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THE SEPARATION OF URANIUM AND PLUTONIUM ISOTOPES IN CHEMICAL EXCHANGE SYSTEMS

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THE SEPARATION OF URANIUM AND PLUTONIUM ISOTOPES

IN CHEMICAL EXCHANGE SYSTEMS

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by

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Chemical Research Sub-Section  
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Environmental Engineering

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THE SEPARATION OF URANIUM AND PLUTONIUM ISOTOPES  
IN CHEMICAL EXCHANGE SYSTEMS

INTRODUCTION

The separation of isotopes by chemical exchange has been largely confined to relatively light elements, such as carbon, nitrogen and oxygen. The decreasing separation factors obtainable with increasing atomic weight have previously been calculated by means of partition functions. The separation factor for two isotopes in equilibrium between two chemical species may be expressed in terms of the concentration  $C$  as

$$\alpha = \frac{C_B C_{A'}}{C_{B'} C_A}$$

where  $A$  and  $B$  denote the chemical species, and the primed values refer to the lighter isotope. The factor may also be expressed as the ratio of partition functions  $Q$ :

$$\alpha = \frac{Q_B Q_{A'}}{Q_{B'} Q_A}$$

For further development see page 5.

The small magnitude of the calculated separation factor has been a deterrent in the application of chemical exchange to the separation of heavy metal isotopes, and the few heavy element isotope experiments completed have borne this out. Since the number of heavy element exchange experiments completed is very small, conclusions based on the results are necessarily tentative. The results can, however, be used to test the theory and set up an order of effectiveness for various exchanging species.

OBJECTIVES

The purpose of this paper is to examine the theory and results of chemical exchange experiments for separation of heavy metal isotopes. Since solvent extraction systems are of considerable interest, attention is given to both aqueous and organic media. The aim is to find a means of predicting those chemical exchange systems likely to produce large isotopic separation factors. Realization of this aim involves the correlation of available data and an evaluation of the feasibility of gathering additional infrared and Raman spectroscopic data in this laboratory as an aid to making these predictions.

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SUMMARY AND CONCLUSIONS

1. A correlation of available spectral data has been made, based upon the Bigeleisen and Mayer approximate equation for the partition function. The spectral data indicate:
  - a. that the partition function per bond increases with decreasing weight of attached atom in the order  
$$\text{bromine} \cong \text{chlorine} \ll \text{fluorine} \cong \text{oxygen}$$
  - b. that the partition function for coordinate-covalent bonds with nitrogen is lower per bond than covalently bound oxygen or fluorine.
2. Normally in an aqueous-organic exchange system for maximum isotope separation, the largest possible value for the partition function is desired in the organic phase; the smallest in the aqueous phase. This situation arises because the metal species present in the organic phase necessarily involves covalent bonding which results in partition functions greater than unity; purely ionic species, on the other hand, have partition function values of unity.

For aqueous media, a consideration of the ionic species present indicates that the partition functions of U(IV) and Pu(IV) are probably at a minimum in 1 to 2 M hydrochloric or perchloric acids; however, the minimum value may never reach unity. The greater complexing ability of nitrate and sulfate reduce their desirability. Disproportionation of Pu(IV) into Pu(III) and Pu(VI) will complicate and probably decrease the exchange separation. The strong tendency of Pu(IV) to polymerize may be expected to increase the partition function above that of U(IV) at the same pH.

For organic media, it is desirable to make full use of the maximum coordination number of eight for both Pu(IV) and U(IV). The central atom should be bound to light elements such as oxygen, or possibly nitrogen. While the cupferride complex used by Oak Ridge personnel fulfills these requirements, a somewhat higher partition function may be achieved by employing the acetyl-acetonate complex.

3. While knowledge of vibrational frequencies and isotopic shifts is necessary for an exact evaluation of the partition function, the time and effort required to work out the structure and force constants for complexes do not seem justifiable at this time. The evaluation would almost certainly require greater effort than performing the actual exchange experiment. The possibility of several species existing in the aqueous phase makes an exact evaluation still more difficult.
4. Chemical exchange systems are proposed which could yield high separation factors, viz., up to 1.0027 per stage for U235-238. Suggested systems

**Include:**

- a. uranium(IV) acetylacetonate in a solvent extraction system or in contact with a resin of low cross-linkage,
  - b. uranium(IV) chloride at pH of 1.5 or higher in contact with a resin,
  - c. uranium peroxide if solubilized.
5. Extrapolation of the correlation of spectroscopic data to plutonium 239-240 systems seems reasonable. Based on the considerations presented for uranium, the maximum separation factor per stage for analogous plutonium systems is estimated to be 1.0007 to 1.0009. The precision of the fission counting method for plutonium isotope analysis is estimated as three percent. A ~~series~~ of forty stages would, therefore, be necessary to demonstrate an effect in an ideal chemical exchange experiment at room temperature.

**THEORY**

The equilibrium distribution of a given set of isotopes between two chemical species may be determined by statistical mechanics. A detailed description of the method appears in the literature<sup>(1)</sup>. It should be pointed out that the considerations involve equilibria, and say nothing of the kinetics involved.

Consider the isotopic exchange between the chemical species A and B (the parent molecule contains the light isotope):



The free energy, F, of a substance is given by the relationship

$$F = -RT \ln Q \quad (2)$$

where Q, the partition function, represents the summation of probabilities for all possible energy states in the molecule. For reaction (1) the separation factor

$$\alpha = K = e^{-\Delta F/RT} = \frac{Q_B Q_{A'}}{Q_{B'} Q_A} \quad (3)$$

The separation factor can, therefore, be calculated when the partition functions are known.

The partition function ratio for the distribution of two isotopes in the species "A" is given by<sup>(1)</sup>

$$\frac{Q_A}{Q_{A'}} = \frac{\sigma'}{\sigma} \left[ 1 + \sum G_i \frac{e^{-u_i}}{e^{-u_i'}} \right] \quad (4)$$

where  $\sigma$  and  $\sigma'$  represent the symmetry numbers of isotopes A and A', (and  $u_i = u_i' - u_i$  is always positive). Further,  $G_i = \left( \frac{1}{2} - \frac{1}{u_i} + \frac{1}{(exp u_i) - 1} \right)$ , (5)

where  $u_i = \frac{hc \nu_i}{RT}$

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$\nu_1$  is the  $i^{th}$  vibration frequency of the species,  $h$  is Planck's constant,  $c$  is the velocity of light,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. If there is only one atom of the exchanging isotope per molecule the symmetry number equals one. The contributions of translational and rotational levels may be neglected at room temperature.

The ratio  $Q_B/Q_A$  may similarly be calculated for the species B and the separation factor for equation (1) may then be calculated from equation (3).

In the case of an aqueous-organic exchange system, the conditions for maximum separation result when the species in the aqueous phase is completely ionic and the species in the organic phase is highly complexed or bonded. When this is so, the partition function ratio of the heavy and light isotopes in the aqueous phase is unity; in the organic phase, however, the partition function ratio of the heavy and light isotopes is not equal to unity. If, in equation (3), the subscript A represents the aqueous species and B represents the organic species of such an "ideal" system, then the expression becomes

$$S = \frac{Q_B}{Q_A}$$

The separation factor is thus defined solely by the ratio of the partition functions of the heavy and light isotopes in the organic phase. Evaluation of the partition functions shows this ratio,  $\frac{Q_B}{Q_A}$  to be greater than unity, hence the heavy isotope

tends to concentrate in the organic phase. In a more general system, in the more highly complexed species. Experimental results indicate, however, that the ratio in the aqueous phase may be greater than one.

Calculation of a separation factor by equation (4) thus requires a knowledge of the vibrational frequencies and the corresponding isotopic shifts.

Unfortunately, the frequencies of the uranium compounds have been assigned in only a few of the simpler molecules, and only one estimate of the isotopic shift for heavy elements has been found<sup>(2)</sup>, that of uranyl ion. No data have been found for plutonium compounds.

A shortened form for the partition function ratio of equation (4) is given by Bigeleisen and Mayer<sup>(1)</sup>:

$$\frac{Q_A}{Q_A'} = \frac{g_A}{g_A'} \left[ 1 + \frac{A - A'}{24 MM'} nm(\nu_1)^2 \right] \quad (6)$$

- where  $f$  is the vibrational contribution to the partition function, where  $M$  is the isotopic mass difference ( $M - M'$ ).
- $n$  = the number of bonds formed with atoms of mass  $m$  by the central atom.
- $\nu_1$  = the previously given function of  $\nu_1$ , the symmetrical vibrational stretching frequency.

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Equation (4) neglects the anharmonicity of the vibrations and the interaction of vibrational and rotational modes. The isotopic shift is also assumed to be small. Equation (6) makes the approximation  $G = u/12$  which holds well for values of  $u_1$  less than three. At  $u = 4$ , ( $\nu_1 = 833$ ) the value of  $G$  calculated by this approximation is 25 percent high, and the deviation is still greater when  $u$  is larger. However, this can be corrected by actually calculating the  $G_i$ 's in equation (5). A second assumption implicit in equation (6) neglects all force constants except those concerned with symmetrical stretching of bonds with the central atom. This results in lower values obtained from equation (6), and tends to cancel the previous effect.

Correlation of the Bond Stretching Frequencies

Available values for the vibrational stretching frequency of numerous halides and oxides are given in Table I. The central atoms are well distributed throughout the atomic chart. The data has been correlated by making use of the latter portion of equation (6).

It was desirable to determine which neighboring atoms provide the highest value of partition function. As the mass "m" is increased, the vibrational frequency " $\nu_1$ " is decreased. Therefore, certain elements should be more desirable as neighbors from the standpoint of maximizing the partition function.

In Figure 1, the atomic weight of the central atom has been plotted as a function of  $\frac{m \nu_1^2}{M^2}$ , where m is the mass of the bonded atom and M is the mass of the central atom.

The abscissa is expressed in terms of  $\nu_1$  since  $u_1$  is temperature dependent. This function indicates the contribution per bond to the partition function since the numerator is proportional to the force constant of the bond. The lines on Figure 1 have been drawn by the method of least squares.

Despite the wide difference in types of molecular groupings, the data for both fluorides and chlorides lie relatively close to logarithmic straight lines. The four bromide frequencies found lie close to the chloride line. (Extrapolation of the correlation from uranium to plutonium, i.e., mass 238 to mass 239, seems reasonable.)

The value of the function  $\frac{m \nu_1^2}{M^2}$  for attached atoms increases in the order

bromine > chlorine < fluorine > oxygen

The trend toward increasing partition function per bond with the light elements suggests the desirability of nitrogen bonding. This will be discussed in a subsequent section.

Since the force constant for the vibrational frequency is proportional to  $m \nu_1^2$ , the force constant for oxygen bonding is greater than for the corresponding chlorine bonding.

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TABLE I

ASSIGNED SYMMETRICAL STRETCHING FREQUENCIES

<u>Grouping</u>	$\nu_1, \text{cm}^{-1}$	$\frac{\nu_1^2}{M^2}$	<u>Reference</u>
CF <sub>4</sub>	908	107,800	Herzberg, p. 167
SiF <sub>4</sub>	800	15,400	Herzberg, p. 167
SiF <sub>6</sub> <sup>-</sup>	600	8,720	Zeits, F. physik. Chemie B 19,231(1932), Redlich, et al.
PF <sub>3</sub>	890	15,650	Herzberg, p. 164
SF <sub>6</sub>	776	12,100	Hibben, p. 352
AsF <sub>3</sub>	707	1,700	Herzberg, p. 164
SeF <sub>6</sub>	710	1,535	Hibben, p. 352
MoF <sub>6</sub>	703	1,130	J. Chem Phys 20,447 (1952)
TeF <sub>6</sub>	697	963	Hibben, p. 352
WF <sub>6</sub>	772	370	J. Chem Phys 20,449 (1952)
UF <sub>6</sub>	678	126	Rabinovitch, p. 436
CCl <sub>4</sub>	458	51,700	Herzberg, p. 167
SiCl <sub>4</sub>	423	8,100	Herzberg, p. 167
PCl <sub>3</sub>	510	9,600	Herzberg, p. 164
TiCl <sub>4</sub>	386	2,350	Herzberg, p. 167
GeCl <sub>4</sub>	336	1,060	Herzberg, p. 167
AsCl <sub>3</sub>	410	1,560	Herzberg, p. 164
SnCl <sub>4</sub>	366	335	Herzberg, p. 167
SnCl <sub>6</sub> <sup>-</sup>	348	250	Zeits, F. physik. Chemie B 19,231 (1932)
SbCl <sub>3</sub>	360	309	Herzberg, p. 164
HgCl <sub>2</sub>	322	92	Hibben, p. 339
HgCl <sub>4</sub> <sup>-</sup>	269	62	Hibben, p. 459
CBr <sub>4</sub>	287	10,600	Herzberg, p. 167
PBr <sub>3</sub>	380	11,900	Herzberg, p. 164
GeBr <sub>4</sub>	234	830	Herzberg, p. 167
SnBr <sub>4</sub>	220	273	Herzberg, p. 167
NO <sub>2</sub>	1,320	142,200	Herzberg, p. 161
SO <sub>2</sub>	1,060	17,800	Herzberg, p. 178
ClO <sub>4</sub> <sup>-</sup>	735	11,100	Herzberg, p. 167
CrO <sub>4</sub> <sup>=</sup>	858	4,350	Hibben, p. 443
AsO <sub>4</sub> <sup>=</sup>	837	2,000	Hibben, p. 443
SeO <sub>3</sub>	662	1,910	Hibben, p. 388
UO <sub>2</sub>	360	210	Dieke & Duncan, p. 52
UO <sub>3</sub>	307	227	R.H. Moore, priv. communic.

Herzberg, G., Infrared and Raman Spectra of Polyatomic Molecules (1945).  
 Hibben, J.H., Raman Effect and its Chemical Applications (1939).  
 Katz, J.J. and Rabinovitch, E., The Chemistry of Uranium, Part I, (1951).  
 Dieke, G.H. and Duncan, A.R.F., Spectroscopic Properties of Uranium Compounds (1949).

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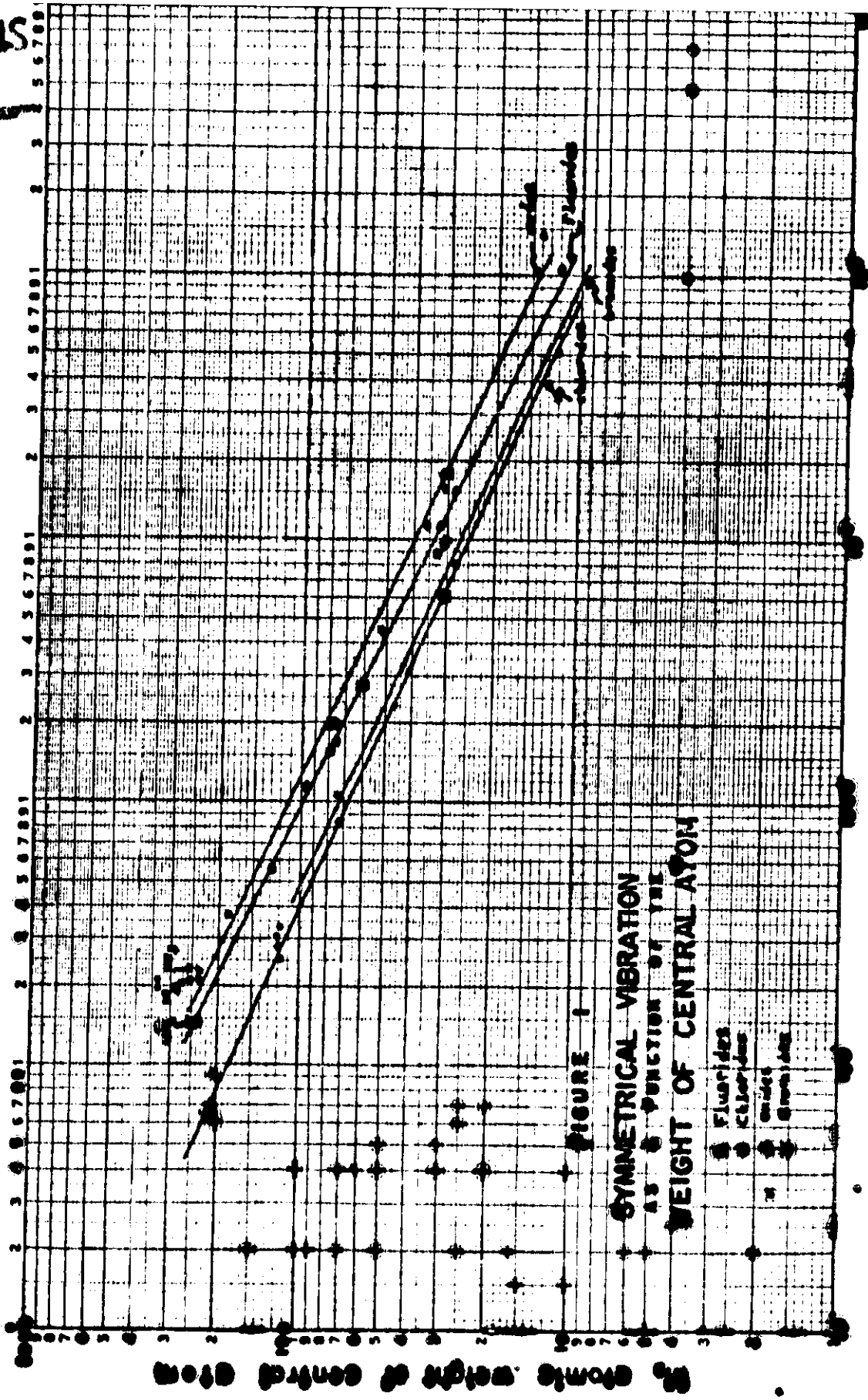


FIGURE 1

SYMMETRICAL VIBRATION  
 $\nu_s$  AS A FUNCTION OF THE  
WEIGHT OF CENTRAL ATOM

- Fluorides
- Chlorides
- △ Bromides
- ◇ Iodides

$\nu_s$  Symm. weight of central atom

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For calculations at 300°K and for  $\nu_1 = 830 \text{ cm}^{-1}$  equation (6) is amended for use with Figure 1 as follows:

$$\frac{f_1}{f_2} = 1 + 9.59 \times 10^{-7} M (n) \left( \frac{\nu_1^2}{\nu_2^2} \right) \quad (6a)$$

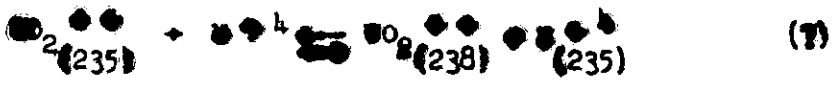
It must be remembered that Figure 1 represents molecular groupings in which the adjoining atom is bound only to the central atom. It is not directly applicable to organo-metallic complexes, unless correction is made for the additional weight of the organic portion of the complex.

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DISCUSSION

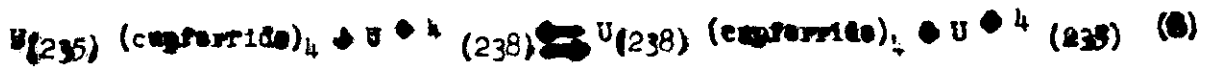
Previous Uranium Exchange Experiments

The isotopic shift for the uranyl ion is estimated by Dick and Duncan (2). Calculations of the separation factor for the system



are given in the literature (3). The assumption was made that only the ionic species of tetravalent uranium exists in solution, hence its  $\alpha$  value equals 1.0000. The separation factor calculated by both equations (4) and (6) was 1.0011, with the lighter isotope anticipated to concentrate in the simpler species. When this separation was performed experimentally (3) at pH of 1.5, the factor per stage was found to be close to 1.001, but the U-235 concentrated in the uranyl ion.

Experiments were also made with the system (3):



in 1 M hydrochloric acid. Here the equilibrium was found to shift to the right, i.e., the U-235 concentrated in the uncomplexed species. On the basis of these observations and other considerations, it was concluded that tetravalent uranium has a complexity intermediate between the cupferron complex and the uranyl ion. However, no consideration was given to the fact that the tetravalent uranium was present at different acidities in the two experiments.

Aqueous Media

The assumption that the uranyl(IV) ion was the sole exchanging species in aqueous media at pH of 1.5 is a considerable oversimplification, since it neglects hydrolysis and polymerization. The larger contribution to the partition function of uranium to oxygen bonds (such as would be produced by the latter reactions) is indicated by Figure 1. The value of  $\beta$  would accordingly be larger than unity, i.e., significantly greater than for the uncomplexed uranyl(IV) ion.

The hydrolysis of tetravalent uranium in chloride solution



has been ascribed a pH value of about 1.9 (4). Even in 0.5 M perchlorate solution at pH of 1.6, Krus and Nelson (5) report that tetravalent uranium is 51 percent hydrolyzed.

The fact that uranyl(VI) is oxygenated is also indicated by the rapid rate of the U(IV)-U(VI) exchange (6). Large changes in the magnetic susceptibility of the uranium species in this pH region (7) suggest polymer formation also.

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Additional evidence that the exchanging species is a hydrolysis (or polymerization) product lies in the fact that the rate of exchange for the U(IV)-U(VI) reaction is an inverse function of the acidity<sup>(8)</sup>. The rate constant is 21 times greater at pH = 1.9 than at pH = 1.1.

The importance of pH in the uranium(IV) exchange reaction suggests that at higher acidities, where hydrolysis and polymerization are suppressed, the reaction will change from



(n is an integer less than five; the arrows are exaggerated to indicate relative rate constants). Experimental results would thus be reconciled with theory. In acidic, non-complexing media (e.g., perchloric acid) the U<sub>235</sub> may then be expected to concentrate in the tetravalent anion.

Even in the chloride system, at high acidities association complexes are formed, ranging from the monochloro- to the hexachloro-uranium(IV) ions. From Figure 1, the partition function for (UCl)<sub>6</sub><sup>4-</sup> is estimated to be 1.0010, and that for the (UCl)<sub>3</sub> ion must be considerably less. For a two phase system, a high complexing acid content is, therefore, undesirable if one wishes to maintain a low-valued partition function in the aqueous phase. The high acid content may also affect the stability of the organic complexing agent by promoting decomposition of other undesirable side reactions.

Based on the calculated value of 1.0311 for uranyl ion and a separation factor of 1.001 for the uranium(IV) - uranium(VI) experiment, the partition function for a solution of uranium(IV) chloride at pH of 1.5 is approximately 1.0021. A minimum value for the partition function might then be expected in 1 to 2 M acid, where only 2 to 3 percent of the uranium is hydrolyzed and the chloride complexes are present in small amount.

No significant difference in the absorption spectra of uranium(IV) chloride, bromide, or iodide solutions has been noted<sup>(9)</sup> indicating that the species present in bromide and iodide systems are similar to those in the chloride system previously described.

In uranium(IV) nitrate and sulfate systems, there is a greater tendency toward complexing than in the chloride system. With increasing acid concentration, ion association occurs, resulting in species of the types U(NO<sub>3</sub>)<sub>4</sub><sup>3-</sup>, U(NO<sub>3</sub>)<sub>5</sub><sup>2-</sup> and U(SO<sub>4</sub>)<sub>3</sub><sup>2-</sup>. Therefore, higher values of the partition function may be expected.

The situation with respect to plutonium(IV), is analogous but far more complicated. In addition to hydrolysis and polymerization, disproportionation also occurs. For example, in dilute (0.0015 M) plutonium solution, 1.5 M in hydrochloric acid, 70 percent of the plutonium is present as Pu(IV), the remainder being in the III and VI valence states<sup>(10)</sup>. Excluding the perchlorate, least complexing occurs in the

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chloride system. Increasing the hydrochloric acid concentration represents the hydrolysis<sup>(11)</sup>,



but increases complex formation which in relatively dilute solution may be represented by<sup>(11)</sup>,



Considering only these reactions, in 0.1 M plutonium solution the maximum Pu<sup>4+</sup> concentration is at 0.4 M hydrochloric acid. However, this neglects polymerization and disproportionation. Since polymerization produces a plutonium species which may be expected to have a higher partition function than the chloride complex, it would be safer to operate at 1 M acid to repress this reaction.

Plutonium(IV) nitrate forms a series of complexes  $Pu(NO_3)^{+3}$  to  $Pu(NO_3)_6^{-}$  with increasing nitrate concentration<sup>(12)</sup>. Similar complexes are known to exist in sulfate solution<sup>(13)</sup> (e.g.,  $Pu(SO_4)_3^{+}$ ).

In aqueous solution, therefore, it would seem desirable to make use of a perchlorate or chloride system (one to two molar in acid) to minimize the partition function of the U(IV) and Pu(IV) species. To operate at higher acidities increases the degree of complex formation while decreasing the acidity results in the formation of hydrolytic and polymeric species.

It is doubtful that a partition function of 1.0000 can be reached, particularly in plutonium solutions initially in the tetravalent state. However, by proper control of acidity, it should be possible to achieve a value less than 1.0005.

Organic Media

The difficulties of postulating a molecular model and calculating frequencies from infrared and Raman shift data are great, particularly so for complexes. The labor involved in the accumulation of such data in order to calculate partition functions would be so great that it would be less difficult to conduct the exchange experiments in the laboratory. However, it should be possible to make predictions based on equation (6) which can lessen the exploratory work considerably.

Organic complexing agents of uranium and plutonium offer a means of forming a molecule with a high partition function. From equation (6), this condition requires:

1. Large number of bonds.
2. High molecular weight of bound atoms.
3. The vibrational stretching frequency to be as high as possible.

Conditions (2) and (3) oppose each other, since the greater the weight of the bound atoms, the slower will be the vibration.

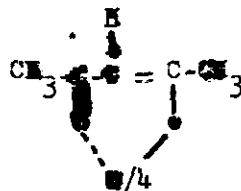
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As a result of exchange experiments with the uranium(IV) cupferride-aqueous uranium(IV) system<sup>(3)</sup>, a separation factor of about 1,001 was estimated. The aqueous system in this series of batch extractions was 1 N in hydrochloric acid at the outset, so that if no acid were extracted into the organic phase, the conditions were optimum for minimum partition function in the aqueous phase.

The cupferron complex with uranium involves interaction with eight surrounding oxygen atoms. From Figure 1, uranium-oxygen bonds provide partition functions somewhat larger than fluorides. Since advantage is taken of maximum coordination in the cupferride complex, improvement must be sought by increasing the vibrational frequency of the uranium-oxygen bond in the complex. This may be accomplished by reducing the weight of the organic portions of the molecule. In the cupferride complex the molecular weight of the organic residue is 70.0 per uranium-oxygen bond, if the equivalent of six uranium to oxygen bonds is assumed.

The beta-diketones of uranium(IV) have the formula  $U_2(O_2R)_4$ . The acetyl acetonate may then be represented as



This constitutes one of the lightest molecules which will permit full coordination of the uranium, the organic residue having a molecular weight of 46.7 per uranium-oxygen bond. Morgan<sup>(15)</sup> tentatively gives the stretching frequency of the uranium-oxygen bond in uranium(IV) acetyl acetonate as  $651 \text{ cm}^{-1}$ . While the coordination number of 8 is achieved in this complex<sup>(16)</sup>, it is not likely that the four coordinate covalent bonds contribute as much to the partition function as the four covalent bonds do. On the other hand, there is evidence that the eight bonds are equivalent in the complex. Assuming that the contribution of the coordinate covalent bonds is half as great as for covalent bonds, the equivalent number of bonds is then six and the partition function for the complex is calculated to be 1.0021.

It is interesting to note that the value of  $\frac{1}{2} \frac{v^2}{\omega^2}$  for the uranium to oxygen bond is reduced to 120 in this complex. The effect of the organic residue is to lower the contribution per bond below that of the uranium-fluorine bond (ca. 150).

To confirm the order of magnitude a simplified comparison may be made with the uranium(IV) cupferride complex for which approximate experimental results are available<sup>(3)</sup>. The latter indicate that the partition function of the complex is 1.0011. If the vibration of the uranium to oxygen bond is harmonic, the square of the vibration frequency is inversely proportional to the attached mass. The lower weight of the acetyl acetonate should then result in a value for the partition function minus one greater by a factor of 1.6 than that of the cupferride complex. The function would then have a value of 1.0018 which compares favorably with the 1.0021 calculated above.

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From the standpoint of stability and availability, the uranium(IV) triethylphosphate complex has been considered for an extraction exchange system. If a coordinate covalent uranium-oxygen bond contributes one-half the effect of a fully covalent bond to the partition function, from Figure 1, the partition function of this complex is estimated to be 1.0012. The estimate is based on four covalent chlorine and two coordinate covalent oxygen bonds. In six molar hydrochloric acid (as required to give a suitable distribution coefficient), the predominant aqueous uranium(IV) species may be the hexachloro-complex. The partition function for this has previously been estimated as 1.0010. If an organic phase containing the complex were contacted with an aqueous phase 6 M in acid, little or no separating effect may be expected. This experiment has been previously conducted in this laboratory and mass spectrographic analyses indicate that little or no isotopic separation occurred.

#### The Contribution of Nitrogen Bonding

As mentioned earlier in this report, Figure 1 indicates a trend toward increasing partition function with decreasing weight of the adjoining atoms. If this trend continues, improvement may be obtained by substituting nitrogen (or a still lighter element) for oxygen as the adjoining atom.

No Raman shift data are available which definitely fix the stretching frequency of metal to nitrogen bonds. However, the most intense Raman shift is generally ascribed to the symmetrical stretching frequency  $\nu_1$  (18). Hibben has tabulated (19) observed Raman shifts for Werner type nitrogen complexes, and the strongest frequencies are reproduced in Table II. No data have been found for inner complexes with nitrogen.

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TABLE II

OF THE COMPLEXES OF AMMONIA AND ETHYLENE DIAMINE

Compound	Molar Weight	Boiling Point (°C)
$Cu(NH_3)_4 SO_4$	418	
$Cu(NH_3)_4 Cl_2$	418	
$Zn(NH_3)_6 Cl_2$	418	
$Pt(NH_3)_4 Cl_2$	518	
$Pt(NH_3)_2 Py_2 Cl_2$	418	
$Ni(En)_2 Cl_2$	272	
$Zn(En)_5 Cl_2$	318	
$Rh(En)_3 Cl_3$	318	
$Ir(En)_3 BF_4$	371	
$Pt(En)_2 Cl_2$	318	
$Pt(En)_3 Cl_4$	318	

Py = Pyridine

(\*\* En = ethylenediamine)

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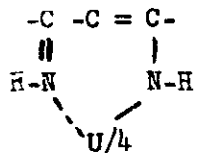
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The ammonia complexes tend to group between 400-500  $\text{cm}^{-1}$ , the frequency increasing with increasing weight of the central atom. The ethylenediamine complexes group in the 500-600  $\text{cm}^{-1}$  range. These data do not correlate as well as the halides but would occupy positions intermediate between the chlorides and fluorides on Figure 1, or in some cases even below the chlorides. Extrapolation of the data to uranium indicates that even if a complex exists which forms eight coordinate covalent bonds with uranium, it would have a partition function of only about 1.0015. Completely coordinate covalent bonding of nitrogen to uranium or plutonium does not appear promising. A platinum complex,  $\text{Pt}(\text{NH}_3)_2 \text{Py}_2^{++}$ , yielded one frequency sufficiently high to be of interest. However, no relative intensity is given.

This evidence does not preclude the attractiveness of the inner complex type compound



The actual magnitude of partition functions of the nitrogen complexes with respect to those of the oxygen complexes remains uncertain until more data for the covalent nitrogen bond is available.

Proposed Exchange Systems

1. The Uranium(IV) Acetylacetonate Complex in a Solvent Extraction System. The separation factor for uranium exchange between an organic phase containing uranium(IV) acetylacetonate and an aqueous phase containing uranium(IV) in one molar perchloric or hydrochloric acid should be approximately 1.002. However, extractability into the organic phase is limited at this acidity.
2. Uranium(IV) Acetylacetonate vs. a Uranium(IV) Resin. The considerations previously described should apply equally well to an ion-exchange process. In the resin the oxygen to heavy element bond is reported to be ionic, hence the partition function should be 1.000. A high value for the partition function in the other phase is desirable. A methanol water solution of uranium or plutonium acetyl acetonate should be acceptable.

Limitations to this proposed exchange system may arise in the rate of exchange. Since the organic complex is a relatively large molecule, diffusion to the inner exchange sites will probably be slow. Hence, a resin with a low degree of cross-linkage would be most desirable.

The separation factor per stage for this system may exceed 1.002 if the resin bonding is purely ionic; the U-235 should concentrate on the resin. Initial experiments with this system have indicated adsorption of the organic complex in one percent cross-linked resin to be excessive.

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3. Uranium(IV) Chloride at pH of 1.5 vs. a Uranium(IV) Resin. If the Oak Ridge data are correct for the enrichment of uranium-238 in uranium(IV) chloride at pH of 1.5, a partition function of 1.0021 is indicated. This system should then provide a separation factor of the same magnitude.
4. Uranium Peroxide. The partition function for uranium peroxide is anticipated to be uniquely high. Based on the Figure 1 value for uranium trioxide, the value calculated for the peroxide is 1.00265; however, the low solubility of this compound limits its usefulness.

Comments thus have have been related chiefly to uranium exchange systems. The highest separation factor per stage for the separation of the 235 and 238 isotopes in the systems considered has been 1.0021 to 1.0026. If the corresponding plutonium system is entirely analogous, the separation factor for the 239 and 240 isotopes may be anticipated to be 1.0007 to 1.0009.

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