the most probable fission yield is about 15 times the symmetric yield for photofission. This value can be compared with a corresponding value of 130 obtained for the fission of thorium induced by pile neutrons reported by Niday and Turkevich.²⁴

Table II

Relative Photofission Yields for Thorium
by 68 Mev Synchrotron Beam

Atoms 89/Atoms 91	1.30
Atoms 89/Atoms 111	9.7
Atoms 89/Atoms 112	12.
Atoms 89/Atoms 113	14.

6. Kinetics and Equilibria of Inorganic Reactions

6.1 Kinetics of the Periodate Oxidation of Manganese

The oxidation of manganese by periodate was followed by measuring the light absorption of permanganate in a recording spectrophotometer. A number of the variables were tested. The dependence on perchloric acid was complex. The reaction was shown to be autocatalytic so that the rate was dependent on the permanganate concentration. Iodate by itself did not, at low concentrations, have much influence on the reaction rates but it did enhance the catalysis by permanganate. At a particular perchloric acid concentration the rate of the reaction at an inflection point was given by

$$\frac{d(\text{MnO}_4^-)}{dt} = k (\text{Mn}^{++})(\text{H}_5\text{IO}_6)(\text{MnO}_4^-)^{1/2} \quad (1)$$

In these experiments it was found that in high iodate concentrations the manganese could be placed in a relatively stable intermediate oxidation state which was probably an iodate complex of manganese (III). Concentrations of this species approaching 10^{-5} molar were achieved and the solutions had a pale violet color which superficially resembled permanganate but was much less intense. The absorption spectrum was distinctly different from that of permanganate in that it did not possess the narrow twin peaks. When solutions of this species were oxidized by periodic acid, it was found that the rates indicated negligible autocatalysis and were satisfactorily described by the expression

$$\frac{d(\text{MnO}_4^-)}{dt} = k(\text{Mn}^{\text{III}})(\text{H}_5\text{IO}_6)^2 \quad (2)$$

This complex is believed to be an important intermediate in the oxidation. The observed rate dependencies can be explained by a process which involves the series of simple steps listed below. Rapidly established equilibria are proposed to be:

The effective oxidation then requires two steps.

and

6.2 Equilibria in the Manganese-Iodate Systems

The solubility of manganese (II) iodate has been measured in water and in solutions of sodium chloride, iodic acid, and manganese(II) perchlorate at 3° and 25°C. Activity coefficients, the solubility product and the heat of solution were calculated. The behavior of this compound was typical of a normal strong 2-1 electrolyte. The solubility product at 25° was 4.8×10^{-7} and the heat of solution, ΔH° was 2200 cal/mole.

Attempts to evaluate the disproportionation equilibrium constant, reaction 4, have not been successful as yet. The methods have involved dilution of solutions in contact with solid manganese (II) iodate and measurement of the changes in total soluble manganese and in the absorbancy by the violet complex. Difficulties may involve the decomposition of the solutions, formation of a precipitate involving an oxidation state of manganese greater than 2, or possibly the formation of a manganese (IV) solution species which is not in equilibrium with other forms. Additional work is needed to clarify this system.

6.3 Activity Coefficients of Methanol-Water Solutions

Work reported elsewhere²⁵ concerning hydration equilibria required information about variations of the activity of water in aqueous methanol solutions. It was particularly important to measure the hydration at the lowest temperatures possible in aqueous solutions; however, previous measurements of methanol-water activities have all been at 25°C or above. Consequently, vapor pressures of various methanol-water solutions have been measured at 0°C and the activity coefficients computed for the entire composition range.

ANALYTICAL CHEMISTRY GROUP

1. Beryllium Research

- 1.1 Spectrophotometric Determination of Beryllium in Aluminum with Sulfosalicylic Acid. H. V. Meek and Charles V. Banks, Anal. Chem., 22, 1512-1516 (1950). (AECU-846).

Abstract

A method of determining small amounts of beryllium in aluminum depends upon the fact that the beryllium-sulfosalicylate complex ion has an absorption maximum at a longer wave length than does the sulfosalicylate alone. The optimum wave length is 317.0 mμ. The procedure is designed to accommodate the range of 0.0015 to 0.23% beryllium in aluminum, but may be conveniently changed to accommodate much higher or lower ranges. Interference by the aluminum-sulfosalicylate complex ion is eliminated by complexing the bulk of the aluminum with N,N,N',N'-tetrakis-(carboxymethyl)-ethylenediamine and by adding approximately the same amount of aluminum to the standards as is present in the samples. Copper and iron, particularly the latter, must not be present in more than trace amounts. Interference by iron is eliminated by extraction with bis-(2-chloroethyl)-ether.

- 1.2 Composition and Stability of the Beryllium-Sulfosalicylate Complex Ion. H. V. Meek and Charles V. Banks. (ISC-81) (Accepted for publication in J. Am. Chem. Soc., (1951).

Abstract

The composition and stability of the "colorless" beryllium-sulfosalicylate complex ion was studied by means of its ultraviolet absorption spectra. The Vosburgh and Cooper extension of Job's method of continuous variations was used to show that in the optimum pH range (9 to 11) only one complex ion is present in appreciable quantity and that the mole ratio of sulfosalicylate to beryllium in this complex ion is 2 to 1.

Evidence is presented that the phenolic hydrogen of the participating sulfosalicylate ions is removed in the process of forming the beryllium-sulfosalicylate complex ion. The true equilibrium constant for the dissociation of $\text{Be}(\text{O}_3\text{SC}_6\text{H}_3(\text{O})\text{COO})_2^{-4}$ into $\text{O}_3\text{SC}_6\text{H}_3(\text{OH})\text{COO}^{-2}$ and an unknown beryllium species, Be_x , was found to be approximately 2.1×10^{-9} at $25^\circ \pm 1^\circ$.

2. Calcium Research

- 2.1 The Polarographic Determination of Small Amounts of Chromium in Calcium. Doris V. Stage and Charles V. Banks, Anal. Chim. Acta, 4, 551-555 (1950). (ISC-108).

Abstract

A polarographic method for the determination of small amounts of chromium in calcium metal is proposed. The diffusion current of the first chromium wave, occurring at -1.0 volt vs. the saturated calomel electrode in 1 M calcium chloride, was found to be directly proportional to the concentration. Factors affecting the diffusion current are discussed, and optimum conditions for the determination are described.

- 2.2 Spectrophotometric Determination of Nickel in Calcium Metal Using 1,2-Cyclohexanedionedioxime. Raymond C. Ferguson and Charles V. Banks, Anal. Chem., 23, 448-453 (1951). (ISC-93).

Abstract

In the course of searching for a method that would be satisfactory for the routine determination of nickel in calcium metal containing more than trace amounts of iron, the possibility of using the vic-dioximes was investigated. The reactions of 1,2-cyclohexanedionedioxime (nioxime) and 1,2-cycloheptanedionedioxime (heptoxime) with nickel in the presence of an oxidizing agent in alkaline solution are similar to the reaction of dimethylglyoxime in that, in each case, unstable, reddish-brown colors are produced having absorption spectra which are very similar. However, the

red inner-complex compound of nickel(II) with 1,2-cyclohexanedione-dioxime can be stabilized with gum arabic, is insensitive to pH changes, absorbs most strongly at 550 mμ, and conforms to Beer's law. The applicability of this method to the spectrophotometric determination of nickel has been established. The effects of diverse ions are discussed and the method is applied to the determination of nickel in calcium metal.

2.3 Determination of Aluminum, Iron and Carbon in Calcium

A spectrophotometric method of determining both aluminum and iron on the same sample of calcium metal has been developed. The iron in the sample is converted to tris(1,10-phenanthroline)iron(II) ion by the addition of hydroxylammonium chloride and 1,10-phenanthroline. The iron is determined and the aluminum is extracted as tris(8-quinolinol)aluminum(III) with a chloroform solution of 8-quinolinol.

It has been found that water purified by mixed-bed ion exchange resins is at least as satisfactory for use in micro-Kjeldahl determinations as is Barnstead water. Deionized water has a lower conductivity, gives comparable nitrogen blanks, and is less troublesome to prepare than Barnstead water.

Progress is being made on developing a satisfactory combustion method for determining carbon in calcium. Highly ignited zirconia seems to make a satisfactory lining for the combustion boats.

3. Thorium Research

A method for determining the amount of sulfate present in thorium fluoride has been developed. The method consists of pyrohydrolysing the sample, fuming off the hydrofluoric acid from the pyrohydrolysis condensate with perchloric acid, and determining the sulfate nephelometrically.

A large amount (500 grams) of 1-(o-arsonobenzeneazo)-2-naphthol-3,6-disulfonic acid has been prepared and is available to other AEC laboratories at a reasonable price. This reagent, sometimes called "Thoron", is very useful in the spectrophotometric determinations of thorium.

4. Zirconium Research

The following procedure has been found to be satisfactory for determining tin in zirconium-tin alloys: dissolve in hydrofluoric-sulfuric acid mixture, fume, reduce the tin in carbon dioxide atmosphere with metallic lead, titrate at 10°C with cerium(IV) sulfate solution using tris(1,10-phenanthroline)iron(II) sulfate as the indicator.

Zirconium-antimony alloys are being analyzed for antimony by dissolving in acid, precipitating antimony trisulfide, filtering, dissolving the precipitate in concentrated hydrochloric acid, removing hydrogen sulfide with nitrogen, and titrating the antimony(III) with cerium(IV) sulfate which has been standardized against antimony(III). Tris(1,10-phenanthroline)iron(II) sulfate is used as the indicator.

The solubility of zirconyl chloride in various water-hydrochloric acid and water-hydrochloric acid-acetone mixtures is being determined.

Preliminary work has been started on spectrophotometric methods for determining aluminum and zinc in zirconium and zirconium compounds.

5. Miscellaneous Research

- 5.1 1,2-Cycloheptanedionedioxime as a Micro-Gravimetric Reagent for Nickel. Raymond C. Ferguson, Roger C. Voter and Charles V. Banks. (ISC-120) (Accepted for publication in *Mikrochemie ver. Mikrochim. Acta.* (1951).)

Abstract

1,2-Cycloheptanedionedioxime (heptoxime), previously reported as a water-soluble gravimetric reagent for nickel, has been applied successfully to the micro-gravimetric determination of this ion. The procedure, modified from the macro-determination, consists of precipitating nickel heptoxime in a micro-filter beaker and weighing the precipitate after drying at 110-120°C. The commonly encountered cations and metallic ions do not interfere or may be masked by complexing agents. The method has been tested on standard nickel solutions and standard steel samples.

- 5.2 A Polarographic Investigation of Iron-Sulfosalicylate Complex Ions. Charles V. Banks and James H. Patterson. (ISC-124) (Accepted for publication in J. Am. Chem. Soc. (1951).)

Abstract

The yellow iron(III)-sulfosalicylate complex ion formed in neutral and alkaline solutions was studied by the half-wave potential method. It was found to contain three triply ionized sulfosalicylate ions for each iron(III) ion, and have a molar hydrolysis constant of approximately 10^{-42} at ionic strength 1. No evidence was found for complex ion formation between iron(II) and sulfosalicylate ions. The second molar dissociation constant, K_{A2} , of sulfosalicylic acid was determined spectrophotometrically to be 3.23×10^{-3} at 25° and ionic strength 0.1.

- 5.3 Spectrophotometric Determination of Nickel Using 1,2-Cycloheptanedionedioxime (Heptoxime). Raymond C. Ferguson and Charles V. Banks. (ISC-126) (Accepted for publication in Anal. Chem., (1951).)

Abstract

Since 1,2-cycloheptanedionedioxime (heptoxime) was found to be a very satisfactory analytical reagent for both the macro- and micro-gravimetric determination of nickel, it was of interest to study its reaction with nickel in the presence of oxidizing agents in strongly basic solutions. A comparison of the sensitivity of the reaction of nickel with dimethylglyoxime, heptoxime, and nioxime in the presence of an oxidant and ammonium hydroxide was made. Although heptoxime does not seem to have any particular advantage over either dimethylglyoxime or nioxime with respect to stability of color produced it does provide a more sensitive method for the spectrophotometric determination of nickel.

- 5.4 Desk and Power Supply for the Beckman Spectrophotometer. Anton B. Carlson, A. S. Ayers, and Charles V. Banks. (ISC-131) (Accepted for publication in J. Chem. Education, (1951).)

Abstract

A desk designed specifically for the Beckman spectrophotometer is described. The accompanying power supply provides for charging the storage batteries at a rate equal to the discharge rate. Plywood boxes for storing certain accessories are also briefly discussed.

SPECTROCHEMISTRY GROUP

1. Analytical Applications of Fluorescent Spectra of Aqueous Solutions of the Rare Earths

The chemical properties of the rare earths are so strikingly similar that mixtures of these elements defy analysis by the usual methods of analytical chemistry, except in a few cases (cerium and europium) where changes in oxidation state may be effected. Since uniqueness in any of the properties of the individual members of the series is of potential usefulness for analytical purposes, it has been one of the general objectives of this laboratory to explore and exploit such differences. Although a majority of the rare earths can be determined by means of the characteristic absorption spectra of aqueous solutions of their salts, the intensity of the bands are not sufficient for measuring rare earth concentrations below several per cent. Thus, for following the large scale rare earth fractionations being carried out in these laboratories, a more sensitive procedure is required. Also, some of the rare earths do not possess any analytically useful absorption bands, and alternate analytical methods are required. Previous reports and publications²⁶ from this laboratory have described arc emission spectra methods for obtaining this analytical information. The possible analytical applications of the fluorescent spectra of rare earth ions in aqueous solution have been under investigation. The scope and limitations of these spectra for the determination of cerium, praseodymium, gadolinium, and terbium have now been established.

A direct ϕ -C. measuring technique was used in which a modified Beckman spectrophotometer served as a fluorimeter. The modifications were directed along the lines of simplicity and minimum outlay of additional equipment with a maximum of effectiveness for detecting light at low levels of intensity on a routine basis. A Nestor hydrogen lamp with electronically regulated power supply served as excitation source. The excitation light was brought into the top of the cuvette-racking compartment by means of a lens and mirror so that the monochromator was used to disperse the fluorescent light produced by the solution contained in the cuvette. A filter between excitation source and sample was not necessary. In fact, no filter or filtering solution was found which did not greatly reduce the excitation effectiveness of the transmitted radiation. A 1P28 photomultiplier phototube was used in a position normally occupied by the light source on the spectrophotometer and was incorporated in the circuit in such a way that all the compensating features of the Beckman instrument were used in the same manner as in transmission measurements.

Cerium, praseodymium, and terbium were determined in a concentration range from about 0.005 to 35 mg oxide per 10 ml of solution. The fluorescent response in order of decreasing sensitivity was cerium, terbium, and praseodymium. Although the fluorescence of gadolinium solutions may easily be obtained, stable fluorescent solutions of this element could not be prepared, and fluorescence served only for the detection of gadolinium. The analytically useful bands were at 277 mμ for praseodymium, 311.5 mμ for gadolinium, 360 mμ for cerium, and 545 mμ for terbium. The fluorescences of all were influenced (quenched) by those ions which absorb in the excitation region such as nitrate, ferric and uranyl ions. Praseodymium was unusual in that it appeared to be slightly self quenching and was greatly influenced by ions of such common elements as sodium, calcium and aluminum. Cerium was determined in thorium, lanthanum and praseodymium matrices in a range as low as 0-50 ppm.

The neodymium absorption bands interfered with the determination of cerium in preparations of that element. Praseodymium was determined in lanthanum and neodymium preparations but its fluorescence was completely quenched when praseodymium occurred as a minor constituent in cerium preparations. Terbium was determined in adjacent rare earth preparations with no apparent difficulty. Highly purified salts of this element were not available and conclusions with respect to its fluorescence may have to be revised. At present, the fluorescent method is the only available technique for determining major amounts of terbium; emission spectra methods are being developed.

For quantitative determinations, 100 mg of the ignited oxide were dissolved in HCl, the resulting solution evaporated to dryness, and then made up to a volume of 10 ml with water. Solutions of the chlorides appeared less subject to quenching or enhancing effects. Sulfate ion enhanced the fluorescence of many of the rare earths. Although the increase in emission from sulfate solutions was desirable the variable nature of the effect precluded its use. With this experimental arrangement the fluorescences of samarium, dysprosium, erbium and thulium could not be excited. Fluorescent spectra of these rare earths, however, have been observed by others under more effective excitation conditions.

2. Quantitative Spectrographic Analysis of Zirconium-Hafnium Mixtures. V. A. Fassel and C. H. Anderson. J. Opt. Soc. Am., 40, 742-7 (1950). (AECU-919).

Extensive studies have been carried out by others of this Laboratory to effect the separation of hafnium from zirconium. To follow these separation studies, an emission spectrographic method for the analysis of zirconium-hafnium mixtures has been developed. A paper based on this research has been published as follows:

Abstract

A spectrographic method for the analysis of zirconium-hafnium mixtures covering the hafnium/zirconium concentration ratio range from 0.001 to 100 is described. The samples are excited as conducting pellets prepared from mixtures of the combined oxides with powdered flake graphite. An overdamped condenser discharge is used for excitation. By utilizing a series of internal standard line pairs, the complete concentration range can be covered by a single exposure. At the same time, photographic photometry errors can be reduced by restricting the intensity ratio range over which these line pairs are measured. The unique similarity in the physical and chemical properties of zirconium and hafnium combined with the use of line pairs of similar excitation characteristics, provides a system in which ideal internal standard conditions can be achieved. Experimental results indicate that, within the wide limits investigated, variations in excitation conditions, extraneous elements, graphite-oxide ratio in the pellets, crystal structure of the oxides, and chemical form of the samples, have no apparent effect on the analytical results. Precision determinations showed a standard deviation of about 1.5 to 2.0 per cent.

3. An Instrument for Internal Standard Flame Photometry and its Application to the Determination of Calcium in the Rare Earths. R. H. Heidel and V. A. Fassel, Anal. Chem. 23, 784-788 (1951). (ISC-107).

Abstract

Microquantities of many elements not readily determined by usual methods of analytical chemistry can be conveniently measured by flame photometric methods. A common technique in flame photometry

is to compare the spectral line intensity of the unknown with a series of standards. This procedure does not take advantage of the usually greater precision and freedom from extraneous influences afforded by use of the internal standard principle. Although flame photometers utilizing this principle have been described, these instruments have been restricted to a single element, lithium, as an internal standard. In this paper details are given for simple modifications of a laboratory monochromator to provide both internal standardization and greater flexibility in choosing line pairs. Need for auxiliary amplification is eliminated by using multiplier phototubes in a differential photometer circuit. A minimum sample is consumed through the use of an atomizing system with provisions for recycling and sample recovery. In the determination of calcium in the rare earths in a concentration range from 0.025 to 2.5%, the average deviation was about 1.5%. The basic design is applicable to most spectrometers or spectrographs. The method should be useful not only for calcium determinations in a number of other matrices but in addition, with proper modifications of the experimental setup, for the determination of other elements susceptible to flame excitation.

4. Miscellaneous Research in Progress

(a) Spectrographic determination of common impurities in zirconium, thorium and calcium metal.

(b) Application of X-ray fluorescence spectroscopy to analytical problems.

(c) Possible analytical applications of diatomic rare earth oxide band emission spectra when excited in flames.

(d) Continuation of development of emission spectrographic methods for the analysis of rare earth mixtures.

(e) Direct spectral line intensity measurements using photomultiplier tubes and associated electronic circuits.

5. Service Analyses

A total of 5252 service spectroscopic analyses were completed during this period.

X-RAY CHEMISTRY GROUP

1. The Structure of Thorium Dicarbide by X-Ray and Neutron Diffraction. E. B. Hunt and R. E. Rundle. (Accepted for publication in J. Am. Chem. Soc. (AECD-3021).)

Abstract

Good X-ray powder diagrams show that ThC_2 is not tetragonal, as previously reported. Single crystals have been obtained and the lattice has been established as C-centered monoclinic with $a_0 = 6.53$, $b_0 = 4.24$, $c_0 = 6.56$ Å, $\beta = 104^\circ$, $Z = 4$. The space group is C2/c or Cc . Thorium positions, determined by X-ray diffraction, are the same in either group, and satisfactory carbon positions have been found in C2/c by neutron diffraction.

The structure contains C_2 groups, but the C-C distance is about 1.5 Å, so that acetylene ions are eliminated. The arrangement of thoriums about the C_2 group combines ethane-like, ethylene-like and acetylene-like character, and considerable covalent character for the Th-C bonds is indicated.

2. Hydrogen Positions in Uranium Hydride by Neutron Diffraction. R. E. Rundle. (Accepted for publication in J. Am. Chem. Soc.)

Abstract

The hydrogen positions in UD_3 have been determined by neutron diffraction, showing that the bridge structure previously proposed is incorrect. The hydrogens lie in distorted tetrahedra, equidistant from four uranium atoms, with $\text{U-D} = 2.32$ Å. There are two types of uranium atoms in the structure, each with twelve nearest D atoms at this distance. The structure is illustrated.

3. The Crystal Structures of Thorium and Zirconium Dihydrides by X-Ray and Neutron Diffraction. R. E. Rundle, C. G. Shull and E. O. Wollan. (Accepted for publication in Acta Crystallographica.)

Abstract

Thorium forms a tetragonal lower hydride of composition ThH_2 . The hydrides ThH_2 , ThD_2 and ZrD_2 have been studied by neutron diffraction in order that hydrogen positions could be determined. The hydrides are isomorphous, and have a deformed fluorite structure. Metal-hydrogen distances in thorium hydride are unusually large, as in UH_3 .

Thorium and zirconium scattering amplitudes and a revised scattering amplitude for deuterium are reported.

4. The Structure of Dimethylberyllium. A. I. Snow and R. E. Rundle. (Accepted for publication in Acta Crystallographica.) (ISC-118).

Abstract

Dimethylberyllium₀ is body-centered orthorhombic, with $a_0 = 6.13$, $b_0 = 11.53$, $c_0 = 4.18$ Å, and a structure similar to SiS_2 . In the

chains, the C-Be-C angle within the four membered ring is somewhat greater than tetrahedral, and the Be-C-Be angle is only 66° . The electron deficient Be-C bonds are 1.93 Å in length.

This structure is in agreement with the rule that electron deficient bonding results from the tendency of metals, with fewer valence electrons than low energy orbitals, to use all their low energy orbitals in forming bonds, even though combined with elements or groups containing no unshared pairs.

5. The Structure of TiBe_{12} . R. F. Baeuchle and R. E. Rundle
(ISC-125) (Accepted for publication in Acta Crystallographica.)

Abstract

TiBe_{12} is hexagonal with $a_0 = 29.44$, $c_0 = 7.33 \text{ \AA}$, $Z = 48$. There is a pseudo-cell, however, with $A_0 = 4.23$, $C_0 = 7.33 \text{ \AA}$, $Z = 1$, one Ti per pseudo unit at 000 or $00\frac{1}{2}$, and it is the alternation between these two positions which leads to the larger cell. Idealized beryllium positions have been found for the pseudo-cell.

The structure is disordered, and though the general reason for the disorder is apparent, the particular type of disorder observed has not been explained.

6. The Structure of Tetramethylammonium Pentaiodide. Ralph J. Hach and R. E. Rundle. (ISC-122) (Accepted for publication in J. Am. Chem. Soc.)

Abstract

Tetramethylammonium pentaiodide is end-centered monoclinic with $a_0 = 13.34$, $b_0 = 13.59$, $c_0 = 8.90 \text{ \AA}$, $\beta = 107.95^\circ$, $\rho_{\text{calcd.}} = 3.06$, $Z = 4$. The structure, based on space group, $C2/c$, consists of nearly square iodine nets within which V-shaped I_5^- ions can be distinguished. Iodine-iodine distances within the ion are $2.91 \text{ \AA}$ and $3.09 \text{ \AA}$, versus $2.67 \text{ \AA}$ for the sum of the covalent radii. Other iodine-iodine distances within one net are $3.62 \text{ \AA}$ or greater, while the nets are $4.3 \text{ \AA}$ apart.

The structure of the I_5^- ion bears no relation to the square ICl_4^- ion, where the I-Cl distance is close to the sum of the covalent radii. It is suggested that iodide does not tend to use its d-orbitals above the valence shell for covalent bonds with iodine, and that the complex ions result from the interaction of an iodide ion with polarizable iodine molecules. Resonating structures result in enough covalent character of the iodide-iodine bond to weaken the iodine-iodine bond.

The relation between polyhalide ions and "polyiodine" polymer complexes is discussed briefly.

7. Structure of the Silver Perchlorate Benzene Complex. R. E. Rundle and Jeanne H. Goring. J. Am. Chem. Soc., 72, 5337 (1950). (AECU-904).

Benzene acts as a Lewis base under a number of circumstances, but it is as yet unknown whether the acid is bonded to one carbon, or by π -bonds, to two, or as more often suggested,²⁷ equally to six carbons. The problem is interesting due to possible implications in organic reaction mechanisms.²⁸ We have examined the silver perchlorate-benzene complex to aid in settling this question.

Crystals, $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$, prepared by crystallization of AgClO_4 from benzene, are orthorhombic, $a_0 = 7.96$, $b_0 = 8.34$, $c_0 = 11.7$ Å., $\rho_{\text{obsd.}} = 2.4$, $Z = 4$, space group Cmcm , Cmc or C2cm . Patterson and, subsequently, Fourier projections on (100), (010) and (001) have been made. On Fouriers, carbon and oxygen peaks are resolved, leading to a complete structure based on Cmcm . Ag and Cl are in 4(c) with $y_{\text{Ag}} = 0.04$, $y_{\text{Cl}} = 0.44$. Benzene centers are in 4(a) with the normal to the ring making an angle of about 40° with c_0 . Bond lengths C-C and Cl-O appear normal. The complete structure, after refinement, will be published elsewhere.

Definite, though weak, Ag-benzene interactions are indicated by Ag-C distances of 2.6 Å., leading to an electron density of 0.15 pair per bond by Pauling's rule and radii.²⁹ Each silver is bonded equally to two carbons of each of two rings, lying above and below the rings, suggesting π -bonding. The perchlorates are pushed away from one side of Ag^+ to make room for benzene.

Benzene may act differently with other Lewis acids or with Ag^+ in solution. But if the silver positions in the crystals are influenced by the availability of π -electrons from benzene, as appears to be the case, then the axial position cannot be materially more favorable than a position over two carbon atoms, and it may be considerably less favorable.

8. Compounds of Thorium with Transition Metals. I. The Thorium Manganese Compounds

Like uranium, thorium forms no compounds with chromium, a few with manganese, the number increasing through nickel, and decreasing sharply with copper. The structures of the compounds of thorium with manganese reported in detail here, are unlike those with iron, cobalt and nickel, which are generally similar. The entire systems, some not completely known, are summarized in Table III.

ThMn_2 is hexagonal with the MgZn_2 (C14-type) structure, with $a_0 = 5.48 \pm 0.01$ Å, $c_0 = 8.95 \pm 0.01$ Å. A parameter evaluation gives no indication of deviation from ideal parameters:

$$\begin{aligned} &4 \text{ Th in } \pm (1/3, 2/3, z); \pm (2/3, 1/3, 1/2 + z); \quad z = 1/16 \\ &2 \text{ Mn in } (000), (00\frac{1}{2}). \\ &6 \text{ Mn in } \pm (x, 2x, \frac{3}{4}); \pm (2x, x, \frac{3}{4}); \pm (x, \bar{x}, \frac{1}{4}); \quad x = 1/6. \end{aligned}$$

For these positions, the discrepancy factor,

$$R = \frac{\sum ||F_{\text{obsd.}}| - |F_{\text{calcd.}}||}{\sum |F_{\text{obsd.}}|}$$

is 0.12 for (HK·0) data and 0.15 for (HH·L) data.

Table III

Compounds of Thorium with First Period Transition Metals

Cr	Mn	Fe	Co	Ni	Cu
		$\text{Th}_7\text{Fe}_3^{a,b}$	$\text{Th}_7\text{Co}_3^{a,b}$	$\text{Th}_7\text{Ni}_3^{a,b}$	
(none)		$\text{ThFe}^{b,c}$	$\text{ThCo}^{b,c}$	$\text{ThNi}^{b,c}$	Th_2Cu
	$\text{ThMn}_2(\text{C14})^d$	$\text{ThFe}_2^{c,e}$	$\text{ThCo}_2^{c,e}$	$\text{ThNi}_2(\text{AlB}_2)$	$\text{ThCu}_2(\text{AlB}_2)$
	$\text{Th}_6\text{Mn}_{23}^b$				
	ThMn_{12}^b	$\text{ThFe}_5(\text{CaZn}_5)^e$	$\text{ThCo}_5(\text{CaZn}_5)$	$\text{ThNi}_5(\text{CaZn}_5)$	
		$\text{ThFe}_{12}^{b,f}$	$\text{ThCo}_{12}^{b,f}$	$\text{ThNi}_{12}^{b,f}$	

^aN. C. Baenziger, Thesis, Iowa State College (1948).

^bNew Structural type

^cStructure not yet fully known

^dStrukturbericht designation

^eExistence suspected from limited data which suggest it is isomorphous with corresponding Co and Ni compounds.

^fNot identical with manganese compound, but structural work not complete.

Table IV summarizes the interatomic distances found in this compound.

Table IV
Interatomic Distances in ThMn_2

Th I ($1/3 \ 2/3 \ 1/6$)	4 Th	3.35 Å
Mn I (000)	12 Mn	3.21 Å
	6 Th	3.21 Å
	6 Mn	2.74 Å
Mn II ($1/3 \ 1/6 \ 1/4$)	6 Th	3.21 Å
	6 Mn	2.74 Å

$\text{Th}_6\text{Mn}_{23}$ is face-centered cubic, $a_0 = 12.523 \pm 0.001 \text{ Å}$, and Laue symmetry O_h , as determined by single crystal data. There are no systematic absences except those required by a face-centered lattice. The final structure, as found from Patterson and Fourier projections, including some three dimensional sections is:

- 24 Th in 24 (e) of $\text{Fm } 3m$ with $X_{\text{Th}} = 0.203$.
- 4 Mn in 4 (b) of $\text{Fm } 3m$ (Parameterless)
- 32 Mn in 32 (f) of $\text{Fm } 3m$ with $X_1 = 0.178$
- 32 Mn in 32 (f) of $\text{Fm } 3m$ with $X_2 = 0.378$
- 24 Mn in 24 (d) of $\text{Fm } 3m$ (Parameterless).

The 4 Mn in 4 (b) are placed there to fill a hole in the structure. The scattering is too slight to be demanded by intensity considerations. Similarly 4 Mn are excluded from 4 (a) on the grounds that Th + Mn distances would be far too small. Putting 4 Mn in this position does not hurt the intensity agreement. R (defined above) = 0.10 for all data when corrected for temperature factor and absorption.

Interatomic distances are given in Table V. The structure is interesting in that Th_6 octahedra are arranged in a face-centered cubic array, with each octahedron surrounded by 44 Mn atoms. Between octahedra, the structure approximates a body-centered packing of Mn atoms.

Table V
Interatomic Distances in $\text{Th}_6\text{Mn}_{23}$

Th(0202 0 0)	4 Th	3.59 Å
	4 Mn	3.08
	4 Mn	3.16
	4 Mn	3.18
Mn (1/2 1/2 1/2)	6 Th	3.71
Mn (0.378 0.378 0.378)	8 Mn	2.64
	3 Th	3.08
	3 Mn	2.69
	3 Mn	2.73
Mn (0.178 0.178 0.178)	3 Mn	3.05
	1 Mn	2.64
	3 Th	3.16
	3 Mn	2.55
Mn (1/4 1/4 0)	3 Mn	2.56
	3 Mn	2.69
	4 Th	3.18
	4 Mn	2.56
	4 Mn	2.73

ThMn_{12} is body-centered tetragonal, $a_0 = 8.74 \pm 0.01$ Å, $c_0 = 4.95 \pm 0.01$ Å, $A = 2$. The Laue symmetry is D_{4h} with no systematic absences other than those required of a body-centered lattice. The structure, derived from Patterson and Fourier data has:

- 2 Th at 000, $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
- 8 Mn in 8f of $I 4/mmm$ (Parameterless)
- 8 Mn in 8 (i) of $I 4/mmm$, $X_1 = 0.361 \pm 0.002$
- 8 Mn in 8j of $I 4/mmm$, $X_j = 0.277 \pm 0.002$.

Refinement of parameters by least squares gives the above limits for standard errors. R (defined above) is 0.10 for the final structure.

Each thorium atom is surrounded by 20 Mn atoms. The thorium atoms distort a tendency toward a body-centered arrangement of Mn atoms.

9. The Structure of Beryllium Chloride

Beryllium chloride is orthorhombic, $a_0 = 9.86$ $b_0 = 5.22$ $c_0 = 5.33$ Å, space group Ibam or Iba from systematic absences. The structure is based on Ibam, and is isomorphous with that of dimethylberyllium (the SiS_2 structure).

Chains, , with an essentially tetra-

hedral configuration about Be, run parallel to c_0 . $\text{Be-Cl} = 2.01$ Å. The angles within the four-membered rings are: $\angle \text{Cl-Be-Cl} = 98.6^\circ$, $\angle \text{Be-Cl-Be} = 81.4^\circ$, contrasting with angles: $\angle \text{C-Be-C} = 114^\circ$, $\angle \text{Be-C-Be} = 66^\circ$ in dimethylberyllium. Arguments are presented, based on these angles, which indicate that chlorine uses an unshared pair in the bonding so that all Be-Cl bonds contain an electron pair, whereas the bonds in dimethylberyllium are necessarily electron deficient.

10. The Structure of Nickel Dimethylglyoxime

Nickel dimethylglyoxime is being examined structurally in an attempt to learn what makes a specific analytical reagent specific. This compound is orthorhombic. The connexity of the bonds, not entirely beyond dispute, heretofore, is:

It is of special interest that the $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bond appears to be unusually short ~ 2.38 Å. Banks and Voter (another part of this report) have found that the usual O-H frequencies are absent in this compound. The two results suggest that this may be the first known case of a symmetric $\text{O}\cdots\text{H}\cdots\text{O}$ bond.

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