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# The System Pentaether-Uranyl Nitrate-Nitric Acid-Water

C. N. Stover, Jr. and H. W. Crandall

April 6, 1950

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# THE SYSTEM PENTAETHER-URANYL NITRATE-NITRIC ACID-WATER

C. N. Stover, Jr. and H. W. Crandall

April 6, 1950

## ABSTRACT

The system pentaether-uranyl nitrate-nitric acid-water has been studied in the liquid-liquid region. Aqueous solutions containing 0.0M to 8.2M nitric acid and 0.0M to 2.3M uranyl nitrate were equilibrated with pentaether, and the effects of nitric acid concentration, uranyl nitrate concentration and temperature are discussed. Phase diagrams for the system are presented and approximate $\Delta H$ values are given.

Conclusions have been made concerning the mechanism of extraction of uranyl nitrate by pentaether and the feasibility of the use of this solvent for uranium recovery.

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# THE SYSTEM PENTAETHER-URANYL NITRATE-NITRIC ACID-WATER

C. N. Stover, Jr. and H. W. Crandall

April 6, 1950

## I. INTRODUCTION

In connection with the study to locate a suitable solvent extraction process for uranium in the absence of non-volatile salting agents, a "shotgun survey"[1] indicated pentaether (dibutoxytetraethylene glycol) as one of the most promising solvents. Other workers have studied pentaether,[2-17] but it was felt more detailed information was needed. Therefore, a study was initiated in this laboratory to determine the equilibria of the system pentaether-uranyl nitrate-nitric acid-water.

The effects of nitric acid concentration, uranyl nitrate concentration, and temperature are considered and phase diagrams are presented. Approximate $\Delta H$ values are presented.

## II. EXPERIMENTAL

The technical grade pentaether (Carbide and Carbon Chemicals Corporation) was distilled at 10 mm. and the heart-cut boiling at $192.5^{\circ} \pm 0.5^{\circ}C$.* was used for this study.

The stock solutions were prepared from the commercially pure uranium nitrate hexahydrate (Mallinckrodt) and concentrated nitric acid, C. P. (Merck), and were standardized before use by the ignition technique described in the Appendix.

Equal aliquots of stock solution and pentaether were equilibrated for one hour at $25^{\circ}C$. After the volume changes were recorded, aliquots of each phase were evaporated, ignited, and weighed as $U_3O_8$. Material balances were calculated in each case and found to check within $\pm 2\%$.

---

*No thermometer stem corrections were made.

Water was determined in the organic phase by using the standard Karl Fischer reagent with a magic eye deadstop titrimeter similar to that of Mitchell and Smith.[18] The water concentration of the aqueous phase was calculated from specific gravity values.

Acid was determined in both phases using the oxalate method of Shepard, Ice, and Alkire.[19]

The pentaether concentration in the aqueous phase was determined by index of refraction measurements. The pentaether concentration of the organic phase was calculated from specific gravity values.

More detailed descriptions of the analytical methods used will be found in the Appendix.

## III. DISCUSSION OF RESULTS

In each of the systems studied the molar concentration of each component was determined by the methods described in the Appendix. The mole percent and weight percent of each component were then calculated. In the case of the four-component systems having a constant total nitric acid concentration, further calculations were made on a nitric acid-free basis, normalizing the remaining three components. Similar calculations on a uranyl nitrate-free basis were made for the four-component systems having a constant total uranyl nitrate concentration. Only liquid-liquid equilibria were considered in this study.

### A. Pentaether-Nitric Acid-Water System

To study the distribution of nitric acid between pentaether and water, solutions of nitric acid varying from 0.0702M to 8.18M were used. It should be noted that preliminary tests by J. B. Chrisney showed negligible decomposition of pentaether in contact with 8M nitric acid for a period of several weeks as

evidenced by lack of color formation or any other change in physical properties such as rate of settling.

It may be seen from Table I and Fig. 1 that very little nitric acid enters the pentaether at low nitric acid concentrations. The distribution ratio of the

Table I*

Nitric Acid Distribution Between Pentaether and Water

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| M $H^+$ (initial) | 0.0702 | 0.344 | 0.596 | 1.269 | 2.74 | 5.97 | 8.18 |
| M $H^+$ (aqueous) | 0.069 | 0.291 | 0.535 | 0.910 | 1.64 | 3.42 | 5.03 |
| M $HNO_3$ (organic) | 0.004 | 0.057 | 0.162 | 0.484 | 1.17 | 2.45 | 3.44 |

*It should be pointed out that material balance differences in this and succeeding tables are due to volume changes and not to experimental inaccuracies, since duplicate determinations always gave excellent checks. While the total volume remained constant within experimental error in all experiments herein reported, the organic volume change was always positive and the aqueous volume change was always negative, the changes being roughly proportional to the number of moles of uranium nitrate and nitric acid transferred. Since there were no volume changes when equal volumes of pentaether and water were equilibrated, all volume changes observed may be explained by assigning molal volumes of 100 ml./mol for nitric acid and 170 ml./ mol for uranium nitrate in both phases.

acid (organic/aqueous) then increases to a maximum of 0.97 at an initial acid concentration of about 2M, decreasing to 0.64 at the higher acid concentrations. This change of distribution ratio is also illustrated in Fig. 2 by the curvature of the equilibrium line.

Fig. 2 also indicates the small amount of pentaether which enters the aqueous phase. Although this value was found to be small in all the systems investigated, variations did occur between systems. These variations were probably due to the effect of very small quantities of impurities on the refractive index measurements, the quantity varying slightly from system to system.

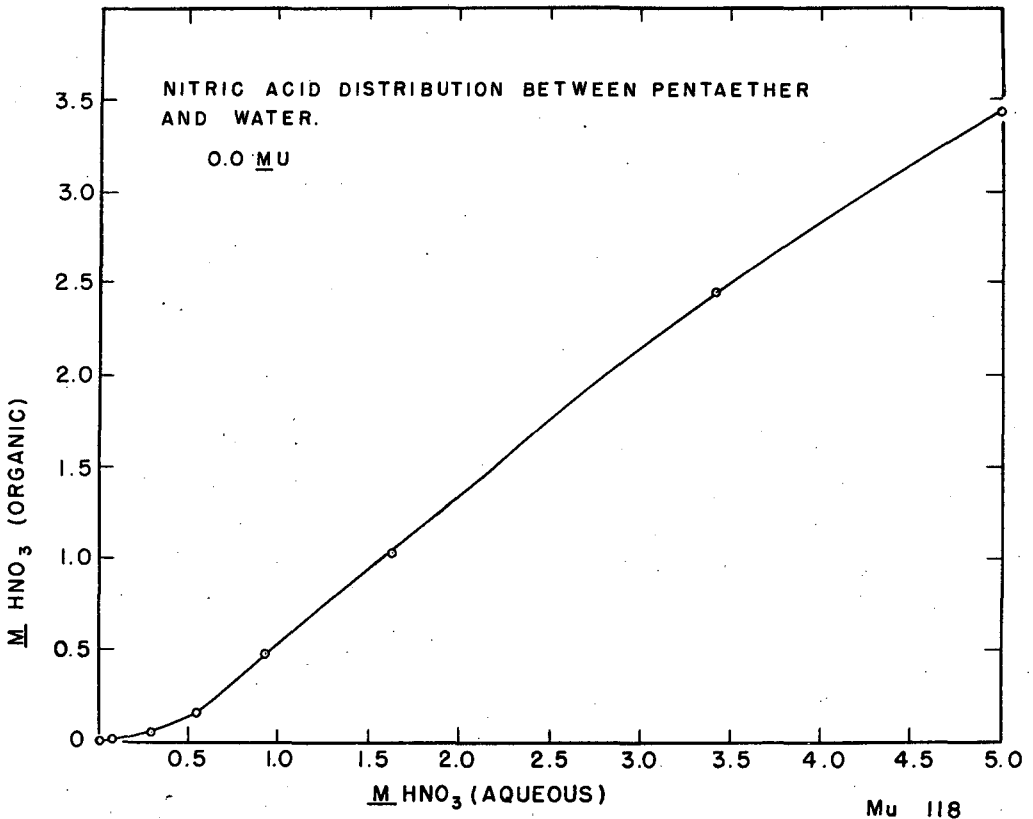


FIG. 1

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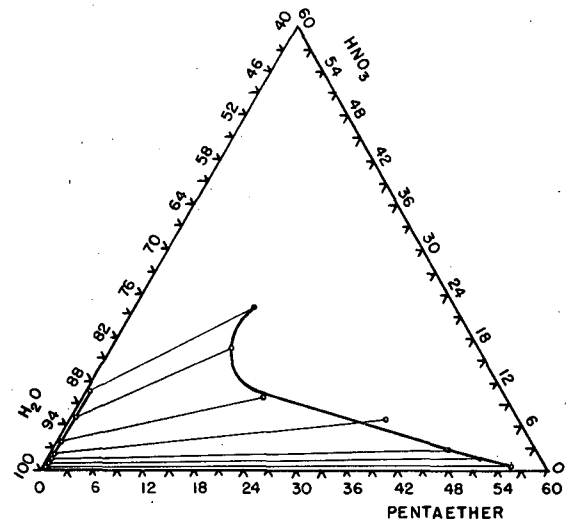
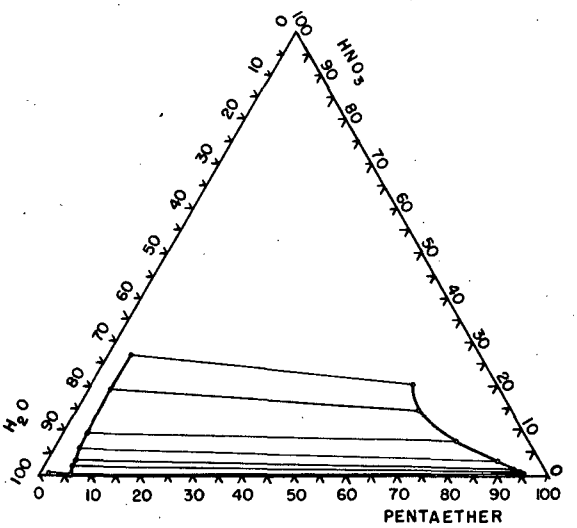



PENTAETHER—NITRIC ACID—WATER SYSTEM MOLE PERCENT

FIG. 2




PENTAETHER-NITRIC ACID—WATER SYSTEM WEIGHT PERCENT

FIG. 3 Mu 119

Therefore, the lower values appearing in this report should be considered the most accurate.

Table II and Fig. 3 present the data for this system on a weight percent basis. It should be pointed out that the weight percent values for pentaether in the aqueous phase correspond on a volume percent basis to less than 2% under all conditions studied.

Table II

Pentaether-Nitric Acid-Water System

| Aqueous Phase | | | | Organic Phase | | | |
|---|---|---|---|---|---|---|---|
| Density | Wt.% $HNO_3$ | Wt.% Penta-ether | Wt.% $H_2O$ | Density | Wt.% $HNO_3$ | Wt.% Penta-ether | Wt.% $H_2O$ |
| 0.996 | 0.45 | 1.5 | 98.1 | 0.952 | 0.02 | 95.5 | 4.46 |
| 1.006 | 1.81 | 5.1 | 93.1 | 0.955 | 0.38 | 94.9 | 4.73 |
| 1.011 | 3.34 | 5.2 | 91.5 | 0.951 | 1.07 | 93.1 | 5.79 |
| 1.027 | 5.59 | 5.0 | 89.4 | 0.965 | 3.16 | 89.0 | 7.84 |
| 1.048 | 9.84 | 4.8 | 85.3 | 1.004 | 7.35 | 77.8 | 14.8 |
| 1.112 | 19.4 | 4.6 | 76.0 | 1.051 | 14.7 | 66.8 | 18.5 |
| 1.158 | 27.3 | 4.4 | 68.3 | 1.065 | 20.4 | 62.8 | 16.9 |

The decrease in the water concentration in the organic phase with increasing acid concentration, which is evident in Figures 2 and 3 and Table II, may be qualitatively explained by the approach to the saturation of the coordination power of the pentaether. For the two highest nitric acid concentrations the ratio ($\underline{M}$ $HNO_3$ + $\underline{M}$ $H_2O$)/$\underline{M}$ pentaether equals approximately six, or one more than the number of oxygen atoms in the solvent molecule.

## B. Pentaether-Uranyl Nitrate-Water System

This system was studied over the range from 0.09M to 2.3M initial aqueous uranyl nitrate concentration. Solid uranium nitrate hexahydrate was added to the 2.3M solution in some experiments. The saturation of pentaether with uranyl nitrate is discussed in a later portion of this report.

It is evident from Table III and Fig. 4 that the aqueous phase is favored in the uranium distribution at very low concentrations. However, the distribution ratio of uranyl nitrate (organic/aqueous) begins to increase rapidly with initial concentrations of approximately 0.2M reaching a maximum of 1.34 in the range from 0.5M to 1.5M initial concentration, and then decreasing to 0.73 at the higher concentrations.

Table III

Uranyl Nitrate Distribution Between Pentaether and Water

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| M $UO_2^{++}$ (initial) | 0.092 | 0.230 | 0.552 | 0.92 | 1.38 | 2.30 | 2.30+ |
| M $UO_2^{++}$ (aqueous) | 0.091 | 0.174 | 0.414 | 0.577 | 0.780 | 1.26 | 1.87 |
| M U (organic) | 0.001 | 0.006 | 0.161 | 0.374 | 0.649 | 1.15 | 1.59 |

This change in distribution ratio may also be seen in Table IV and from the change of slope of the equilibrium tie lines in Fig. 5.

Although the region studied was considerably below the saturation point of pentaether, Fig. 6 shows a decreasing water concentration at high uranyl nitrate concentration, which indicates an approach to saturation of the coordination power of pentaether.

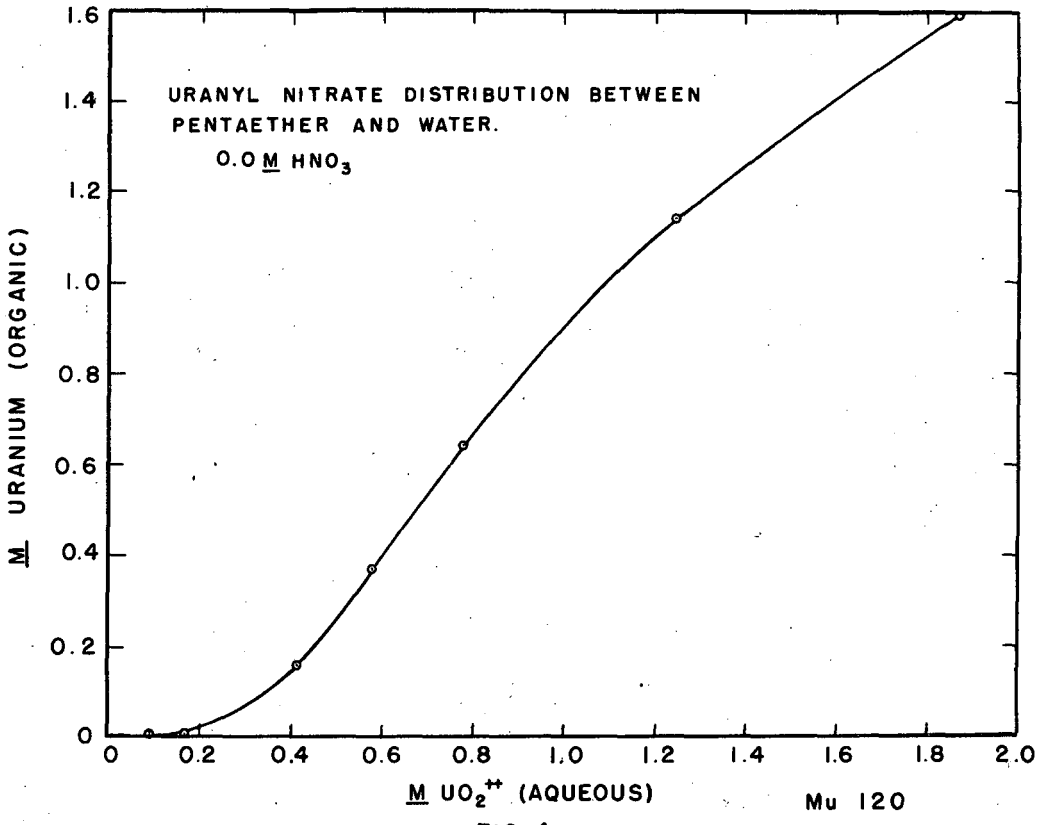



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FIG. 4

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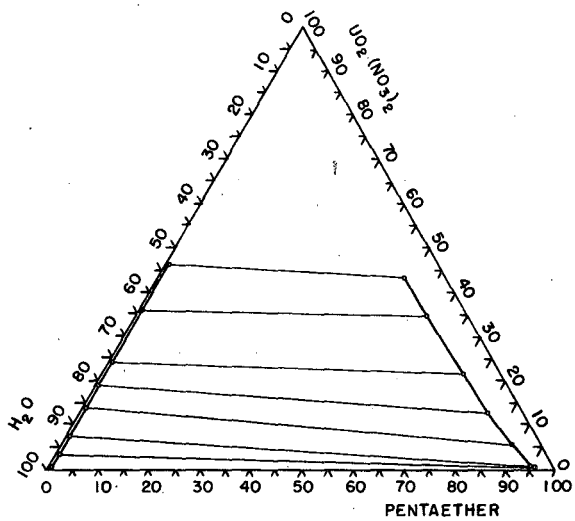
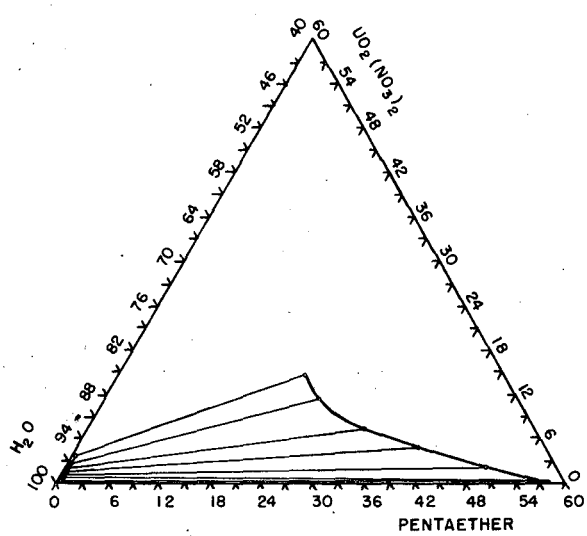



PENTAETHER–URANYL NITRATE–WATER SYSTEM WEIGHT PERCENT

FIG. 5




PENTAETHER-URANYL NITRATE-WATER SYSTEM MOLE PERCENT

FIG. 6

Mu 121

14750-1

Table IV

Pentaether-Uranyl Nitrate-Water System

| Aqueous Phase | | | | Organic Phase | | | |
|---|---|---|---|---|---|---|---|
| Density | Wt.% $UO_2(NO_3)_2$ | Wt.% $H_2O$ | Wt.% Penta-ether | Density | Wt.% $UO_2(NO_3)_2$ | Wt.% $H_2O$ | Wt.% Penta-ether |
| 0.091 | 3.57 | 95.8 | 0.7 | 1.003 | 0.04 | 4.02 | 95.9 |
| 0.174 | 6.53 | 92.8 | 0.7 | 0.989 | 0.24 | 4.37 | 95.4 |
| 0.414 | 14.5 | 85.2 | 0.3 | 1.062 | 5.98 | 5.14 | 88.9 |
| 0.577 | 19.2 | 80.5 | 0.3 | 1.112 | 13.3 | 6.51 | 80.2 |
| 0.780 | 24.6 | 75.2 | 0.3 | 1.191 | 21.5 | 7.78 | 70.8 |
| 1.255 | 35.1 | 64.7 | 0.2 | 1.312 | 34.4 | 8.60 | 57.0 |
| 1.874 | 46.0 | 53.8 | 0.2 | 1.466 | 42.8 | 8.45 | 48.7 |

At the lower uranyl nitrate concentrations the increasing water concentration in the organic phase (Table V) suggests that water is being brought into the organic phase in parallel with the uranyl nitrate. That this may be true is illustrated in Fig. 7 which indicates that four molecules of water accompany each uranium atom

Table V

Uranyl Nitrate and Water Concentrations in Organic Phase
(Pentaether-Uranyl Nitrate-Water System)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| M U (organic) | 0.001 | 0.006 | 0.161 | 0.374 | 0.649 | 1.15 | 1.59 |
| M $H_2O$ (organic) | 2.24 | 2.40 | 3.03 | 4.02 | 5.15 | 6.27 | 6.88 |

into the organic phase. This slope of four has been observed in systems involving other solvents including isobutyl alcohol, diethyl cellosolve, methyl isobutyl ketone, and diethyl ether.[22,23] The decrease in this slope at the higher uranyl

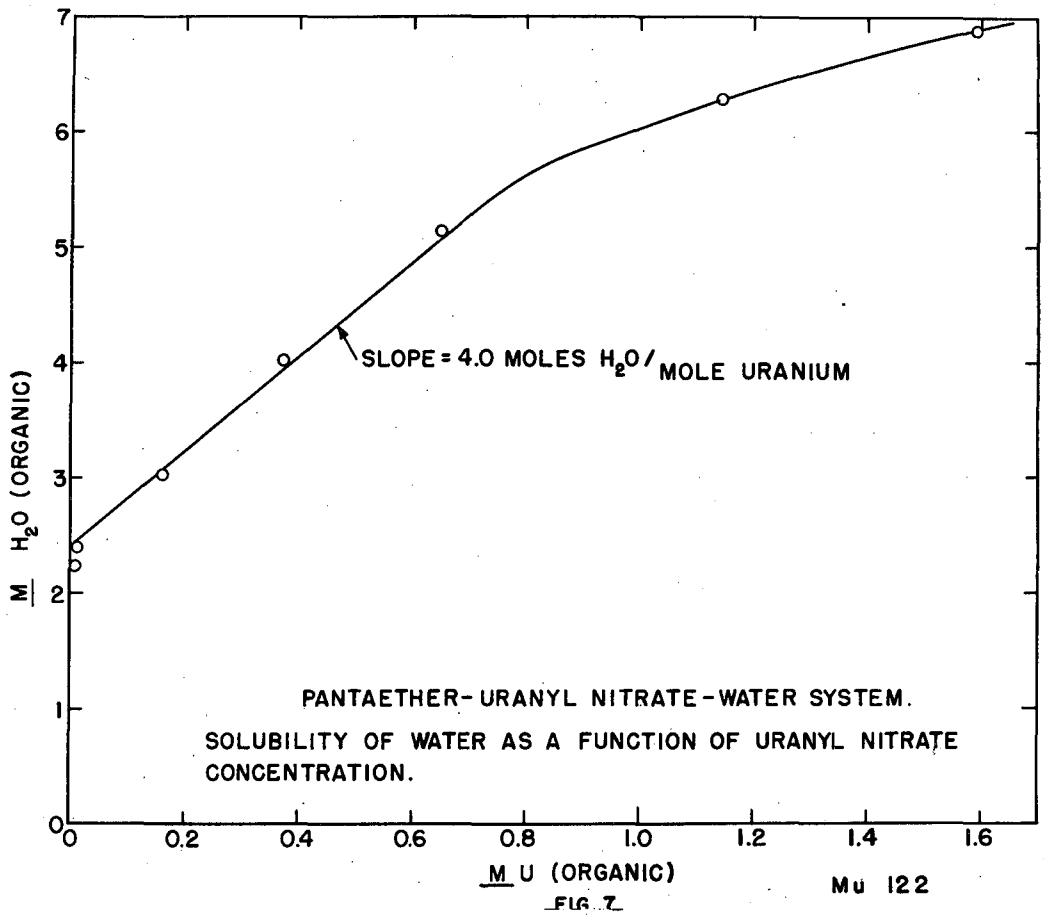



FIG. 7

Mu 122

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nitrate concentrations may be due to partial saturation of the coordination power of the pentaether, thus diminishing the solubility of "free" water, i.e., that water which is not coordinated with uranium.

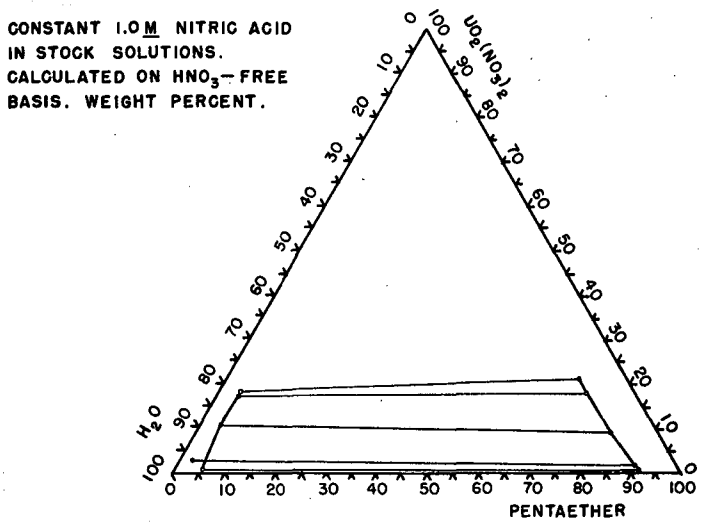
These data, however, should not be considered as proof that four molecules of water are coordinated with each uranium atom in the organic phase, because one might expect the solubility of water to increase due to dielectric effects, e.g., increased water solubility with the transfer of nitric acid.

### C. Pentaether-Nitric Acid-Uranyl Nitrate-Water System

This four-component system was studied with three constant initial aqueous nitric acid concentrations (1.0M, 2.0M, and 4.0M). The data for these series are presented in Table VI. Further calculations were then made on a nitric acid-free basis, normalizing the remaining three components. Phase diagrams for these three systems are presented on a weight percent basis in Figures 8,10, and 12 for initial aqueous nitric acid concentrations of 1.0M, 2.0M, and 4.0M, respectively. The corresponding phase diagrams on a mole percent basis are presented in Figures 9, 11, and 13, respectively. These may be compared with data in Table II and Figures 2 and 3 which has no nitric acid present.

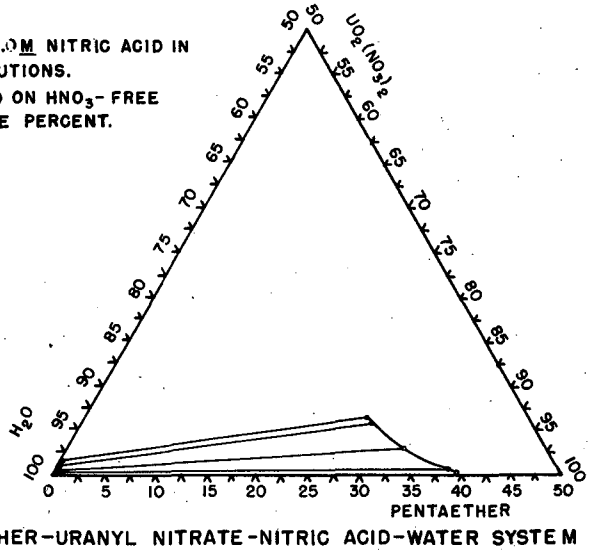
It may be seen from the phase diagrams that these systems are very similar. In each case very little solvent enters the aqueous phase. However, the water concentration of the organic phase increases with increasing nitric acid concentration. Table VI and Figures 8 through 13 also illustrate the decreasing water concentration with increasing uranyl nitrate concentration, the effect being more pronounced with increasing nitric acid concentration.

Although the density differences between phases are comparatively small, phase separation was always quick and complete, the separation being somewhat more rapid at the higher acid concentrations.




PENTAETHER-URANYL NITRATE-NITRIC ACID-WATER SYSTEM

FIG. 8




PENTAETHER-URANYL NITRATE-NITRIC ACID-WATER SYSTEM

FIG. 9

Mu 123

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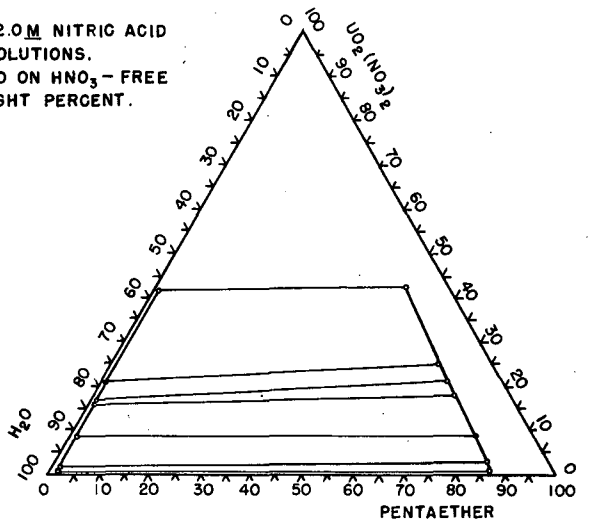
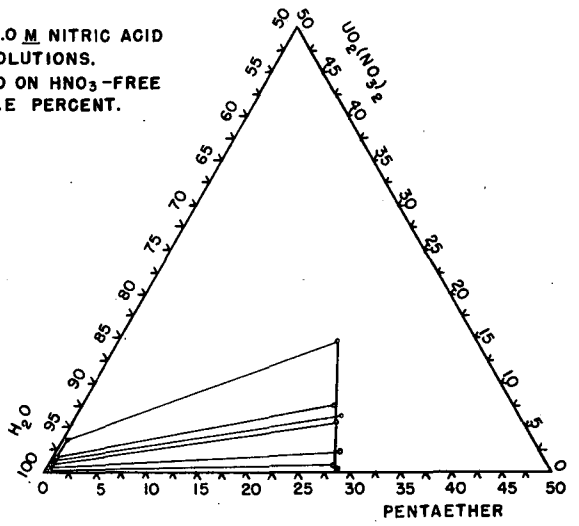
CONSTANT 2.0 M NITRIC ACID IN STOCK SOLUTIONS. CALCULATED ON $HNO_3$ - FREE BASIS. WEIGHT PERCENT.




PENTAETHER-URANYL NITRATE-NITRIC ACID-WATER SYSTEM

FIG. 10

CONSTANT 2.0 M NITRIC ACID IN STOCK SOLUTIONS. CALCULATED ON $HNO_3$-FREE BASIS. MOLE PERCENT.




PENTAETHER-URANYL NITRATE-NITRIC ACID-WATER SYSTEM

FIG. 11

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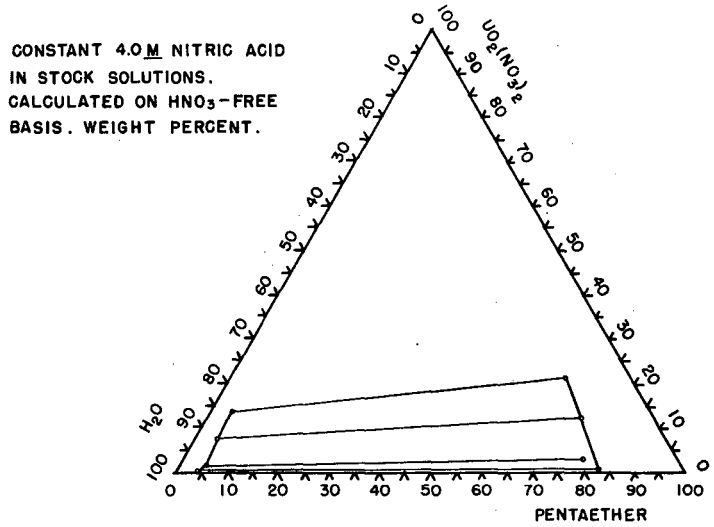
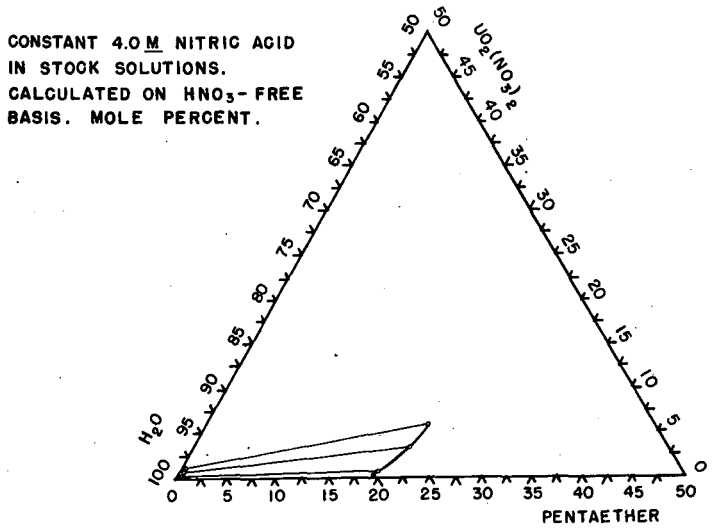



PANTAETHER-URANYL NITRATE - NITRIC ACID- WATER SYSTEM
FIG. 12




PANTAETHE-URANYL NITRATE-NITRIC ACID-WATER SYSTEM
FIG. 13

Mu 125

14754-1

Table VI

Pentaether-Uranyl Nitrate-Nitric Acid-Water Systems

| Soln. No. | Composition Stock Solution | | Aqueous Phase | | | | | Organic Phase | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | M $UO_2(NO_3)_2$ | M $HNO_3$ | Density | Wt.% $UO_2(NO_3)_2$ | Wt.% $HNO_3$ | Wt.% $H_2O$ | Wt.% Penta-ether | Density | Wt.% $UO_2(NO_3)_2$ | Wt.% $HNO_3$ | Wt.% $H_2O$ | Wt.% Penta-ether |
| 1 | 0.10 | 1.00 | 1.044 | 2.42 | 4.32 | 90.6 | 2.67 | 0.975 | 1.41 | 2.31 | 8.14 | 88.1 |
| 2 | 0.50 | 1.00 | 1.110 | 9.79 | 3.66 | 82.7 | 3.88 | 1.043 | 8.65 | 2.48 | 9.13 | 79.7 |
| 3 | 1.00 | 1.00 | 1.184 | 16.8 | 3.37 | 75.7 | 4.10 | 1.118 | 17.6 | 2.46 | 9.53 | 70.5 |
| 4 | 1.12 | 1.00 | 1.206 | 17.9 | 2.99 | 75.1 | 4.06 | 1.115 | 20.1 | 2.38 | 9.51 | 68.0 |
| 5 | 0.10 | 2.00 | 1.061 | 1.81 | 7.31 | 89.8 | 1.10 | 1.014 | 2.09 | 5.05 | 12.0 | 80.8 |
| 6 | 0.50 | 2.00 | 1.126 | 7.96 | 6.87 | 84.1 | 1.03 | 1.084 | 8.18 | 4.72 | 11.1 | 76.0 |
| 7 | 1.00 | 2.00 | 1.196 | 14.8 | 6.63 | 77.7 | 0.96 | 1.170 | 18.1 | 4.25 | 10.4 | 67.3 |
| 8 | 1.12 | 2.00 | 1.227 | 16.4 | 6.25 | 76.4 | 0.94 | 1.192 | 20.1 | 4.02 | 10.0 | 65.8 |
| 9 | 1.37 | 2.00 | 1.262 | 19.6 | 6.17 | 73.3 | 0.91 | 1.228 | 23.8 | 3.83 | 10.0 | 62.4 |
| 10 | 1.37+ | 2.00 | 1.578 | 40.3 | 3.94 | 55.0 | 0.79 | 1.461 | 41.6 | 1.78 | 8.32 | 48.3 |
| 11 | 0.10 | 4.00 | 1.087 | 1.29 | 14.1 | 80.1 | 4.46 | 1.038 | 2.19 | 10.9 | 16.5 | 70.4 |
| 12 | 0.50 | 4.00 | 1.125 | 6.17 | 13.9 | 76.1 | 3.84 | 1.115 | 10.6 | 9.09 | 13.5 | 66.8 |
| 13 | 1.00 | 4.00 | 1.204 | 11.7 | 14.1 | 70.6 | 3.59 | 1.190 | 19.5 | 8.44 | 11.6 | 60.4 |

The change in the slopes of the equilibrium tie lines in Figures 8 through 13 indicates enhanced extraction of uranyl nitrate with increasing acid concentrations. That this is true is shown in Fig. 14 which shows the uranium distribution at the different acid concentrations. The effect of acid is particularly evident at the low concentrations of uranyl nitrate which enters the organic phase preferentially with acid concentrations of greater than 1.0M. The salting effect of nitric acid is also illustrated by the increasing distribution ratios of 0.99, 1.17, and 1.65 for 1.0M, 2.0M, and 4.0M initial nitric acid concentrations, respectively. The ease of stripping uranium from pentaether with water is illustrated by the curve for zero nitric acid.

Further calculations were also made on a uranyl nitrate-free basis for the systems having the same total uranyl nitrate concentration, normalizing the remaining three components, nitric acid, pentaether, and water. Solutions 1, 5, and 11 were used for Fig. 15 which presents the phase diagram (in weight percent) of the 1.0M nitric acid system on this basis. The same system on a mole percent basis is presented in Fig. 16. Similar diagrams determined from solutions 2, 6, and 12 and from solutions 3, 7, and 13 gave almost identical points.

A comparison between Figures 3 and 15 reveals that the presence of uranyl nitrate produces very little change in the distribution of nitric acid which indicates little or no direct coordination between nitric acid and the uranyl nitrate in the organic phase.

In Fig. 17 the distribution of nitric acid as a function of initial uranium concentration shows that increased concentrations of uranyl nitrate force more nitric acid into the organic phase at low acid concentrations. At high acid concentrations the trend is reversed with the acid being forced back into the aqueous phase. This clearly indicates a mutual salting effect, with the uranyl nitrate being extracted preferentially.

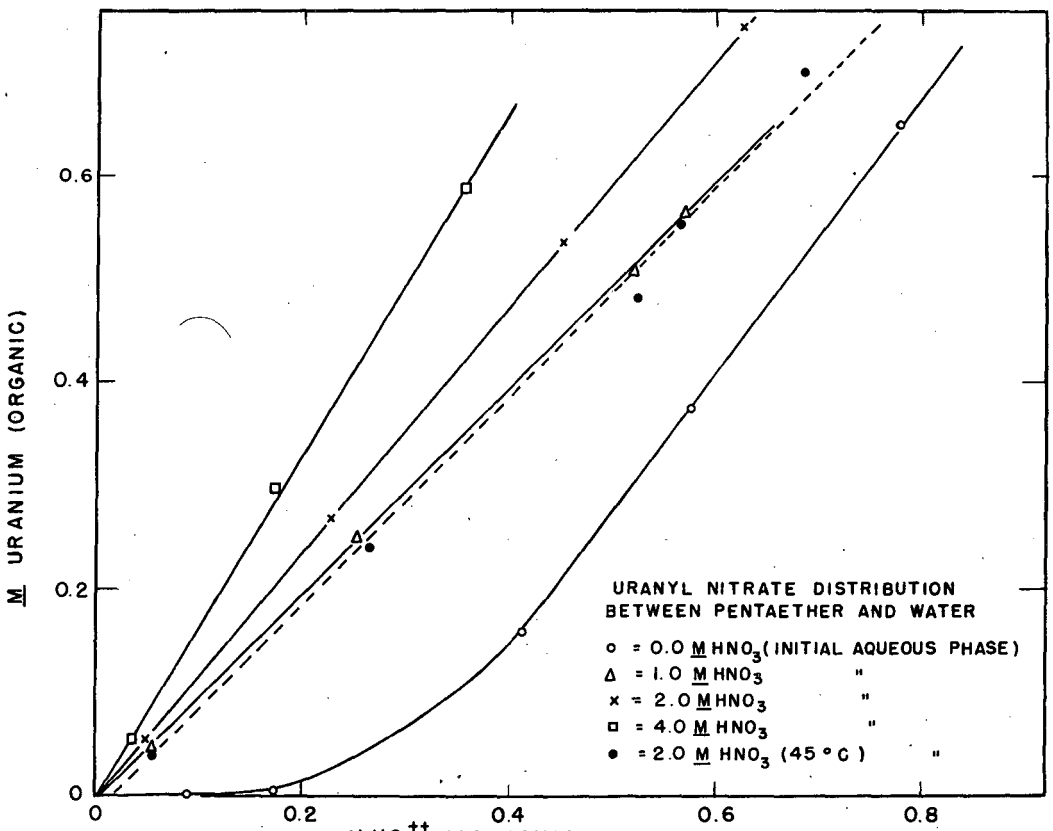
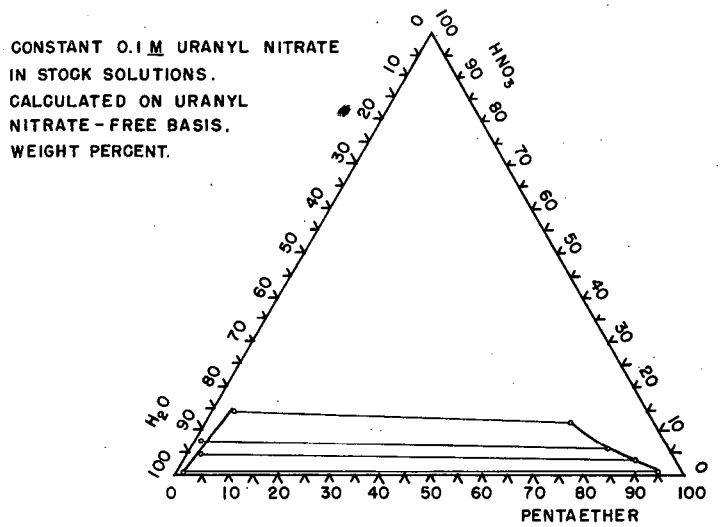
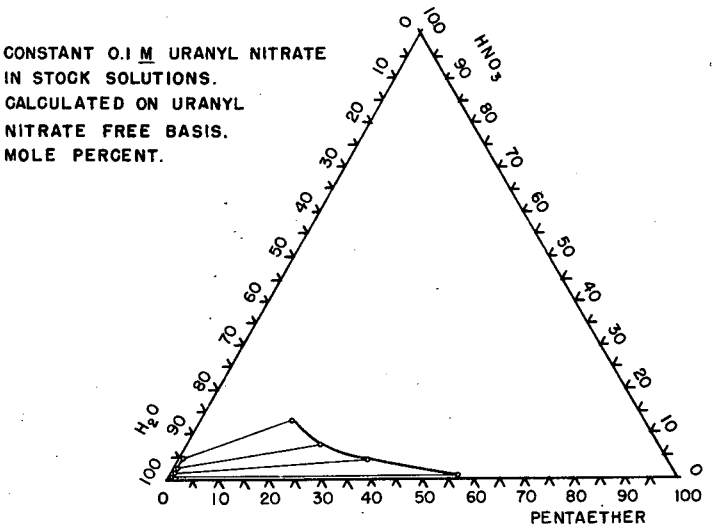



FIG. 14 Mu 126 14755-1




PENTAETHER-URANYL NITRATE-NITRIC ACID-WATER SYSTEM

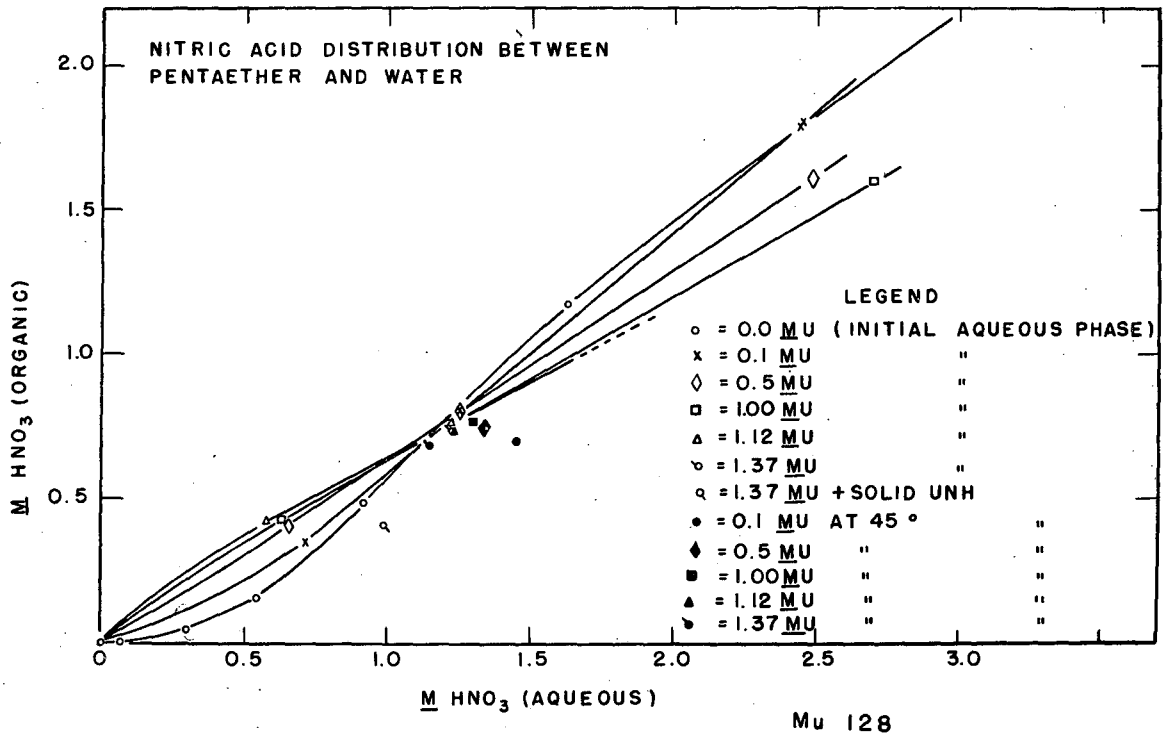
FIG. 15




PENTAETHER-URANYL NITRATE-NITRIC ACID-WATER SYSTEM

FIG. 16

Mu 127 14756-1




Mu 128

FIG. 17

14757-1

## D. Saturation of Pentaether with Uranyl Nitrate

All the systems discussed thus far were studied below the saturation point of uranyl nitrate in pentaether, although this point was approached in some of the systems. To further study this region solid uranyl nitrate hexahydrate was dissolved in pentaether at 25°C. until saturation was reached. The uranyl nitrate concentration of the organic phase at this point was 3.6M with the pentaether concentration being 2.1M. No measurement was made of the water concentration in the organic phase.

These data indicate that in this solution 1.7 moles of uranyl ion are associated with each mole of pentaether. This indicates that more than one atom of oxygen per molecule of pentaether is effective in extracting uranyl nitrate.

## E. Temperature Studies

To study the effect of temperature on the system pentaether-nitric acid-uranyl nitrate-water the 2.0M total initial nitric acid series (see Table VI and Figures 10 and 11) was repeated at 45°C. The data for this study are presented in Table VII.

Table VII

Pentaether-Uranyl Nitrate-Nitric Acid-Water System (45°C.)

| Aqueous Phase | | | | | Organic Phase | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Density | Wt.% $UO_2(NO_3)_2$ | Wt.% $HNO_3$ | Wt.% $H_2O$ | Wt.% Pentaether | Density | Wt.% $UO_2(NO_3)_2$ | Wt.% $HNO_3$ | Wt.% $H_2O$ | Wt.% Pentaether |
| 1.057 | 1.96 | 8.68 | 86.8 | 2.59 | 0.969 | 1.77 | 4.50 | 6.97 | 86.8 |
| 1.126 | 9.30 | 7.49 | 80.5 | 2.69 | 1.033 | 9.23 | 4.59 | 7.81 | 78.4 |
| 1.209 | 17.1 | 6.46 | 74.5 | 1.97 | 1.114 | 17.1 | 4.32 | 7.83 | 70.8 |
| 1.235 | 17.4 | 6.29 | 74.4 | 1.97 | 1.129 | 19.3 | 4.13 | 7.80 | 68.7 |
| 1.278 | 21.1 | 5.68 | 71.4 | 1.89 | 1.176 | 23.5 | 3.68 | 7.87 | 65.0 |

It may be seen from Figures 18 and 19 that considerably less water enters the organic phase at this temperature. The amount of pentaether entering the aqueous phase remains essentially unchanged.

A comparison of Figures 11 and 19 indicates a shift in the uranyl nitrate distribution toward the aqueous phase at the higher temperature. This is more clearly illustrated by the 45°C. line in Fig. 14, the slope of the line being less than the 1.0M total initial nitric acid line at 25°C. A similar effect is noticed for nitric acid which is also forced toward the aqueous phase. These points are included in Fig. 17 and lie in the same order as the corresponding points at 25°C.

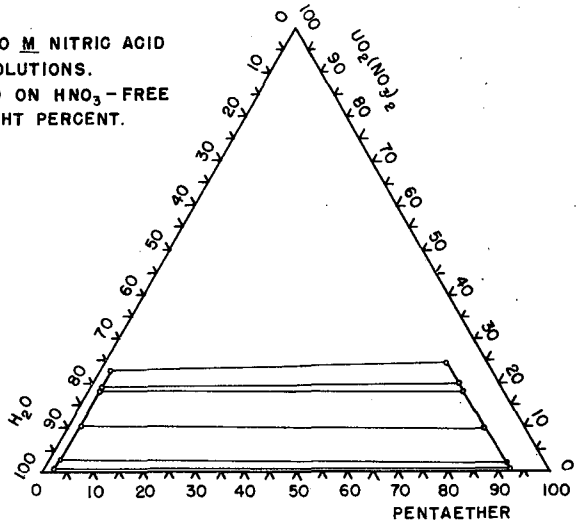
As previously noted, phase separation was always quick and complete in spite of the small density differences between phases. It may be seen from a comparison of Tables VI and VII that the density differences are greater at the higher temperature. This trend, coupled with the change in distribution ratio at temperatures above room temperature, would facilitate "stripping" operations, i.e., the transfer of uranium from pentaether back into water.

From thermodynamic considerations and the data at these two temperatures an order of magnitude for the $\Delta H$ of extraction may be estimated. Such estimations indicate the $\Delta H$ for extraction of uranyl nitrate by pentaether is approximately -5 to -10 Kcal/mole. Preliminary calculations based on qualitative data (temperature rise of extraction/specific heat x number of moles transferred) give the same order of magnitude.

Similar calculations indicate the $\Delta H$ for extraction of nitric acid is approximately -10 to -15 Kcal/mole. Therefore, heat is evolved in extraction and is absorbed in stripping operations.

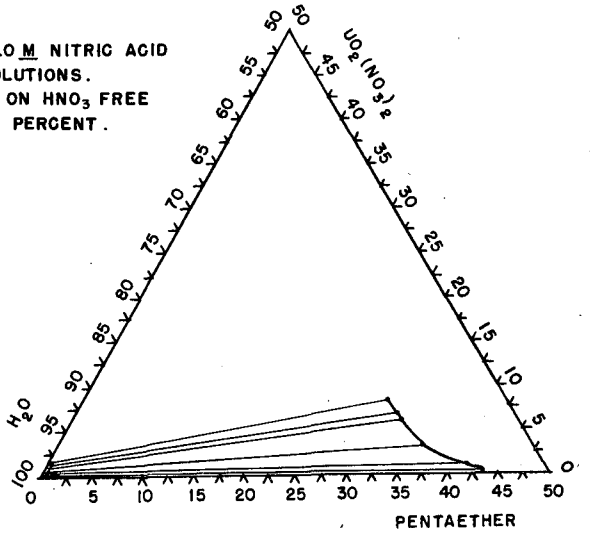
The saturation of pentaether with uranyl nitrate was also studied at 45°C. by dissolving solid uranyl nitrate hexahydrate in the solvent. The uranyl

CONSTANT 2.0 M NITRIC ACID IN STOCK SOLUTIONS. CALCULATED ON $HNO_3$-FREE BASIS. WEIGHT PERCENT.




PENTAETHER-URANYL NITRATE-NITRIC ACID-WATER SYSTEM (45°C.)
FIG. 18

CONSTANT 2.0 M NITRIC ACID IN STOCK SOLUTIONS. CALCULATED ON $HNO_3$ FREE BASIS. MOLE PERCENT.




PENTAETHER-URANYL NITRATE-NITRIC ACID-WATER SYSTEM (45° C.)
FIG. 19

Mu 129 14758-1

nitrate concentration was found to be 2.1M with the pentaether concentration 1.9M. This indicates that 1.1 moles of uranyl ion are associated with each mole of pentaether which is a further indication that more than one atom of oxygen per molecule of pentaether is effective in the extraction process.

## IV. SUMMARY AND CONCLUSIONS

The liquid-liquid equilibria of the system pentaether-uranyl nitrate-nitric acid-water have been studied by equilibrating aqueous solutions of uranyl nitrate hexahydrate and nitric acid with pentaether. In these initial aqueous solutions nitric acid concentrations from 0.0M to 8.2M and uranyl nitrate concentrations from 0.0M to 2.3M were covered. The effects of nitric acid concentration, uranyl nitrate concentration, and temperature are discussed.

The following conclusions have been reached:

1. Nitric acid, probably as $NO_3^-$, acts as a salting agent primarily in accordance with the equation:

$$UO_2^{++}\ (aq.) + 2NO_3^-\ (aq.) = UO_2(NO_3)_2\ (org.).$$

2. Competition exists between water, nitric acid, and uranyl nitrate for the coordinative positions of the pentaether, i.e., for the oxygen atoms in the pentaether molecule. This conclusion is based on the following points:

   a. The decrease in water concentration at high uranyl nitrate or nitric acid concentrations.

   b. Similar competition in the system pentaether-TTA-nitric acid-water.[20]

   c. The decrease in nitric acid concentration in the organic phase with increasing uranyl nitrate concentration, the initial nitric acid concentration remaining constant.

   d. Saturation experiments show that in concentrated solutions one pentaether is coordinated to more than one uranyl ion.

3. There is evidence that four molecules of water accompany each uranyl ion into the organic phase. No further identification of the species extracting was made.

4. The feasibility of the use of pentaether as a possible solvent for processing uranium has been demonstrated by the following points:

a. The solvent is sufficiently immiscible with water.

b. Suitable extraction coefficients for uranyl nitrate can be obtained with the use of 1-2M $HNO_3$ as a salting agent.

c. The salting effects of $HNO_3$ indicate that stripping uranyl nitrate from pentaether with water is a feasible operation.

d. Density differences are small, increasing with temperature. Other work[21] indicates these density differences are sufficient for operation in contacting equipment. Phase separation was always sufficiently quick and complete in these experiments.

# APPENDIX

## ANALYTICAL METHODS

### Uranium

After equilibration, aliquots of each phase were placed in ignited, weighed crucibles and were evaporated, ignited at 850°C., and weighed as $U_3O_8$. The $U_3O_8$ obtained by this method from weighed samples of pure uranium nitrate hexahydrate agreed with the calculated amount within ±0.001 millimole.

### Nitric Acid

The acid concentration of both phases was determined by the oxalate method of Shepard, Ice, and Alkire.[19] To the sample aliquot was added sufficient potassium oxalate (solution) to complex the uranium. After vigorous stirring at 0°C., the glass and calomel electrodes were placed in position and the solution was titrated potentiometrically with standard sodium hydroxide.

Material balances checked within ±1%.

### Water

The water concentration of the organic phase was determined with the standard Karl Fischer reagent ($I_2$, $SO_2$, pyridine and methanol) using a magic eye deadstop titrimeter similar to that of Mitchell and Smith.[18] Methanol was added to aliquots of the samples and the mixture titrated to the endpoint with Fischer reagent. An excess of reagent was then added and the solution back-titrated with standard water-in-methanol, since this endpoint is more accurate and more reproducible.

The reagent was standardized daily, originally against a known mixture of water and absolute methanol. Later, sodium acetate trihydrate (crystalline) was adopted as the primary standard. A similar choice has been made by others.[22,23,24]

To check the applicability of the method to the uranium nitrate-nitric acid-pentaether-water system weighed samples of pure uranium nitrate hexahydrate were dissolved in methanol, and the water of hydration titrated in the usual manner. In addition, known solutions of uranium nitrate hexahydrate in pentaether, nitric acid in pentaether, and uranium nitrate hexahydrate and nitric acid in pentaether were titrated similarly. In all cases the value obtained agreed with the calculated value within ±1%.

The water concentration of the aqueous phase was calculated from specific gravity values.

## Pentaether

Aliquots of the aqueous phase were equilibrated with benzene for one hour at 25°C. The refractive index of the benzene phase was then measured at 25°C. (using a standard tungsten lamp), and the concentration of pentaether in the aqueous phase was calculated from a calibration curve of the system benzene-pentaether. This method was found to be reproducible within ±1%. No correction was made for decomposition products in the solvent, since the same cut was used throughout the study.

The pentaether concentration of the organic phase was calculated from specific gravity values and volume changes.

The work described in this report was performed under the auspices of the Atomic Energy Commission.

BIBLIOGRAPHY

1. C. N. Stover, Jr., H. W. Crandall, D. C. Stewart, and P. C. Mayer, "Survey of Solvents for Uranium Extraction Without Salting Agents," UCRL-576, January 13, 1950.

2. D. C. Stewart, "Solubility of Plutonium in Organic Solvents; Partition with Aqueous Media," NNES-PPR Vol. 14A, Ch. V (Oct. 1946)(to be issued).

3. L. Yaffe, J. Herbert, and C. E. Mackintosh, "Solvents for Uranium Extraction," M-2305, May 21, 1945.

4. R. H. Smellie, Jr. and D. P. Krause, "Solvent Extraction," B-4.380.216, July 16, 1947.

5. E. F. Orleman and A. G. Jones, "The Use of Pentaether for the Analytical Determination of Uranium," C-4.360.3 (1945).

6. Orleman, "The Efficiency of the Pentaether Extraction of Small Amounts of Uranium," CD-2233 (1945).

7. C. A. Krause, "Determination of Uranium by Extraction Methods," BT-40 (A-2301).

8. Orleman, "Progress Report, Department 192," CD-2213 (1945).

9. C. C. Casto, "Division of Chemical Research and Development Period Progress Report," C-4.100.26 (1946).

10. Casto, "Division of Chemical Research and Development Period Progress Report," C-4.100.27 (1946).

11. A. V. Henrickson and D. F. Musser, "Adaptations of the Standard Pentaether Procedure for Determination of Uranium in Salvage Operations," B-4.360.1 (1945).

12. Orleman, "Division of Chemical Research and Development Period Progress Report," CD-2253 (1945).

13. W. R. Grimes, ibid., C-4.100.29 (1946).

14. J. E. Powell and A. S. Newton, CC-2293 (1945).

15. Orleman, "Period Progress Report, Department 192," CD-2220 (1945).

16. Orleman, ibid., CD-2224 (1945).

17. Orleman, ibid., CD-2228 (1945).

18. Mitchell and Smith, "Aquametry," Interscience Publishers, Inc., N. Y. (1948).

19. D. F. Shepard, G. H. Ice, and G. J. Alkire, "A Modified Oxalate Method for Determination of Free Nitric Acid in Redox Solutions," HW-10828, August 31, 1948.

20. D. L. Heisig and H. W. Crandall, report in printing.

21. B. Rubin and H. R. Lehman, private communication.

22. Leonard I. Katzin and James C. Sullivan, "The System Uranyl Nitrate-Water-Organic Solvent," AECD-2537, December, 1948.

23. Katzin and Sullivan, "Form of Uranyl Nitrate Extracted from Aqueous Solution by Organic Solvents," ANL-4145, May 5, 1948.

24. G. G. Warren, Can. Chem. Process Inds., 29, 370 (1945).

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