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Isotope Separation

AEC RESEARCH AND DEVELOPMENT REPORT

THE SEPARATION OF URANIUM AND PLUTONIUM ISOTOPES

IN CHEMICAL EXCHANGE SYSTEMS

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by

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ENGINEERING DEPARTMENT

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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

$$\text{bromine} \cong \text{chlorine} < \text{fluorine} \cong \text{oxygen}$$
 - 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 minimum 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⁽¹⁾. 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 primed 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⁽¹⁾

$$\frac{Q_A}{Q_{A'}} = \frac{\sigma'}{\sigma} \left[1 + \sum_i G_i \Delta u_i \right] \quad (4)$$

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

$$\text{where } u_i = \frac{hc Y_i}{kT}$$

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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 $u = 4$, ($\gamma_1 = 833$) 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 " γ_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 $\frac{m \gamma_1^2}{M^2}$, 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 γ_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 $\frac{m \gamma_1^2}{M^2}$ for attached atoms increases in the order

$$\text{bromine} \cong \text{chlorine} < \text{fluorine} \leq \text{oxygen}$$

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 $m \gamma_1^2$, the force constant for oxygen bonding is greater than for the corresponding chlorine bonding.

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TABLE I

ASSIGNED SYMMETRICAL STRETCHING FREQUENCIES

Grouping	γ_1, cm^{-1}	$\frac{m(\gamma_1)^2}{M^2}$	Reference
CF ₄	904	107,800	Herzberg, p. 167
SiF ₄	800	15,400	Herzberg, p. 167
SiF ₆ =	600	8,720	Zeits, F. physik. Chemie B 19,231(1932), Redlich, et al.
PF ₃	890	15,650	Herzberg, p. 164
SF ₆	776	11,100	Hibben, p. 352
AsF ₃	707	1,700	Herzberg, p. 164
SeF ₆	710	1,535	Hibben, p. 352
MoF ₆	741	1,130	J. Chem Phys 20,447 (1952)
TeF ₆	697	563	Hibben, p. 352
WF ₆	772	370	J. Chem Phys 20,449 (1952)
UF ₆	656	146	Rabinovitch, p. 436
CCl ₄	458	51,700	Herzberg, p. 167
SiCl ₄	424	8,100	Herzberg, p. 167
PCl ₃	510	9,600	Herzberg, p. 164
TiCl ₄	386	2,350	Herzberg, p. 167
GeCl ₄	396	1,060	Herzberg, p. 167
AsCl ₃	410	1,060	Herzberg, p. 164
SnCl ₄	366	335	Herzberg, p. 167
SnCl ₆ =	314	250	Zeits, f. physik. Chemie B 19,231 (1932)
SbCl ₃	360	309	Herzberg, p. 164
HgCl ₂	322	92	Hibben, p. 339
HgCl ₄ =	265	62	Hibben, p. 459
CBr ₄	267	34,400	Herzberg, p. 167
PBr ₃	380	11,900	Herzberg, p. 164
GeBr ₄	234	830	Herzberg, p. 167
SnBr ₄	220	273	Herzberg, p. 167
NO ₂	1,320	142,200	Herzberg, p. 161
SO ₃	1,069	17,800	Herzberg, p. 178
ClO ₄ -	935	11,100	Herzberg, p. 167
CrO ₄ =	858	4,350	Hibben, p. 443
AsO ₄ =	837	2,000	Hibben, p. 443
SeO ₃	862	1,910	Hibben, p. 388
UO ₂ ⁺ +	860	210	Dieke & Duncan, p. 52
UO ₃	897	227	R.H. Moore, priv. communic.

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$$\frac{m Y, 2}{M^2}$$

A
0.83

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For calculations at 300°K and for $\gamma_1 < 830 \text{ cm}^{-1}$ equation (6) is amended for use with Figure 1 as follows:

$$\frac{f}{f'} = 1 + 9.59 \times 10^{-7} \Delta M (n) \left(\frac{m \gamma_1^2}{M^2} \right) \quad (6a)$$

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 Dieke 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 "f" 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 N 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 uranium(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 f would accordingly be larger than unity, i.e., significantly greater than for the uncomplexed uranium(IV) ion.

The hydrolysis of tetravalent uranium in chloride solution

has been ascribed a pK value of about 1.5⁽⁴⁾. Even in 0.5 M perchlorate solution at pH of 1.6, Kraus and Nelson⁽⁵⁾ report that tetravalent uranium is 61 percent hydrolyzed.

The fact that uranium(IV) 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.

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⁽⁸⁾. 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-235 may then be expected to concentrate in the tetravalent uranium.

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 $(\text{UCl}_6)^=$ is estimated to be 1.0010, and that for the $(\text{UCl})_{+3}$ 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 or other undesirable side reactions.

Based on the calculated value of 1.0011 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⁽⁹⁾ 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 $\text{U}(\text{NO}_3)^{+3}$, $\text{U}(\text{NO}_3)_6^-$ and $\text{U}(\text{SO}_4)_3^-$. 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 +3 and +6 valence states⁽¹⁰⁾. Excluding the perchlorate, least complexing occurs in the

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chloride system. Increasing the hydrochloric acid concentration represses the hydrolysis⁽¹¹⁾,

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

Considering only these reactions, in 0.1 M plutonium solution the maximum Pu^{+4} 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 $\text{Pu}(\text{NO}_3)^{+3}$ to $\text{Pu}(\text{NO}_3)_6^-$ with increasing nitrate concentration⁽¹²⁾. Similar complexes are known to exist in sulfate solution⁽¹³⁾ (e.g., $\text{Pu}(\text{SO}_4)_3^-$).

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 atom, 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⁽³⁾, 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 UX_4 ⁽¹⁴⁾. The acetyl acetate 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 44.7 per uranium-oxygen bond. Morgan⁽¹⁵⁾ tentatively gives the stretching frequency of the uranium-oxygen bond in uranium(IV) acetyl acetate as 651 cm^{-1} . While the coordination number of 8 is achieved in this complex⁽¹⁶⁾, 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 $m \nu_1^2 / M^2$ 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⁽³⁾. 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 acetate 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) tributylphosphate 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 separative 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 γ_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.

TABLE IICHARACTERISTIC RAMAN SHIFTS OF AMMINE TYPE COMPLEXES

<u>Compound</u>	<u>Most Intense Raman Shift, cm⁻¹</u>
$\text{Cu}(\text{NH}_3)_4 \text{ SO}_4$	418
$\text{Cu}(\text{NH}_3)_4 \text{ Cl}_2$	419
$\text{Zn}(\text{NH}_3)_6 \text{ Cl}_2$	418
$\text{Pt}(\text{NH}_3)_4 \text{ Cl}_2$	508
$\text{Pt}(\text{NH}_3)_2 \text{ Py}_2 \text{ Cl}_2^*$	1015
$\text{Ni}(\text{En})_2 \text{ Cl}_2^{**}$	571
$\text{Zn}(\text{En})_5 \text{ Cl}_2$	560
$\text{Rh}(\text{En})_3 \text{ Cl}_3$	500
$\text{Ir}(\text{En})_3 \text{ BF}_3$	571
$\text{Pt}(\text{En})_2 \text{ Cl}_2$	525
$\text{Pt}(\text{En})_3 \text{ Cl}_4$	550

* Py = pyridine

(** En = ethylenediamine)

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The ammonia complexes tend to group between 400-500 cm^{-1} , the frequency increasing with increasing weight of the central atom. The ethylenediamine complexes group in the 500-600 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 acetate 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.

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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