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MOUND LABORATORY CHEMISTRY AND PHYSICS PROGRESS REPORT:
JANUARY-MARCH 1969

AEC Research and Development REPORT

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MIAMISBURG, OHIO

OPERATED FOR

UNITED STATES ATOMIC ENERGY COMMISSION

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Foreword

The Mound Laboratory Chemistry and Physics Progress Report, issued quarterly, is intended to be a means of reporting items of current technical interest in research and development programs. Since this is an informal progress report, the results and data presented are preliminary and subject to change.

These reports are not intended to constitute publication in any sense of the word. Final results either will be submitted for publication in regular professional journals or will be published in the form of MLM topical reports. Questions concerning the material compiled here should be directed to G. R. Grove, Director, Nuclear Operations.

Previous reports in this series are:

MLM-1531	MLM-1456
MLM-1526	MLM-1443
MLM-1520	MLM-1417
MLM-1494	MLM-1405

Summary

INORGANIC CHEMISTRY

Nuclear Magnetic Resonance of Actinide Complexes The pseudo-contact shift is dependent on the geometrical factor, which may be used to determine structures of paramagnetic complexes. This fact is useful only if the pseudo-contact shift can be separated from the contact shift, and the technique for this determination is discussed for the β -isopropyl-tropolone complex of uranium. The structure of $\text{ThCl}_4 \cdot 2\text{Bu}_3\text{PO}$ is also discussed. (Page 6)

Effects of Including Pentavalent Plutonium Ions in the Scheme of the Disproportionation of Tetravalent Plutonium Ions in Dilute Aqueous Acid Some consequences of including pentavalent plutonium in the scheme of the disproportionation of plutonium(IV) have been investigated. These consequences are contrasted with current ideas of this disproportionation reaction which omit plutonium(V). (Page 8)

SEPARATION CHEMISTRY

Residue Adsorption Microgram amounts of protactinium-231 adsorbed on glass were desorbed with isopropanol containing 1-5M HCl. The desorption was found to be slow but significantly high. In preliminary tests at the milligram level, the solubility of protactinium(V) in 3M HCl (in isopropanol) was estimated to be of the order of 10 mg/ml. (Page 17)

Uranium-234 Recovery The latest uranium-234 product (A9) contained 0.66 g of uranium-234 at an isotopic purity of 99.90%—the highest isotopic purity observed to date. Analysis of samples taken during previous homogeneous oxalate precipitations of plutonium indicates that very little uranium is coprecipitating with the plutonium. Dissolution of old heat source material, estimated to contain over 1 g of uranium-234, was begun. (Page 20)

Thorium-229 Recovery A shipment of 1092 gal of uranium-233 purification raffinate, containing approximately 300 mg of thorium-229 product, has been received. Analytical and test thorium separation work is under way

on the material. A batch of 8.559 kg of uranium-233 with low uranium-232 content (~6 ppm) has been received and is being stored for thorium-229 ingrowth. (Page 22)

Lead-206 Recovery Lead-206 obtained from an aged polonium-210 heat source has been purified. The total inventory of purified lead-206 is 1.71 g. One sample of the product had an isotopic purity of 99.5% lead-206. (Page 23)

NUCLEAR PHYSICS

The $^{20}\text{Ne}(d,n)^{21}\text{Na}$ Reaction The $^{20}\text{Ne}(d,n)^{21}\text{Na}$ reaction has been studied from 3 to 6 MeV bombarding energy. The results showed that the differential cross sections for the neutron groups involved are generally isotropic with values of the order of 1 mb/sr. No evidence was found for the existence of a 4.86-MeV level in sodium-21. It was determined that the spin assignment made earlier by other workers for the 2.81-MeV level is in error. The width of the 4.12-MeV level was found to be 134 keV, in good agreement with the results of other workers using (p, γ) experiments. (Page 25)

Neutron Total Cross Section for Oxygen-16 and Calcium-40 The neutron total cross sections were measured with 2-keV resolution for 0.82 to 1.8-MeV neutrons on calcium-40 and also for energies near 3 MeV on oxygen-16. A narrow 3006-keV resonance was found in oxygen-16. (Page 32)

MATERIALS DEVELOPMENT

Coating Beryllium Oxide Particles Ceric oxide and beryllium oxide particles were coated with nickel by the thermal decomposition of nickel carbonyl by means of a two-step process. Deposit thicknesses of 4 to 8 μm were achieved, but coating times of 4 to 5 hr were necessary. Therefore, a satisfactory one-step process was developed. Beryllium oxide particles in two size ranges, 125 μm to 149 μm and approximately 50 μm in diameter, have been nickel coated. With this one-step process thicknesses of 5 to 10 μm have been achieved in 2 hr of coating time. (Page 36)

Inorganic Chemistry

NUCLEAR MAGNETIC RESONANCE OF ACTINIDE COMPLEXES

In a recent paper it was shown that the large chemical shifts observed for some uranium β -diketone complexes could be adequately discussed in terms of a contact shift and a pseudo-contact shift.¹ The contact shift arises from delocalization of an electron from a paramagnetic metal to the ligand molecule, while the pseudo-contact shift is determined by the position of the nucleus undergoing resonance relative to the magnetic dipoles of the metal and appears only if these dipoles are anisotropic.

The positional dependency of the pseudo-contact shift makes the observation of this effect a very powerful tool for obtaining structural information for a species in solution. For an axially symmetrical molecule the magnetic dipoles of the metal may be described by two quantities, $g_{\parallel}$ and $g_{\perp}$, which are the magnetic g -factors parallel and perpendicular to the ligand field axis; the ratios of the shifts for any two nuclei within the same molecule may be described as:

$$\left(\frac{\Delta H}{H}\right)_i : \left(\frac{\Delta H}{H}\right)_j : \left(\frac{\Delta H}{H}\right)_k = \left(\frac{3\cos^2\chi - 1}{r^3}\right)_i : \left(\frac{3\cos^2\chi - 1}{r^3}\right)_j : \left(\frac{3\cos^2\chi - 1}{r^3}\right)_k \quad (1)$$

Here r is the distance of the radius vector from the metal to the nucleus undergoing resonance and χ is the angle this radius vector makes with the ligand field axis. Of course, in order to be able to use the pseudo-contact shift to gather structural information, one must be able to separate the pseudo-contact shift from the contact shift. The use of the pseudo-contact shift to determine molecular structure is currently being used in two problems.

Muetterties has listed several possible configurations for an octacoordinate metal complex with four bidentate ligands.² The different configurations may be expected to give rise to considerably differing pseudo-contact shifts. When considering structures in solution it is most desirable to study a system in a non-donor solvent so as to eliminate for the most part any coordination by the solvent. Thus, the β -isopropyltropolone complex of uranium(IV), which is soluble in chloroform, was chosen as the molecule to study.

The nuclear magnetic resonance spectra of the paramagnetic uranium and diamagnetic thorium complexes have been obtained. The assignments of the proton resonances are not unambiguous. In most cases the splitting pattern is sufficient to assign the protons; however, for both the single γ proton and one of the α protons, a doublet is expected. As work proceeds the correct assignment should become obvious. The fact that only a single absorbance is observed for the α and β protons suggests the equivalency of all the chelate rings. Thus, the C_2 square antiprism and the D_2 dodecahedron as possible structures may be immediately discarded.

The molecular structure of bistropolonatoncopper has been determined quite accurately by Macintyre et al.,³ and, using the atomic parameters from their results, the ratios of the pseudo-contact shift for the protons in tetrakis β -isopropyltropolonatoncopper(IV) may be calculated. That the calculated and observed ratios are not in agreement for any of the possible structures indicates the presence of a contact shift contribution.

The major problem at the present time is that only ratios of pseudo-contact shifts are known, and not absolute values. One must then vary the pseudo-contact shift at one position, calculate the pseudo-contact shift for the remaining positions, subtract these values from the observed shifts and compare the resulting contact shifts with the theoretical spin distribution on the tropolone molecule. The theoretical spin distribution of the tropolone molecule is not known; however, it may be obtained by using a molecular orbital treatment or experimentally by observing the nuclear magnetic resonance spectrum of a paramagnetic metal complex which has no pseudo-contact shift contribution. The latter method was chosen and the spectrum of the nickel complex is being obtained.

Some preliminary conclusions, nevertheless, may be drawn concerning the structure. The spin densities should give alternate positive and negative values at the carbon atoms, and thus alternate upfield and downfield shifts. For any reasonable value for the pseudo-contact shift this is not the case for the D_{4h} cube and this structure may be eliminated from future consideration. The remaining two structures, the D_2 and D_4 square antiprisms, both give correct qualitative results, and a final conclusion as to the structure must await the spin distribution.

The second system under investigation is the structure of the phosphine oxide adducts of UCl_4 . These are very useful in solvent extraction studies and thus the structure of these adducts would seem to be rather important. In this case the effect of the contact shift may most likely be eliminated since electron delocalization would have to be through σ bonds. On the other hand, since one is dealing with an alkyl group which has certain free rotations, the calculation of the geometrical factor becomes extremely difficult.

The nuclear magnetic resonance absorption of similar protons gives only one signal which may be used in eliminating a very likely model for the adduct. Crystal structures of metal phosphine oxide complexes have all indicated that the M-O-P bond is not linear.^{4,5} In the present case,

however, similar protons in different alkyl chains would have different geometrical factors if the M-O-P bond is bent and thus would give different pseudo-contact shifts.

Approximate calculations on the pseudo-contact shift ratios using a model with a linear M-O-P bond located on the four-fold axis of UCl_4 gave ratios much smaller than those observed. By using a probability function, it is possible to determine the average position of the hydrogen nucleus by integrating over the entire area in which the proton may exist, and one may determine with certainty if the chosen model for the adduct is correct.

These adducts may be studied by other means also. In the case of the triethylphosphine oxide adduct of UCl_4 , the infrared spectrum was used to determine if the two adduct molecules were cis or trans.⁶ The conclusion that they were trans seems to be substantiated by the simplicity of the nuclear magnetic resonance spectra. The Raman spectra of these adducts should also give information as to the importance of the M-O bond in adduct formation. (C. J. Wiedenheft)

EFFECTS OF INCLUDING PENTAVALENT PLUTONIUM IONS IN THE SCHEME OF THE DISPROPORTIONATION OF TETRAVALENT PLUTONIUM IONS IN DILUTE AQUEOUS ACID

The stoichiometry of disproportionation of Pu(IV) as ordinarily written excludes pentavalent plutonium, even though this species is known to be present in plutonium solutions of low acidity which derive from pure Pu(IV). This is a curious anachronism in plutonium chemistry, and may have been perpetuated by the lack of methods for accurately measuring low concentrations of pentavalent plutonium. Recently, stoichiometries of disproportionation of Pu(IV) corrected for small amounts of Pu(V) have been calculated.⁷ Such stoichiometries are of interest because they are an attempt to describe in full the nature of the distribution of plutonium ions in solutions of disproportionated Pu(IV). Another reason why these stoichiometry calculations are of interest is because they allow the rapid and easy estimation of plutonium species which arise from Pu(IV) by disproportionation.⁸ For example, the relative amounts of Pu(III) and Pu(VI) in a 0.474M hydrochloric acid solution containing 0.00425M plutonium are calculated as 26% and 13%, respectively, in good agreement with experimental values.⁹ Similarly, the relative amounts of Pu(III) and Pu(VI) in a 0.244M hydrochloric acid solution containing 0.00138M plutonium are calculated to be 45% and 21%, respectively, also in good agreement with experimental values.¹⁰

In order to illustrate the changing stoichiometry of disproportionation of Pu(IV), the stoichiometries of disproportionation in 1.0, 0.8, 0.6, 0.4, 0.3, 0.2 and 0.1M acid were calculated based on potentials given by Pourbaix.¹¹ Comparison of these stoichiometries with those derived from experimental potential values shows that the potentials given by Pourbaix are somewhat inaccurate in that they predict too much disproportionation. They nevertheless form a consistent set of data with which to study the

predicted behavior of plutonium species at low acidity. Several interesting questions, not adequately handled elsewhere, concerning the behavior of plutonium species are suggested by these stoichiometries.

1. Question: As the acidity of a Pu(IV) solution is decreased, the equilibrium concentration of Pu(V) is observed to increase, as are the concentrations of Pu(III) and Pu(VI). Neglecting the hydrolysis of Pu(IV), is there ever a point at which the concentration of one of these species might decrease with decreasing acidity, or do they always increase their concentrations with decreasing acidity as predicted by the universally accepted equation:

In Figure 1 are plotted the equilibrium concentrations of Pu(III), Pu(IV), Pu(V) and Pu(VI) for a 0.01M plutonium solution calculated with the aid of the equation⁸

$$8.5 = \frac{[\text{Pu(III)}][\text{Pu(VI)}]}{[\text{Pu(IV)}][\text{Pu(V)}]} \quad (3)$$

This graph has several interesting features:

- a) The concentration of Pu(IV) decreases with decreasing acidity, as has frequently been remarked.
- b) The concentration of Pu(V) increases with decreasing acidity, and this increase is pronounced in solutions of acidity lower than 0.6M.
- c) The concentration of Pu(III) increases with decreasing acidity. This increase is rapid until an acid strength of 0.2M is reached, at which point there is a small inflection, so that the rate of increase of Pu(III) abates somewhat.
- d) The concentration of Pu(VI) increases until it reaches a maximum of about 20% at approximately 0.2M acid. The concentration of Pu(VI) then begins to decrease as the acidity is lowered. Thus, the answer to the above question is that one species, Pu(VI), does reach a maximum concentration such that a slight increase or decrease of the solution acidity at this point results in a decrease in the concentration of this species.

Mechanistically, such behavior can be understood as follows. The disproportionation of Pu(IV) occurs in two steps:

and

As the acid concentration is lowered, reaction (a) proceeds toward the right. Reaction (b) also proceeds toward the right, but is acid-independent and does not go to completion. Reaction (a) generates

considerable Pu(III) at the expense of Pu(IV) and this Pu(III) is augmented by some from reaction (b), which also acts to deplete Pu(IV) from the solution. As acid is continually removed from the solution, there comes a time when the accumulated Pu(III) starts to reverse reaction (b) so that equilibrium is maintained in the face of the decreasing Pu(IV) concentration. At this time PuO_2^+ increases its concentration rapidly because it is now generated by both reaction (a) and the reverse of reaction (b). At this point the increase in the Pu(III) concentration abates somewhat as reaction (b) is reversed and some Pu(III), as well as Pu(VI), begins to be removed from the solution via reaction (b). Whether this point is at 0.2M acid, and whether the Pu(VI) concentration at this point is about 20% as indicated by Figure 1, cannot be decided because of the lack of accurate potential data and the neglect of the effect of hydrolysis on the various plutonium species. A plot of $d[\text{Pu(VI)}]/d[\text{Pu(V)}]$ as a function of acidity is shown in Figure 2.

FIGURE 1 - Behavior of plutonium species as a function of acidity (hydrolysis neglected).

FIGURE 2 - Rate of change of Pu(VI) with respect to Pu(V) as a function of acidity.

An interesting relation between the species Pu(VI) and Pu(V) at the point of maximum concentration of Pu(VI) can be developed with the aid of three statements: charge conservation (c), material balance (d), and equilibrium among the species (e):

$$(c) \quad \text{Pu(III)} = \text{Pu(V)} + 2\text{Pu(VI)} \quad (6)$$

$$(d) \quad 0.01 = \text{Pu(III)} + \text{Pu(IV)} + \text{Pu(V)} + \text{Pu(VI)} \quad (7)$$

$$(e) \quad 8.5 = \frac{[\text{Pu(III)}][\text{Pu(VI)}]}{[\text{Pu(IV)}][\text{Pu(V)}]} \quad (3)$$

This relationship is

$$0.085[\text{Pu(V)}] - 17[\text{Pu(V)}]^2 - 25.5[\text{Pu(VI)}][\text{Pu(V)}] = [\text{Pu(V)}][\text{Pu(VI)}] + 2[\text{Pu(VI)}]^2 \quad (8)$$

Differentiating this statement with respect to Pu(V), and setting the term $d[\text{Pu(VI)}]/d[\text{Pu(V)}]$ equal to zero, gives

$$\frac{0.085 - 25.5[\text{Pu(VI)}]}{34} = \text{Pu(V)} \quad (9)$$

If the relative concentration of Pu(VI) at its maximum is 22% (see Figure 1), then the relative concentration of Pu(V) is calculated to be 8%, in agreement with the value of 8% for Pu(V) calculated from the stoichiometry of disproportionation shown in Figure 1.

2. Question: The function $d[\text{Pu(VI)}]/d[\text{Pu(V)}]$ is a decreasing function [i.e., Pu(V) increases faster than Pu(VI)]. In very low acid concentrations does this function decrease at an increasing rate or a decreasing rate?

Figure 3 shows a plot of $d^2[\text{Pu(VI)}]/d[\text{Pu(V)}]^2$ as a function of acidity. This plot shows that this function appears to approach zero asymptotically at low acidities. The implication of this is that $d[\text{Pu(VI)}]/d[\text{Pu(V)}]$ is constant in solutions of low acidity. Mechanistically, this can be seen by considering reaction (a) and reaction (b) when significant amounts of all species are present. At this time a slight increase in Pu(III) and slight decrease in Pu(IV) via reaction (a) produces a fixed shift in reaction (b) to the left, and this shift is nearly constant for small, equivalent changes in reaction (a).

3. Question: The systems Pu(IV)-Pu(III) and Pu(VI)-Pu(V) constitute potential buffer systems. How does the potential (vs. NHE) of a Pu(IV) solution change with decreasing acidity?

Since the potentials of the system Pu(IV)-Pu(III) and Pu(VI)-Pu(V) are related to one another by a constant, either system may be used. It is obvious that the potential must decrease since the ratio Pu(III)/Pu(IV) increases. Figure 4 shows that the potential, plotted with the standard potential of the Pu(IV)-Pu(III) system, does not decrease uniformly with acidity but that the rate of potential change varies somewhat as shown on the graph. The increasing Pu(III)/Pu(IV) ratio may be used as evidence for the necessity of increasing the ratio Pu(V)/Pu(VI), since these two ratios constitute potential buffer systems which must

FIGURE 3 - Change in $d(\text{VI})/d(\text{V})$ with acidity.

FIGURE 4 - Potential of disproportionated Pu(IV) solutions as a function of acidity.

be in equilibrium with one another. Since the Pu(III)-Pu(IV), Pu(V)-Pu(VI) equilibria are rapidly established, it follows that some Pu(V) is necessarily generated by the disproportionation of Pu(IV), even though it is customary to omit any suggestion of the presence of this species when discussing the nature of the Pu(IV) disproportionation reaction.

4. Question: The disproportionation of Pu(IV) is customarily said to display a fourth power dependence on the hydrogen ion concentration.^{1,2} This is so if the disproportionation reaction is considered to generate only one oxygenyl species (i.e., PuO_2^{2+}):

In fact, however, the disproportionation of Pu(IV) generates two oxygenyl species: PuO_2^{2+} and PuO_2^+ . Bearing this in mind, is the hydrogen ion dependence of the disproportionation reaction truly fourth power?

The answer to this question is clarified by the answer to the question, "Fourth power with respect to what?" Past practice has tacitly assumed that the answer to this latter question is fourth power with respect to PuO_2^{2+} (i.e., four hydrogen ions per ion of PuO_2^{2+}). Alternately, the tacit assumption has been made that the reaction is fourth power with respect to the value of K in the expression

$$K = \frac{(\text{Pu}^{3+})^2 (\text{PuO}_2^{2+}) (\text{H}^+)^4}{(\text{Pu}^{4+})^3} \quad (10)$$

These viewpoints are convergent, since the disproportionation of Pu(IV) is always normalized to PuO_2^{2+} (i.e., always written so as to involve only one mole of PuO_2^{2+}). [An alternate viewpoint is to express the reaction per mole of Pu(V).]^{7,8} Since the custom of expressing the disproportionation of Pu(IV) per mole of PuO_2^{2+} is established, it is convenient to follow that custom.

In Figure 5 is plotted the number of hydrogen ions per ion of PuO_2^{2+} generated by the disproportionation of Pu(IV) in solutions of various acidities. This plot is based on disproportionation stoichiometries in 1M to 0.1M acid as described elsewhere.⁷ In low acidities, the number approaches eight hydrogen ions per ion of PuO_2^{2+} . This is because there is almost one mole of PuO_2^+ generated for every mole of PuO_2^{2+} generated when Pu(IV) disproportionates in solutions of approximately 0.1M acid. Both of these species are oxygenyl ions, and the generation of an ion of either is accompanied by the generation of four hydrogen ions. In more acid solutions, less PuO_2^+ is generated per mole of PuO_2^{2+} , so that in the limit the stoichiometry

is approached, and the disproportionation of Pu(IV) is "fourth power in hydrogen ion". This is shown graphically in Figure 5, which shows that the number of hydrogen ions per ion of Pu(VI) approaches 4.00 asymptotically as the acidity of the solution in which the disproportionation occurs is increased.

The viewpoint that the stoichiometry of disproportionation of Pu(IV) in solutions of low equilibrium acidity should not be expected to be exactly fourth power in hydrogen ion raises some interesting historical questions. It seems reasonable to believe that this "fourth power" expectation underlay much of the early work on the Pu(IV) disproportionation equilibrium; at least, examination of early work seems to suggest this.^{9,12,13} Examination of this early work also reveals that considerable frustration was encountered in trying to force the expression $(\text{Pu}^{3+})^2 (\text{PuO}_2^{2+}) (\text{H}^+)^4 / (\text{Pu}^{4+})^3$ to be constant. A variety of reasons was given for this frustration: poor experimental data, hydrolysis, complexation, alpha reduction. That the reaction should not be expected to be exactly fourth power with acidity apparently did not occur to anyone. Some degree of constancy for the expression could be obtained in solutions of higher acidity (i.e., 0.5M to 1M), and more weight was often assigned to the values obtained in this acidity.¹² Artyukhin et al.^{12,14} found that the actual hydrogen ion dependence of the Pu(IV) disproportionation reaction in nitric acid solutions of low acidity was in fact greater than 4.00. They attributed this to complexation of Pu(IV) by nitrate.

FIGURE 5 - Number of hydrogen ions generated by the disproportionation of Pu(IV) per ion of Pu(VI) as a function of disproportionation acidity.

5. Question: Stoichiometries of disproportionation of Pu(IV) per mole of Pu(V) appear cumbersome and are unfamiliar. Is it possible to write these stoichiometries in a more familiar manner?

The stoichiometry of disproportionation of Pu(V) in 1M perchloric acid is

In spite of the large numbers in the above equation, it is well known that 152 moles of Pu(IV) do not react instantaneously to produce Pu(III), Pu(V) and Pu(VI), and no such meaning is intended by the equation. It is customary, however, to write chemical equations so that fractions do not appear (i.e., so that the equation is normalized per mole of that reactant or product with the smallest coefficient). Stoichiometries of disproportionation of Pu(IV) can also be written normalized to Pu(VI) in the familiar manner. In the above case the stoichiometry normalized to Pu(VI) is

showing that the amount of Pu(V) generated by the disproportionation reaction is small compared to other species, in agreement with experience. The equation also shows that the ratio Pu(III)/Pu(VI) is greater than 2.00, in disagreement with the impression perpetuated by the equation

as must be the case if any Pu(V) is generated by disproportionation. Above 0.5M acid, however, the simpler formulation omitting Pu(V) is a good approximation to the true disproportionation stoichiometry. Unfortunately, the distinction between approximate representation and accurate representation of the disproportionation of Pu(IV) by the simpler expression has historically not been made, and the erroneous impression that the simpler expression is the last word on the disproportionation matter has frequently been impressed upon chemists.

6. Question: Plutonium chemistry has advanced well enough without intercession of Pu(V) in the universally accepted equation

Since such intercession seems meddlesome, is there anything to be gained by asking questions 1-5?

Probably not. The suggestion to include Pu(V) in the Pu(IV) disproportionation stoichiometry is many years overdue. Chemists are satisfied with the traditional representation.

The proposed answers to questions 1-5 may be criticized for omitting various important aspects of plutonium chemistry [i.e., the hydrolysis of the Pu(IV) ion]. In Figure 6 is shown the predicted stoichiometry of disproportionation of Pu(IV) corrected for the first hydrolysis of Pu(IV):

If hydrolysis is included, the predicted concentration of the tetravalent state is greater than the predicted concentration when hydrolysis is neglected. Such considerations as hydrolysis can affect the answers to questions 1-5 considerably. The point of questions 1-5, however, is to draw attention to the predicted behavior of Pu(IV) solutions if the time is taken to include Pu(V) in the Pu(IV) disproportionation stoichiometry. Experimental evidence suggests that Pu(V) has a place in this stoichiometry, historical precedent notwithstanding.¹⁵

(G. L. Silver)

FIGURE 6 - Disproportionation of Pu(IV) corrected for first hydrolysis reaction of Pu(IV).

Separation Chemistry

RESIDUE ADSORPTION

A recurrent problem in the chemistry of protactinium is its tendency to hydrolyze in aqueous solutions of simple mineral acids. At macroscopic levels this behavior is manifested by the appearance, over a period of several minutes, hours or days, of a flocculent white precipitate. At trace levels the hydrolyzed protactinium is frequently found adsorbed on the walls of its container. In general, only solutions containing HF are immune to this behavior, although stable aqueous solutions of protactinium in appropriate concentrations of H_2SO_4 and $\text{H}_2\text{C}_2\text{O}_4$ have been prepared.

Protactinium(V) is readily extracted from aqueous acid solutions by a number of organic solvents, notably di-isobutyl or di-isopropyl carbinol, di-isopropyl or methyl isobutyl ketones and solutions of di- or tri-n-octylamine. Characteristically, the extraction coefficient increases with the concentration of hydrogen ions in the aqueous phase and, if the organic phase has not been pre-equilibrated, the acid concentration of the aqueous phase may be reduced to the point where protactinium(V) begins to hydrolyze into "inextractible species". Nevertheless, because of the slowness of the hydrolytic process, protactinium(V) can usually be quantitatively extracted by the organic solvent, and such solutions are, in general, quite stable.

Previous work on the desorption of complex species by non-aqueous solvents^{16,17} suggested that similar work with protactinium might yield information of fundamental significance and, at the same time, produce a new solvent in which protactinium(V) would be permanently stable.

Preliminary work was carried out with a stock solution containing 18 $\mu\text{g}/\text{ml}$ of protactinium-231 in 0.002N HF/0.001N H_2SO_4 . The source was approximately 8 yr old and contained an estimated 0.2 $\mu\text{Ci}/\text{ml}$ of actinium-227 and its decay products.

The solvent tested initially was isopropanol to which were added various amounts of concentrated (ca. 12N) aqueous HCl. Experiments were performed in 10-ml glass vials. Quantification was by gamma spectroscopy with an NaI(Tl) crystal.

In a typical experiment, 0.1 ml of the protactinium-231 stock solution was introduced into the glass vial and 0.5 ml of concentrated aqueous HCl was added. The solution was evaporated to dryness at 98°C and gamma-counted. The residue was leached twice with 0.5 ml of aqueous 0.1N HCl at 98°C and the solutions were transferred to a second vial, which was gamma-counted. The desorbate contained 68% of the gamma activity, but there was no peak at 27 keV, indicating that no protactinium-231 had been desorbed. The residue was then leached twice with ca. 1 ml of isopropanol (10% HCl) at 80°C and the solutions were transferred to a third vial. The desorbate contained 81% of the remaining protactinium-231.

In a reversal of the procedure described above, the organic desorption was carried out first, and this was followed by the aqueous desorption. Essentially the same distribution of nuclides was observed, except that the organic desorbate contained thorium-227 as well as protactinium-231. When pure isopropanol was used as a desorbate in place of the 10% HCl mixture, essentially no activity was desorbed.

In view of the limited amount of information to be gained from NaI(Tl) gamma spectroscopy, it was decided to renew the attempt to develop a technique which would permit the use of alpha spectrometry. As noted in the previous report,¹⁸ organic solvents cannot be readily contained on a flat surface; on the other hand, the use of planchets or other containers distorts the source geometry, primarily because of deposition of the nuclides on the sides of the vessel.

Nevertheless, it was felt that the qualitative information to be derived from alpha spectrometry was sufficient to justify the loss of accuracy and precision. Experiments were, therefore, run in small glass vials (15 mm in diameter and 13 mm high). Typically, the material balances were poor—in one case, the apparent total protactinium-231 recovered was nearly twice as much as was originally introduced. In most cases, a ring was observed around the insides of the small vials, indicating that the protactinium was depositing at the solid-liquid interface, instead of remaining in solution during evaporation. The effect of this deposition was to bring the alpha source closer to the detector, thus increasing the counting efficiency and yielding material balances considerably greater than 100%.

To make the desorbent truly non-aqueous, a solution was prepared by bubbling HCl gas into reagent-grade isopropanol for several hours. The HCl concentration was found by titration to be slightly greater than 5M. Dilution of this solution with isopropanol yielded non-aqueous desorbents which were 1M and 3M in HCl. Approximately 10 ml of the 5M HCl solution was evaporated at 83°C to half its original volume; the final HCl concentration, after cooling to room temperature, was found to be 3.04M.

To eliminate possible interference by H₂SO₄ and to compensate for the low efficiency of the alpha detector, a source containing 0.4 mg/ml of protactinium-231 in 0.01N HF was used. One drop (ca. 50 μl) of this solution, containing approximately 20 μg of protactinium-231, was transferred to

one of the short vials with approximately 0.5 ml of 3M HCl in isopropanol. The solution was evaporated to dryness at 83°C and its alpha spectrum was obtained. The residue was then desorbed by heating for 5 min at 83°C with 0.5 ml of 3M HCl. The desorbate was transferred to a second short vial and dried. The alpha spectra of both fractions were obtained. It was found that approximately 35% of the protactinium-231 had been desorbed. The desorption was repeated, but only 10% of the residual protactinium-231 was transferred. A third desorption was made with enough 3M HCl to fill the small vial (ca. 1.3 ml); this time 38% of the residual protactinium-231 was desorbed.

In a test of the desorption effectiveness of various concentrations of HCl in isopropanol, the protactinium-231 adsorbed in a glass vial was desorbed with 5M HCl and transferred to a second vial where it was dried. The protactinium-231 in the second vial was then desorbed with 3M HCl and transferred to a third vial, from which it was desorbed with 1M HCl. To minimize evaporation, each desorbent was heated for only 1 min at 83°C. The desorption efficiencies of the three concentrations of HCl are given in Table 1.

Table 1

PROTACTINIUM-231 DESORBED BY HCl/ISOPROPANOL

Concentration of HCl (M)	Protactinium-231 Desorbed (%)
5	58.4
3	69.4
1	82.6

It was concluded that the desorption would be effective if sufficient desorbent remained (after heating) to cover the ring of dried protactinium-231. However, because the dissolution is slow and the evaporation rate rapid, this could be accomplished only in a vessel tall enough to cause refluxing of the solvent.

Despite the erratic data obtained by alpha spectrometry, the results were considered sufficiently promising to justify the commitment of several milligrams of protactinium to a test of its non-aqueous solubility. The source selected for this purpose was a composite of numerous small sources previously used for adsorption and hydrolysis experiments. The protactinium-231 had been combined, repurified and dissolved in 10 ml of dilute (ca. 3.5N) H₂SO₄ in June 1966. It was estimated to contain a total of 20 mg of protactinium-231.

The H_2SO_4 solution was transferred in portions to a 10-ml glass vial and evaporated at 98°C overnight. The protactinium-231 crystallized out, as expected. The residual H_2SO_4 was cooled, diluted with isopropanol, mixed and decanted. The crystals were washed three times with 2.0-ml portions of isopropanol and allowed to settle. After each wash, the isopropanol was decanted and gamma-counted. The wash solutions, which contained most of the decay products but very little protactinium-231, were combined and set aside.

The crystals were covered with 2.0 ml of 5M HCl in isopropanol and heated at 83°C for 10 min. The solution was cooled to room temperature, decanted, and gamma-counted. Approximately one-third of the protactinium-231 was dissolved. The dissolution was repeated three times with fresh solvent; after the fourth such treatment, all of the protactinium-231 was in solution.

The solution was evaporated at 83°C over a period of several hours. Incipient crystallization was observed when the volume was reduced to approximately 2 ml, indicating that the solubility of protactinium-231 in this solvent is of the order of 10 mg/ml. The solution was diluted again to approximately 8 ml with 5M HCl in isopropanol and heated to complete solution. The vial was removed from the heat, stoppered and allowed to stand at room temperature. At the time of this report, several days later, there has been no indication of precipitation or crystallization.

An alpha spectrum of the new protactinium solution shows that 96.1% of the total alpha activity is due to protactinium-231 and 2.2% to thorium-227. No estimate can be made of the amount of actinium-227 present, because its principal alpha energy peaks are obscured by those of protactinium-231. As expected, radium-223 and its decay products were quantitatively removed by the crystallization of the protactinium-231 from H_2SO_4 and its subsequent dissolution in a non-aqueous solvent, but there has been some regrowth of radium-223 due to the presence of thorium-227.
(H. W. Kirby)

URANIUM-234 RECOVERY

Mound Laboratory has a continuing program to separate and purify the rare isotope uranium-234 from aged plutonium-238 materials. One process uses homogeneous oxalate precipitation to separate the bulk of the plutonium. The oxalate supernatant solution, containing the uranium and any impurities which may have been present, is concentrated by evaporation and extracted with TOPO (tri-n-octyl phosphine oxide) to separate uranium and plutonium from the impurities. Additional plutonium is separated in a second homogeneous oxalate precipitation from a minimum volume of solution. The supernatant solution from this step is salted with aluminum nitrate and loaded on an anion exchange column. The remaining plutonium and any other impurities are washed off before the uranium is eluted. Finally the uranium is precipitated with hydroxide, dried, and calcined to U_3O_8 . Normally, products are greater than 99% mass 234 and contain less than 10 ppm plutonium.

A second process has been developed which makes use of the waste anion exchange raffinate solutions from plutonium recovery operations. Although this solution is dilute in uranium (1-5 mg/l) it still represents a large source of uranium-234 because of the large volumes generated. The uranium (and any plutonium) in the raffinate solution can be extracted into TOPO with a concentration factor of 100-400 expected for two cycles of TOPO extraction and stripping with sodium carbonate. The concentrate from the extraction step is small enough to permit further concentration and purification by established techniques in normal laboratory type operations.

The purification and preparation of uranium-234 batches designated A9 were described previously.¹⁹ Two portions were combined, precipitated with ammonia, and the precipitate was calcined to constant weight at 850°C. The weight of the oxide was found to be 0.7826 g, which calculates to 0.6619 g of uranium. Mass spectrographic analysis of this sample appears in Table 2.

Table 2
ANALYSIS OF BATCH A9

<u>Uranium Isotope</u>	<u>Concentration (at. %)</u>
234	99.90
235	0.064
236	0.036
238	<0.01

The above value for uranium-234 isotopic purity is the highest found to date in any uranium-234 product; it is due to an extraordinarily high plutonium-238 content in the plutonium parent material and an extremely low uranium contamination level in the original plutonium. The uranium-234 content of this batch was calculated to be 0.6612 g. After removal of samples for alpha spectrometry and impurity analysis, the remaining 0.7685 g of U_3O_8 (0.6494 g of uranium-234) was labeled "A9-1-3-69" and packaged for shipment to the Heavy Elements Research Pool at ORNL.

In previous work using homogeneous oxalate precipitation to separate the bulk of the plutonium from the uranium,²⁰ the question of how much uranium was coprecipitating with the plutonium oxalate was unresolved. During the processing, selected batches of plutonium oxalate were dissolved and reprecipitated in the standard way. The uranium content of the supernatant solution from the second precipitation then should be a reliable indicator of the amount of uranium coprecipitated in the first precipitation. Previous analyses, using a spectrophotometric method, showed

the uranium content to be too low to be accurately determined. Recent analyses by a mass spectrometric isotope dilution technique gave results of 0.5, 1.9 and 0.5 mg of uranium coprecipitated in three separate plutonium precipitations. In each case, 3 to 6 g of plutonium were precipitated from 500-600 ml of solution, with an estimated 100-200 mg of uranium present. No immediate explanation can be given for the one high value. However, from an operating standpoint, the data indicate that a second precipitation is unnecessary either on the basis of uranium contamination of the plutonium (100-300 ppm) or on the basis of loss of uranium product (<1%).

The first portion of an old plutonium-238/zirconium alloy heat source, estimated to contain more than 1 g of uranium-234 in 100 g of plutonium, was selected for uranium-234 recovery and has been designated batch A10. Dissolution of this material in HNO_3 and HNO_3/HF has been complicated by the formation of a fine white precipitate or a thick gelatinous precipitate, which are very difficult to remove by filtration. The precipitates are believed to contain zirconium. The bulk of the A10 material has been dissolved, but oxalate precipitations have not been started.

(P. E. Figgins)

THORIUM-229 RECOVERY

A total of 1092 gal (4133 liters) of waste raffinate from the purification of 120 kg of uranium-233 was received in 42 shipping containers from Nuclear Fuel Services, Erwin, Tennessee. The 30-gal (113-liter) intermediate steel drums were removed from the outer containers and moved into the high-level gamma cave for storage.

Surface gamma readings on the drums varied from negligible values to as high as 150 mr/hr. The shipper reported a uranium-233 content for the shipment of 44.5 g but requested that, in view of the fact that his analytical data were several years old and the values were uncertain, a sample from each drum be returned.

Each drum was stirred for 5 min by means of an electric mixer inserted in one of the bungs of the inner polyethylene container, and a 1-liter sample was drawn off. After a direct surface gamma measurement on each sample bottle, a 250-ml sub-sample was removed. The 42 250-ml sub-samples were shipped to Nuclear Fuel Services.

The gamma readings on the sample bottles varied from less than 0.5 to 40 mr/hr. Test gamma spectra were obtained on some of the sub-samples using a 2-in. X 2-in. (5.08-cm X 5.08-cm) NaI(Tl) detector and pulse height analyzer. All the gamma emission was found to be due to the thorium-228 daughter chain.

The acidity of each of the samples was measured by titration with NaOH, using a pH meter to determine the end point. It was found that the acidity was titrated at an end point of pH 3, while continuation of the titration

to pH 8 gave the total nitrate normality. The difference between the two end points was due to the aluminum nitrate which had been added to some of the solutions to improve tributyl phosphate extraction of the original uranium. Acidities varied between drums from 0.3N to 6N.

A procedure was set up by which the thorium-229 and uranium-233 contents of each drum could be estimated, as well as the efficiency of a proposed single-stage solvent extraction method for separating both the thorium and the uranium from the bulk of the raffinate. This consisted of shaking 10 ml of the raffinate with 5 ml of 0.1M TOPO (tri-n-octyl phosphine oxide) dissolved in diethyl benzene, allowing the phases to separate, and mounting alpha planchets from aliquots of each of the fractions. Gross alpha counts as well as alpha pulse height analyses were then obtained at approximately the same time on the planchets. Estimates of the concentration to be expected by single-stage TOPO extraction and the thorium and uranium contents of the drum can be obtained by calculation from the counting and APHA results.

The above procedure has been performed on samples from 27 of the 42 drums. The calculation of the results of the separations made to date has not been completed. Preliminary estimates indicate that the drums contain at least 300 mg of thorium-229, that practically all the residual uranium-233 is extracted in a single stage with TOPO, but that thorium extraction varies greatly from drum to drum. In some of the drums it appears that the thorium may be hydrolyzed and in colloidal suspension. It is estimated that the thorium-228:thorium-229 alpha activity ratio is approximately 15:1. The ratio for previously produced thorium-229 is approximately 36:1.

Upon completion of the analytical estimates, development of methods for concentrating thorium from those drums which give poor single-stage TOPO extraction will be started. Actual initiation of full-scale recovery of thorium-229 awaits completion of a fume hood and installation of equipment in the processing room.

A shipment of 8.559 kg of uranium-233, as oxide, containing 6 ppm of uranium-232, was received from ORNL. This was transferred to Mound fissionable material storage containers and is being stored in the criticality storage vault for ingrowth of thorium-229. The uranium, believed to have aged approximately 2 yr since the last thorium separation, will be processed for the thorium-229 content at some future date.

(M. R. Hertz and R. M. Watrous)

LEAD-206 RECOVERY

The lead chloride solution from an aged polonium-210 heat source, the initial purification of which was reported previously,²¹ was passed, hot, through additional anion exchange columns containing Bio-Rad AG-1 X 8 resin. This reduced the polonium-210 content to 2 mCi. The material was then converted to nitric acid solution, the polonium-210 was reduced

by selective electroplating to less than 0.1 mCi, and the lead was plated on a platinum anode as the dioxide. A total of 1.44 g of lead-206 was obtained from the heat source. This, plus previously recovered material on hand, constitutes a current inventory of 1.71 g of lead-206.

Valid data on the isotopic purity of the lead-206 are not available from the Mound heavy element mass spectrometer, due to natural lead contamination in the instrument. A recipient of a shipment of Mound lead-206 reports an isotopic purity of 99.5% lead-206. (M. R. Hertz)

Nuclear Physics

THE $^{20}\text{Ne}(\text{d},\text{n})^{21}\text{Na}$ REACTION

The study of the $^{20}\text{Ne}(\text{d},\text{n})^{21}\text{Na}$ reaction was undertaken as an extension of the investigation of the energy levels of sodium-21. This experiment, last performed in 1960 at Los Alamos²² was repeated: (1) to look for the level at 3.677 MeV found in the previous work using the $^{20}\text{Ne}(\text{p},\gamma)^{21}\text{Na}$ reaction;²³ (2) to search for a level around 2.8 MeV, corresponding to the mirror of a newly discovered level²⁴ in neon-21; (3) to verify or deny the existence of a level at 4.85 MeV, observed by the Los Alamos group at a single angle in their experiment and possibly attributed to neon-22 contamination in their target; and (4) to re-measure the differential cross section for the previously unresolved level at 2.81 MeV.

High-purity neon-20 gas targets, operated at pressures of about 0.33 atm, were bombarded with the deuteron beam of the 5.5-MV Van de Graaff accelerator. The fast neutron time-of-flight spectra for the reaction were studied at deuteron energies of 3.6, 4.88, 5.57 and 5.94 MeV. Figure 7 shows typical time-of-flight spectra. For each foreground spectrum obtained, a background spectrum was run with the target cell filled with helium. The spectrum represented by the circles is the foreground; the spectrum represented by the triangles is the background normalized to the foreground using the current integrator. Time increases to the left at about 0.8 nsec/channel, while energy increases to the right as the inverse square of the time. The peaks labeled 0, 1, 2, ... correspond to the neutron groups populating the ground state, first-excited state, second-excited state, ... (see Figure 8). Neutron peak areas were extracted by first subtracting the normalized background from the foreground and then integrating the resulting peaks. Spectra were obtained from 0° to 115° in the lab system at approximately every 15°.

The absolute differential cross sections were obtained from the peak areas, correcting for analyzer live time and for beam heating in the target. Only the neutron groups leading to the 0.33, 2.424, and 4.110-MeV levels of sodium-21 show angular distributions which can be analyzed using direct reaction predictions. The Distorted-Wave Born Approximation (DWBA) code JULIE for stripping reactions,²⁵ without spin-orbit coupling, was used to analyze the data to obtain spectroscopic factors. The calculations were performed using the optical model potential of the form

FIGURE 7 - Typical neutron time-of-flight spectra for the $^{20}\text{Ne}(d,n)^{21}\text{Na}$ reaction ($\bar{E}_d = 5.94$ MeV, $\theta_{lab} = 90^\circ$).

FIGURE 8 - Energy levels of sodium-21 showing gamma-rays and branching ratios corresponding to the peaks of Figure 7.

$$U(r) = U_c(r) - \frac{V}{(e^x + 1)} - i \left[W - W' \frac{d}{dx'} \right] (1 + e^{x'})^{-1} \quad (14)$$

where:

- $x = (r - R)/a$
- $R = r_0 A^{1/3}$
- $U_c(r)$ = the Coulomb potential arising from a uniformly charged sphere of radius $r_0 A^{1/3}$
- V = the real potential
- W = the imaginary potential

The optical model parameters used for the present analysis are presented in Table 3.

Table 3

OPTICAL MODEL PARAMETERS

<u>Parameter</u>	<u>Deuteron</u>	<u>Neutron</u>
-V (MeV)	110	47
W (MeV)	3	0
W' (MeV)	0	24
r ₀ (fm)	1	1.25
r' ₀ (fm)	2.34	1.25
a (fm)	0.8	0.65
a' (fm)	0.47	0.47
r ₀ (fm)	1.3	1.25

The DWBA calculations are based on the assumption that the stripped particle enters a single-particle state. The states of the code JULIE are calculated using shell-model harmonic oscillator wave functions for the bound states. If the particle is not captured in a single-particle state, the experimental cross section will be lower than the calculated one. The spectroscopic factor, S , is a measure of the ratio of the observed cross section to the cross section expected for a single-particle state. It measures the percentage of a single-particle state or states with given ℓ to the total wave function describing the residual state. The spectroscopic factors were obtained from

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{exp}} = 1.5 \frac{2I_t + 1}{2I_1 + 1} S \left(\frac{d\sigma}{d\Omega}\right)_{\text{th}} \quad (15)$$

where the factor 1.5 comes from the use of the Hulthen wave function for the deuteron. The values obtained for the n_1 ($\ell = 2$) and n_3 ($\ell = 0$) neutron groups at the deuteron bombarding energies used in this experiment are listed in Table 4. Spectroscopic factors for the n_8 (4.11-MeV) state were not obtained since this state is unbound. The angular distribution does, however, show an $\ell = 1$ angular momentum transfer which is consistent with the spin assignment of $3/2^-$ for this state. The absolute differential cross sections for these three groups are shown in Figures 9, 10 and 11. The solid curves are the theoretical predictions of the code JULIE. Spectroscopic factors are indicated beside each curve.

Table 4

SPECTROSCOPIC FACTORS

Deuteron Energy (MeV)	n_1 ($\ell = 2$) $E_x = 0.33$ MeV		n_3 ($\ell = 0$) $E_x = 2.424$ MeV		n_8 ($\ell = 1$) $E_x = 4.11$ MeV
	S	max $d\sigma/d\Omega$ (mb/sr)	S	max $d\sigma/d\Omega$ (mb/sr)	max $d\sigma/d\Omega$ (mb/sr)
3.60	0.47	9.3	0.33	46.2	
4.88	0.43	10.7	0.36	72.1	
5.57	0.33	8.8	0.47	98.2	8.68
5.94	0.35	9.8	0.45	96.6	12.9

FIGURE 9 - Values for $^{20}\text{Ne}(d,n_1)^{21}\text{Na}$, $Q = -0.123$ MeV ($\ell_p = 2$).

FIGURE 10 - Values for $^{20}\text{Ne}(d,n_3)^{21}\text{Na}$, $Q = -2.202$ MeV ($\ell_p = 0$).

Since the angular momentum of the target nucleus is 0^+ , the final state, populated by the stripping reaction, will have angular momentum $J_f = \ell \pm 1/2$ and parity $\pi_f = (-1)^\ell$. Then, the spin of the 0.330-MeV state is $3/2$ or $5/2$ and the parity is positive. Previous gamma-gamma correlation data have shown that the spin is $5/2$. The spectroscopic factor for this state is a measure of the strength of $d_{5/2}$ single-particle state of the shell model. The spin of the 2.424-MeV state can only be $1/2^+$ and the spectroscopic factor is a measure of the $s_{1/2}$ single-particle state.

The $\ell = 1$ angular distribution for the 4.11-MeV state establishes the spin of this state as $1/2$ or $3/2$ and the parity as negative. This is in agreement with proton scattering data which established $J^\pi = 3/2^-$ for this level.

The angular distributions of the other neutron groups show no consistent shape as the bombarding energy is changed. These states in sodium-21 are not single-particle states and cannot be described using direct reaction theory. The differential cross sections for these neutron groups are

FIGURE 11 - Values for $^{20}\text{Ne}(d, n_8)^{21}\text{Na}$, $Q = -3.89$ MeV ($\ell_p = 1$).

generally isotropic with values of the order of 1 mb/sr. No evidence was found for the existence of a 4.86-MeV level in sodium-21.²²

Figure 12 shows the differential cross section for the 2.81-MeV level. (Note the suppressed zeros.) The dashed curves in the figure are intended only to guide the eye. These distributions do not show a consistent shape and definitely do not show an $\ell = 0$ angular distribution. The spin assignment $J^\pi = 1/2^+$ made by Endt and Van der Leun,²⁶ based on the earlier work of Ajzenberg-Selove et al.²² where this neutron group was not completely resolved from the neutrons feeding the 2.42-MeV level, is in error.

The neutron peaks, n_8 , in the spectra feed the 4.12-MeV level and again show a large width. Using the data from the 5.94-MeV runs, the width of this level is 134 keV in the laboratory system. This is in good agreement with the value of 125 keV obtained previously²³ in the $^{20}\text{Ne}(p, \gamma)^{21}\text{Na}$ experiments. (F. X. Haas, C. H. Johnson* and J. K. Bair*)

*This work was performed at Oak Ridge National Laboratory. C. H. Johnson and J. K. Bair are staff members of the ORNL Physics Division.

FIGURE 12 - Differential cross section for the 2.81-MeV level $^{20}\text{Ne}(d,n)^{21}\text{Na}$, $Q = -2.59$ MeV.

NEUTRON TOTAL CROSS SECTION FOR OXYGEN-16 AND CALCIUM-40

In an earlier report²⁷ the neutron total cross section measurements with about 2-keV resolution on oxygen-16 are described. Among other results are listed the energies and widths ($\Gamma \leq 2$ keV) for four narrow resonances. A later comparison with the known levels of the mirror nucleus suggested that a level in a particular energy region may have been missed. An early study of $^{19}\text{F}(d,\alpha)^{17}\text{O}$ by Watson and Buechner²⁸ also suggested an additional oxygen-17 level at 6986 ± 15 keV. Now, using finer energy steps over a small energy region, a resonance was found at 3006 keV corresponding to 6970-keV excitation in oxygen-17. Recently, Rose²⁹ also found the level from the $^{14}\text{N}(\alpha,p)^{17}\text{O}$ spectrum. Figure 13 shows the 3006-keV resonance and the other four narrow resonances.

The same techniques were used to repeat measurements on calcium-40 from 0.82 to 1.8 MeV. Previously,³⁰ 4-keV resolution was used for 1.0 to 2.1-MeV neutrons. Figure 14 shows the new 2-keV data up to 1.8 MeV and the old 4-keV data above that. Two symbols are used to show duplicate sets

FIGURE 13 - Neutron total cross section of oxygen-16 in selected energy regions, showing five narrow resonances. Background curves have been drawn to agree with the observed cross sections over wider energy regions.

FIGURE 14 - Neutron total cross section for calcium-40.

of data for each experiment. In the energy region from 1.0 to 1.8 MeV, which was covered in both experiments, about 45 peaks were found with 4-keV resolution and almost twice as many with 2-keV resolution. Perhaps this means that most of the peaks are not yet resolved; nevertheless, the shapes of a few of the peaks indicate that they are resolved single resonances. (F. X. Haas, J. L. Fowler* and C. H. Johnson*)

*This work was performed at Oak Ridge National Laboratory. J. L. Fowler and C. H. Johnson are staff members of the ORNL Physics Division.

Materials Development

COATING BERYLLIUM OXIDE PARTICLES

A two-step process for coating beryllium oxide particles with nickel by the thermal decomposition of nickel carbonyl was investigated. The initial investigation involved the use of ceric oxide as a substitute for beryllium oxide. The first step involved application of a flash coating about 1 μm thick by conventionally heating the particles while passing nickel carbonyl over them. The particles were agitated by stirring to insure a uniform coating on all particle surfaces. The flash-coated particles were then transferred to a radio-frequency induction-heated system. The particles were held in a horizontally mounted glass cylinder which was rotated to expose all surfaces of the particles to the nickel carbonyl. The final coating thickness ranged from 5 to 7 μm on ceric oxide particles. Coatings of 4 to 8 μm have been obtained with beryllium oxide particles using this process.

Problems were subsequently encountered in nickel coating beryllium oxide particles by this process. It was found that coating times of 4 to 5 hr were necessary to achieve coatings approximately 4 μm thick.

The two-step process has been abandoned and resistance heating is being used instead of induction heating. The r-f induction coil has been replaced by one-half of a clam shell furnace. This is the only change which has been made in the previously described apparatus. The process presently being used involves pre-heating the beryllium oxide particles in the stationary cylindrical coating chamber prior to introduction of nickel carbonyl into the system. After the particles have been heated to approximately 120°C, nickel carbonyl is introduced into the system and the coating chamber is then rotated during the coating process to insure even coating of all the particles. As a nickel coating builds up, a small magnet is occasionally moved slowly over the length of the cylinder to disperse the particles evenly through the coating chamber. Coatings 4 to 7 μm thick have been achieved in 2 hr of coating time for batches approximately the same size as those requiring 4 to 5 hr in the two-step process. Batches of approximately 100 g have been successfully coated.

The particles coated were in two size ranges, 125 to 149 μm and approximately 50 μm in diameter. Cross sections showing the coating on particles in the two size ranges are shown in Figures 15 and 16.

FIGURE 15 - Beryllium oxide particles 125 μm to 149 μm in diameter with nickel coating 4 to 8 μm thick (250X).

FIGURE 16 - Beryllium oxide particles $\sim 50 \mu\text{m}$ in diameter with nickel coating 4 to 6 μm thick (250X).

This work was performed at the request of Lawrence Radiation Laboratory as part of a study on cermets which contain small amounts of metal on ceramic particles. The materials are being considered as possible components in the fabrication of personnel and aircraft armor protection. The work was performed at Mound because of this organization's expertise in the coating of particles by various techniques. (B. Richardson)

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