

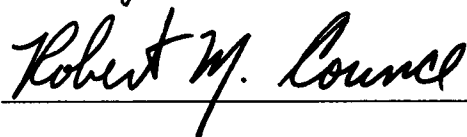
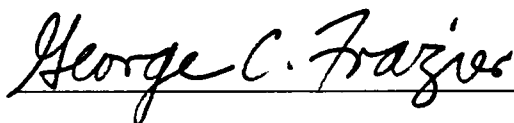
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Frederick E. Weber, Major Professor

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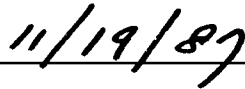
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A MATHEMATICAL MODEL FOR EQUILIBRIUM DISTRIBUTION OF
URANIUM(VI), PLUTONIUM(IV) AND NITRIC ACID IN
PUREX SOLVENT EXTRACTION PROCESSES

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Joon-Hyoun Lee
December 1987

DEDICATION

Dedicated to my parents, Ki-Seong Lee and Ki-Ja Lee,
and to my brother, Tai-Hyoun Lee,
whose encouragement, support and patience
made this study possible.

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I wish to express my sincere gratitude to Dr. Frederick E. Weber, Assistant Professor of Chemical Engineering, under whose direction this study was carried out, for his guidance, advice and support from the start to the completion of this study.

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ABSTRACT

A total of 351 data points for distribution of uranium(VI), plutonium(IV) and nitric acid between aqueous nitric acid solutions containing these components and organic solutions of 20 volume percent tri-n-butyl phosphate (TBP) in a normal paraffin hydrocarbon diluent were collected from the available literature and systematically screened to prune erroneous data.

The seven parameters for nitric acid distribution in a mathematical model for equilibrium distribution of uranium(VI), plutonium(IV) and nitric acid between aqueous nitric acid solution of the components and organic solution of TBP in an aliphatic diluent were re-evaluated using the minimum variance location procedure. With the new parameter values, the prediction for nitric acid distribution coefficients was improved.

A nonlinear simultaneous regression procedure was then used to re-estimate all 21 parameters, except those for TBP concentration effects, in the mathematical model. The coefficients of determination for plutonium and nitric acid were improved, but there was little change in the coefficients for uranium. The use of the nonlinear simultaneous regression procedure to construct an empirical model for equilibrium distribution of uranium(VI), plutonium(IV) and nitric acid was demonstrated.

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INTRODUCTION

Since only a few percent of the fissionable content of nuclear power reactor fuel is consumed during power generation, recycle of the unused portion is economically attractive. Fuel recycle involves the separation of unused uranium and plutonium from fission products and the subsequent purification and refabrication into new fuel elements.

One of the main steps in the reprocessing of an irradiated nuclear fuel is the solvent extraction process. The Purex (Plutonium Uranium Recovery by EXtraction) process was developed for the reprocessing of natural or slightly enriched uranium power reactor fuels and has been widely used for nearly three decades. The process uses tri-n-butyl phosphate (TBP) as an extractant.

The development of such solvent extraction processes for reprocessing spent nuclear power reactor fuels is difficult and costly because of the required containment and radiation shielding. If a reliable mathematical model for such process is available, testing to establish optimum values for operating parameters for solvent extraction treatments of fuel solutions can be minimized through the use of computer modeling of the process. For instance, the number of experimental runs required to establish flowsheet conditions can be reduced by simulating the extraction process, and experimentation is then required to verify a small fraction of the computer-predicted results.

Construction of a mathematical model for the Purex solvent extraction process needs both equations of material balance for each component in the system and an equilibrium distribution model for these components. The formulation of the equations of material balance usually does not present any difficulties. The main problem in the mathematical simulation of the process has been associated with the equilibrium

distribution model. Performance of the computer simulation depends largely on the accuracy of the equilibrium distribution model.

Activities or activity coefficients of the components in the aqueous and organic phases, which are needed for the equilibrium distribution expression, have not been able to be fully described because of the apparent nonideality of the solutions. Therefore, empirical equilibrium distribution models have been used in practice. Richardson's model is one of them and accurately predicts uranium distribution coefficients but less accurately plutonium and nitric acid distribution coefficients. Its corrected later version improved the prediction for plutonium distribution coefficients, but the prediction for nitric acid distribution coefficients is still inaccurate.

The goals of this study are (1) to correct Richardson's model for a better description of nitric acid distribution by minimizing the variance between experimental and calculated distribution coefficients of nitric acid, and (2) to further improve the model by re-estimating the parameters with a nonlinear simultaneous regression procedure.

CHAPTER 1

PUREX SOLVENT EXTRACTION PROCESSES

1.1 History of Nuclear Fuel Reprocessing

Separation of microgram quantities of plutonium from irradiated uranium was first conducted at the Chicago Metallurgical Laboratory of the Manhattan Project by the method of carrier precipitation, called the Bismuth Phosphate process, during World War II. The process was then put into operation for large-scale recovery of plutonium from irradiated fuel at Hanford, Washington, in early 1945. Serious disadvantages of the process were the inability to recover uranium, batch operation, the large amount of process chemicals used and the large volume of wastes[1,2].

The first successful solvent extraction process for large-scale separation of both uranium and plutonium, called the Redox process, was developed at the Argonne National Laboratory soon after World War II. In the Redox process hexone (methyl isobutyl ketone) was used as the organic solvent. Because of the instability of the hexone to attack by concentrated nitric acid, aluminium nitrate was used as the salting agent in the aqueous phase. Large-scale operation of the process began at Hanford in 1952. Advantages of the process over the Bismuth Phosphate process were continuous operation, a large decrease in waste volume and the ability to recover uranium as well as plutonium though it still had disadvantages of the volatility and flammability of the hexone solvent and the large amount of nonvolatile reagents such as aluminium nitrate added to the radioactive wastes[1-3].

While the Redox process was still under development, an improved solvent extraction process, called the Purex process, was developed at Knolls Atomic Power Laboratory and at the Oak Ridge National Laboratory from 1948 to 1950. The Purex

process uses tri-n-butyl phosphate (TBP) diluted in normal paraffin hydrocarbon as the organic solvent. Since TBP is stable in the presence of nitric acid, the process uses nitric acid as the salting agent in the aqueous phase, rather than the aluminium nitrate in the Redox process. The use of nitric acid lowers the waste volume as the nitric acid can be removed from the waste by evaporation and recycled. An undesirable feature of nitric acid is its extractability with TBP, which results in a change of salting strength in the aqueous phase and a decrease of the available, uncomplexed TBP[1]. This new process was put into operation at the Savannah River plant at Aiken, South Carolina in 1954, and its successful operation there led to replacement of the Redox process by the Purex process at Hanford in 1956. The Purex process, with modifications, can be used to reprocess spent fuels from the Liquid-Metal Fast-Breeder Reactor (LMFBR) which are characterized by the higher contents of plutonium (about 20 percent Pu) and radioactive fission products[6]. Several modified Purex processes have been developed for the reprocessing of different types of spent nuclear reactor fuels. The Purex process has four significant advantages over the Redox process[1-3]:

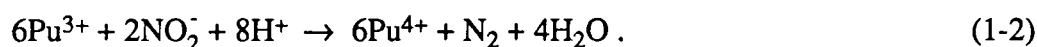
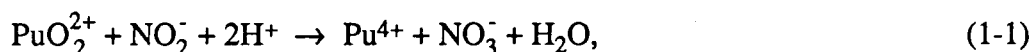
- (1) Waste volumes can be reduced greatly because of employing nitric acid as salting agent which can be removed by evaporation;
- (2) The solvent, TBP, is less volatile and less flammable than hexone;
- (3) TBP is more stable against attack by nitric acid;
- (4) Operating costs are lower.

1.2 Purex Solvent Extraction Flowsheet

Purex solvent extraction processes[1-5] have been widely used to recover both uranium and plutonium from irradiated natural or slightly enriched uranium fuels. Modified Purex processes such as the TBP-25 process, TBP-23 process and Thorex process have been developed for reprocessing spent fuels from different reactor types.

The TBP-25 process with TBP concentration of about 7 volume percent in a hydrocarbon diluent, instead of 30 volume percent TBP for the standard Purex process, has been used to reprocess highly enriched U-235 reactor fuels in which only traces of plutonium are formed, and TBP-23 and Thorex processes were developed for reprocessing thorium-based reactor fuels[7-11].

1.2.1 Fuel Dissolution and Feed Adjustment. A schematic flowsheet of the Purex solvent extraction cycles is shown in Figure 1. Spent fuels, after several months "cooling" period, are charged to a dissolver where the fuels are reacted with nitric acid at near-boiling temperature. After filtering to remove any remaining solids, the acidity of the dissolver solution is adjusted by the addition of nitric acid to the feed adjustment tank. In this step, plutonium is converted to plutonium(IV), which is most extractable with TBP, by the controlled addition of sodium nitrite (NaNO_2). Nitrite ion has the valuable property of reducing plutonium(VI) to plutonium(IV) and of oxidizing plutonium(III) to plutonium(IV) by following reactions[1]:



Since sodium nitrite adds nonvolatile material to the aqueous phase, N_2O_4 or hydroxylamine nitrate (HAN) are now favored[2].

1.2.2 Uranium and Plutonium Co-Extraction. Uranyl nitrate, plutonium nitrate and fission products in the aqueous phase enter the co-extraction bank near the midpoint and the organic extractant, TBP, diluted in normal paraffin hydrocarbon, enters the bottom of the bank. The uranium and plutonium are extracted into the organic phase by complexing with TBP, leaving most of the fission products and impurities in the aqueous phase. After extracting the uranium and plutonium, the organic phase, which

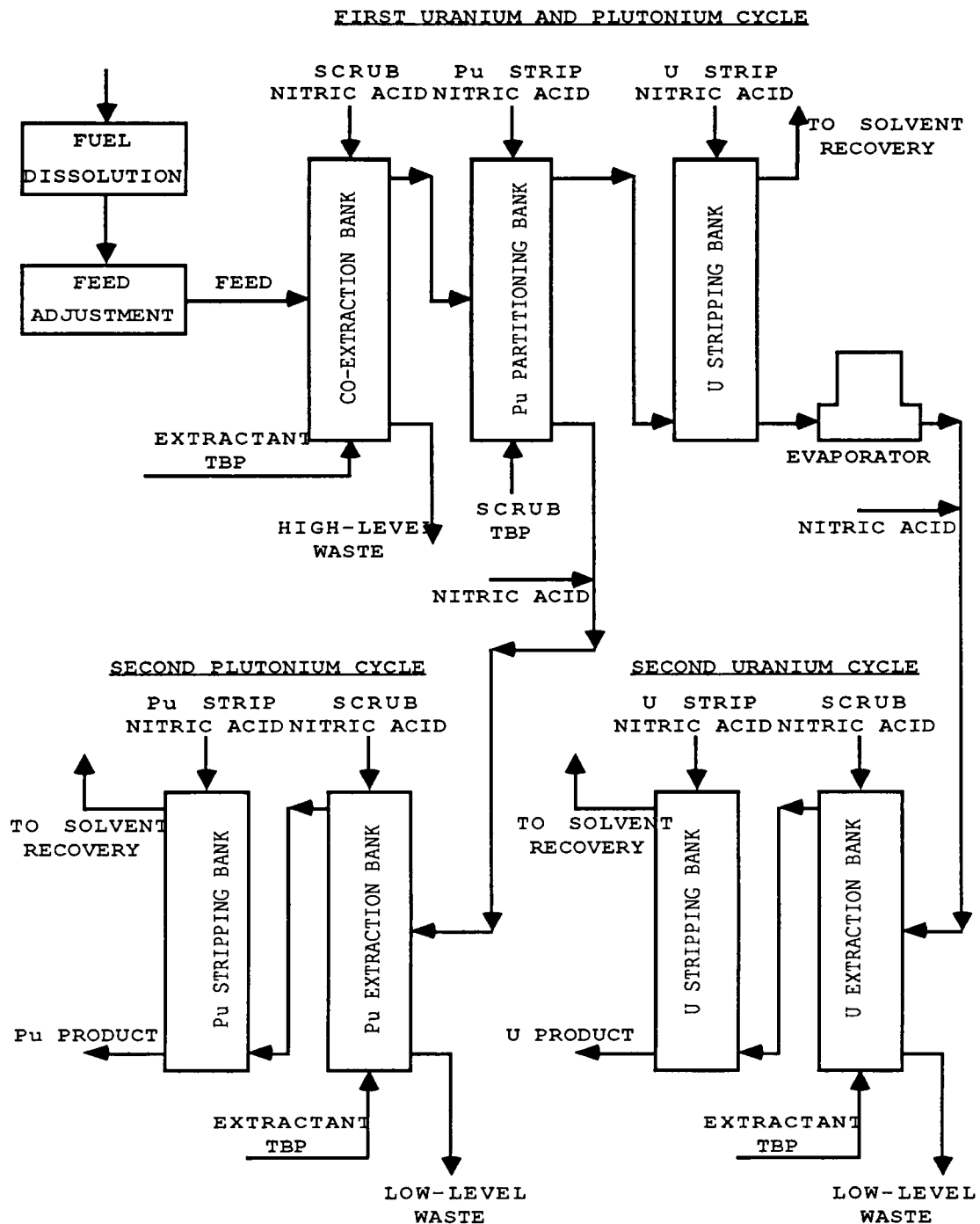
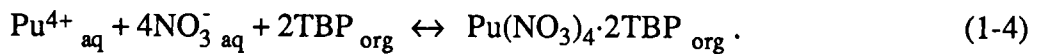
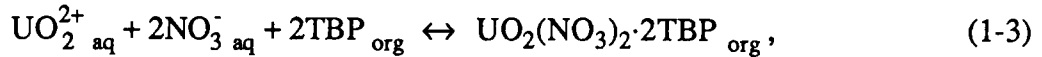


Figure 1. Schematic Flowsheet of the Purex First and Second Solvent Extraction Cycles.

is nearly saturated with the uranium, is scrubbed in the upper part of the bank with nitric acid solutions to backwash any extracted fission products before it flows into the uranium and plutonium partitioning bank. The reactions of uranyl nitrate and plutonium nitrate with TBP are:



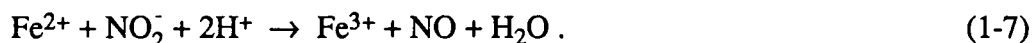
The extraction conditions are controlled for maximum uranium and plutonium and minimum fission products extraction. A high degree of saturation of the organic phase with uranium and plutonium is favored to maximize uranium and plutonium extractions and to restrict fission products extraction. Zr-95, Ru-103, Ru-106 and Nb-95 have been the most troublesome fission products in the Purex solvent extraction processes[12]. Since Nb-95, by itself, does not extract into TBP to any significant extent if silicates are not present[13], its extraction can be reduced by removing silicon with an adequate gelatin head-end treatment. Since the kinetics of Zr-95 and Ru-103 and Ru-106 complexing reactions with TBP are relatively slow compared to uranium and plutonium, rapid extraction such as in centrifugal contactors and slow scrubbing such as in mixer-settlers greatly improves the decontamination from the zirconium and ruthenium. Also, rapid extraction contactors are used for the uranium and plutonium co-extraction to minimize solvent degradation from the intense fission products radioactivity. The co-extraction contactors are usually run at or near room temperature, to reduce the solvent degradation and because the uranium extraction is better at lower temperatures, and the scrubbing contactors are operated at higher temperature, around 60 °C, because the decontamination of ruthenium is more complete at higher temperatures[14].

1.2.3 Uranium and Plutonium Partitioning. In the partitioning bank plutonium is separated from uranium by reducing the plutonium from the tetra-valent state to the tri-valent state, which is relatively inextractable to TBP, by addition of a reductant to the plutonium stripping stream, introduced at the top of the bank, with sufficient nitric acid to keep the uranium almost quantitatively in the organic phase. TBP scrubbing solution is introduced at the bottom of the bank to re-extract any uranium which is stripped from the organic solvent into the aqueous stream with the plutonium.

The reductant which has been widely used for plutonium reduction is ferrous sulfamate ($\text{Fe}(\text{NH}_2\text{SO}_3)_2$). Ferrous ion rapidly reduces plutonium(IV) to plutonium(III) even in moderately strong nitric acid, which assures a clean separation from uranium, and sulfamate ion, which is known as a "holding reductant", rapidly destroys the nitrite ions generated as a result of radiolysis of nitrates[13],

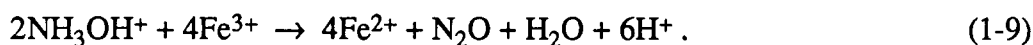
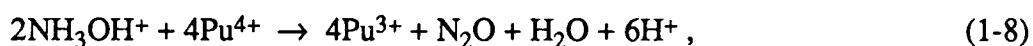


thus minimizing unwanted oxidation of ferrous ion and plutonium(III),



The major disadvantage of ferrous sulfamate is that it adds considerably to the waste volume. Use of hydroxylamine nitrate (HAN)[15,16] and uranous ion (U^{4+})[17] as plutonium(IV) reductants has been studied to resolve this problem. These reductants require addition of hydrazine (N_2H_4) as a holding reductant, and none of these chemical contributes solids to the waste. Slow reduction kinetics for plutonium(IV) with uranium(IV) and the relatively poor stability of uranium(IV) may cause problems in full scale operation, and this technique has thus far not been demonstrated in full scale equipment. Plutonium reduction with HAN is much slower so that sufficient residence

time must be provided for the reduction to proceed to completion. Mixtures of HAN and ferrous sulfamate have been used for plutonium reduction[13], and the waste volume due to ferrous sulfamate has been greatly reduced. It was also found that HAN reduces not only plutonium(IV) but also Fe^{3+} ,



Cathodic reduction of plutonium(IV) is another technique to reduce plutonium(IV) without adding solids to waste volume, but it requires a novel, electrolytic reduction-extraction contactor.

The aqueous plutonium solutions from the partitioning bank continuously flows to the second plutonium cycle, and the organic uranium solutions is fed to the bottom of the uranium stripping bank, where the uranium is stripped back to the aqueous phase by 0.01 M nitric acid solutions.

1.2.4 Second Uranium Cycle. The aqueous uranium product solutions from the first cycle are concentrated by evaporation and adjusted to the proper feed concentration by addition of nitric acid before they are fed to the second uranium cycle. The concentrated uranium solution is introduced near the midpoint of the uranium extraction bank, and the uranium is extracted with TBP to the organic phase and scrubbed with nitric acid stream. The uranium in the organic phase is stripped back to the aqueous phase by 0.01 M nitric acid stripping stream in the stripping bank. The aqueous uranium product solution is concentrated again by evaporation, and further purification is achieved by passing the concentrated uranium solution through a silica gel bed, which absorbs remaining fission products.

1.2.5 Second Plutonium Cycle. The aqueous plutonium product solution is treated with sodium nitrite to destroy any plutonium(IV) reductants still present and to re-oxidize plutonium(III) to plutonium(IV). It is then adjusted to the appropriate salting strength with nitric acid before it is fed to the second plutonium cycle. In the plutonium extraction bank, plutonium is extracted with TBP, together with still remaining trace uranium, into the organic phase and scrubbed with a nitric acid stream, introduced at the top of the bank, to backwash any extracted fission products. The plutonium is again stripped from the organic phase by reducing plutonium(IV) to plutonium(III) with ferrous sulfamate or HAN in the plutonium stripping stream, which contains a small amount of nitric acid to prevent plutonium(IV) hydrolysis. Further purification is done by anion exchange from nitrate solution or precipitation as plutonium oxalate with oxalic acid.

CHAPTER 2

MATHEMATICAL MODELS FOR DISTRIBUTION EQUILIBRIA IN PUREX SOLVENT EXTRACTION

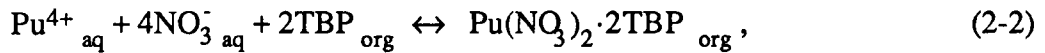
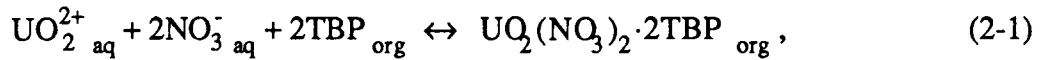
After the high extraction power of TBP for metal nitrates was discovered in 1945[18], enormous work on the equilibrium distribution of uranyl nitrate, plutonium nitrate, nitric acid, water and other metal nitrates was done by researchers from the United States[19-30], Britain[31-46], Russia[47-63] and other countries[64-72]. As a result of their work, the solution chemistry in the aqueous phase is now well known. Considerably less is known about the organic phase which is undoubtedly nonideal except at very low TBP concentrations.

In order to construct a mathematical model in standard thermodynamic terms for the equilibria a good knowledge of the activities or activity coefficients for all the components in a system is necessary. Extensive fundamental work to determine these thermodynamic quantities for uranyl nitrate, nitric acid and TBP has been done[20-26]. The ultimate purpose of the work was to develop a thermodynamically rigorous mathematical model for the distribution behavior of uranyl nitrate, nitric acid, fission products and water between TBP-hydrocarbon diluent solutions and aqueous solutions containing these components[26]. Since activities or activity coefficients for all the components were not available, construction of the thermodynamic mathematical model was not possible.

2.1 Mathematical Model Using Aqueous Total Ionic Strength

Horner[73] developed a mathematical model to estimate the distribution coefficients of uranium(VI), plutonium(IV) and nitric acid as a function of the equilibrium aqueous phase concentrations of these components and a pseudo-

thermodynamic equilibrium constant of each component. This contained an activity coefficients ratio and was expressed empirically as a polynomial function of the aqueous phase ionic strength. It was assumed that the following reactions were applied to the Purex solvent extraction:



where subscripts aq and org represent aqueous and organic phases respectively. The pseudo-thermodynamic equilibrium constants, K^C , having embedded activity coefficients ratio, are respectively:

$$K_U^C = \frac{[\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}]_o}{[\text{UO}_2^{2+}]_a [\text{NO}_3^{-}]_a^2 [\text{TBP}]_o^2}, \quad (2-4)$$

$$K_{\text{Pu}}^C = \frac{[\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP}]_o}{[\text{Pu}^{4+}]_a [\text{NO}_3^{-}]_a^4 [\text{TBP}]_o^2}, \quad (2-5)$$

$$K_H^C = \frac{[\text{HNO}_3 \cdot \text{TBP}]_o}{[\text{H}^{+}]_a [\text{NO}_3^{-}]_a [\text{TBP}]_o}, \quad (2-6)$$

where the quantities in brackets represent molar concentrations of the reacting species. The subscripts a and o mean the aqueous and organic phases, respectively, and the superscript C means the molar concentration base.

The distribution coefficient, D^C , for each component is defined as the ratio of the concentration of the component in the organic phase to the concentration of the component in the aqueous phase. Thus,

$$D_U^C = \frac{[\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}]_o}{[\text{UO}_2^{2+}]_a} = K_U^C [\text{NO}_3^-]_a^2 [\text{TBP}]_o^2, \quad (2-7)$$

$$D_{\text{Pu}}^C = \frac{[\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP}]_o}{[\text{Pu}^{4+}]_a} = K_{\text{Pu}}^C [\text{NO}_3^-]_a^4 [\text{TBP}]_o^2, \quad (2-8)$$

$$D_H^C = \frac{[\text{HNO}_3 \cdot \text{TBP}]_o}{[\text{H}^+]_a} = K_H^C [\text{H}^+]_a [\text{TBP}]_o. \quad (2-9)$$

The quantity $[\text{TBP}]_o$ is the uncomplexed, "free" TBP concentration and is calculated by material balance as follows:

$$\begin{aligned} [\text{TBP}]_o = T_C - 2[\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}]_o - 2[\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP}]_o \\ - [\text{HNO}_3 \cdot \text{TBP}]_o. \end{aligned} \quad (2-10)$$

Here T_C is the equilibrium molar concentration of the total amount of TBP in the organic phase. T_C differs from the initial TBP concentration, T_S , because of volume changes in the organic phase during extraction of the components. Since proper correction tools for the volume changes was not available, the initial concentration was used in place of T_C , and the error introduced by use of T_S instead of T_C was not significant if TBP saturation ("loading") with the components was less than 90 percent[73]. T_S is calculated from the volume fraction of TBP as follows[73]:

$$T_S = \frac{1000 \rho_{\text{TBP}} F}{266.32}, \quad (2-11)$$

By substituting Eqs. (2-7)-(2-9) into Eq. (2-10) and solving the resulted quadratic equation, an equation for $[\text{TBP}]_o$ as a function of the aqueous phase concentrations of the three components and K_U^C , K_{Pu}^C and K_H^C was obtained.

$[\text{NO}_3^-]_a$ is the total nitrate concentration of the aqueous phase and calculated by:

$$[\text{NO}_3^-]_a = 2[\text{UO}_2^{2+}]_a + 4[\text{Pu}^{4+}]_a + [\text{H}^+]_a. \quad (2-12)$$

The pseudo-thermodynamic constants, K^C 's, were correlated as a polynomial function of aqueous phase total ionic strength, I , as follows:

$$K^C = \alpha_0 + \alpha_1 I + \alpha_2 I^2 + \alpha_3 I^3, \quad (2-13)$$

where α_0 , α_1 , α_2 and α_3 are parameters to be determined. The aqueous ionic strength, I , is defined by:

$$I = \frac{1}{2} \sum_{i=1}^n C_i z_i^2. \quad (2-14)$$

Therefore, from the assumed extraction reactions, Eqs. (2-1)-(2-3),

$$I = 3[\text{UO}_2^{2+}]_a + 10[\text{Pu}^{4+}]_a + [\text{H}^+]_a. \quad (2-15)$$

The values of the parameters α_0 , α_1 , α_2 and α_3 were determined by nonlinear least-square fitting of a set of experimental distribution data to the model. The fitting procedure did not produce the same equations for uranium and plutonium, presumably because of the lack of a high degree of accuracy in the distribution data. Hence, the experimental distribution data for uranium and plutonium were fitted separately. For instance, the uranium distribution data were best described by[73]:

$$K_U^C = 18.39 + 5.114 I - 4.174 I^2 + 1.892 I^3, \quad (2-16)$$

$$K_{\text{Pu}}^C = 3.882 - 0.4838 I + 0.05814 I^2 + 0.006005 I^3, \quad (2-17)$$

$$K_H^C = 0.4841 - 0.1445 I + 0.02216 I^2, \quad (2-18)$$

and the plutonium distribution data were best described by:

$$K_U^C = 12.22 + 3.81 I - 4.798 I^2 + 2.477 I^3, \quad (2-19)$$

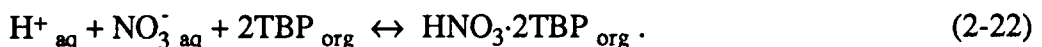
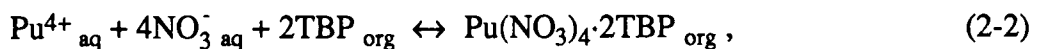
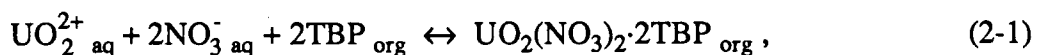
$$K_{\text{Pu}}^C = 2.415 + 0.701 I + 0.05271 I^2 - 0.0333 I^3, \quad (2-20)$$

$$K_H^C = 0.4076 - 0.166 I + 0.03319 I^2. \quad (2-21)$$

Since the fitting of nitric acid distribution data was not successful, the equations fitted to the uranium distribution data was used to calculate the nitric acid distribution coefficients. Later, the parameters were re-evaluated, and the model with new parameter values was adapted to SEPHIS (Solvent Extraction Processes Having Interacting Solutes), a computer code developed to study the transient behavior of countercurrent solvent extraction processes with particular applications to the recovery of spent LMFBR fuels[74]. Similar models, containing the pseudo-thermodynamic equilibrium constants as a polynomial function of the aqueous phase total ionic strength, were developed in West Germany[75-77] and Russia[78].

2.2 Mathematical Model Using Aqueous Total Nitrate Concentrations

Since the equilibrium distribution model in the SEPHIS computer code[74] was restricted to 25 °C and the use of 15 volume percent TBP, a study was initiated to develop a new equilibrium distribution model to extend the code to higher temperatures and TBP concentrations. Richardson[6] found that the pseudo-thermodynamic equilibrium constants used in Horner's work[73] were better correlated as a function of the aqueous total nitrate concentrations, defined in Eq. (2-12), rather than the aqueous phase total ionic strength, and the correlation for nitric acid was improved by assuming that nitric acid forms both mono- and di-solvates with TBP. This has been experimentally confirmed[26,60]. The assumed reactions applied to the Purex solvent extraction were:



Richardson used "solute-free" concentrations (moles solute/liter of solvent), rather than molar concentrations, for use in the correlation because molar concentrations of components change as the solution volume changes during the extraction process. For instance, total equilibrium concentration of TBP, T_C in Eq. (2-10), should be corrected for these volume changes. Accurate density equations are required for the conversions between the molar and solute-free concentrations and discussed in Section (3-3). Richardson converted all collected data to solute-free concentrations and correlated the pseudo-thermodynamic equilibrium constants by plotting the constants versus the aqueous total nitrate concentrations and by including correction factors for temperatures and TBP concentrations.

The pseudo-thermodynamic equilibrium constants were defined by:

$$K_U^S = \frac{(UO_2(NO_3)_2 \cdot 2TBP)_o}{(UO_2^{2+})_a (TBP)_o^2}, \quad (2-23)$$

$$K_{Pu}^S = \frac{(Pu(NO_3)_4 \cdot 2TBP)_o}{(Pu^{4+})_a (TBP)_o^2}, \quad (2-24)$$

$$K_{H1}^S = \frac{(HNO_3 \cdot TBP)_o}{(H^+)_a (TBP)_o}, \quad (2-25)$$

$$K_{H2}^S = \frac{(HNO_3 \cdot 2TBP)_o}{(H^+)_a (TBP)_o^2}, \quad (2-26)$$

where the quantities in parentheses represent the solute-free concentrations of the reacting species, and superscript s means solute-free concentration base.

Distribution coefficients for each component are related as follows:

$$D_U^S = \frac{(UO_2(NO_3)_2 \cdot 2TBP)_o}{(UO_2^{2+})_a} = K_U^S (TBP)_o^2, \quad (2-27)$$

$$D_{Pu}^S = \frac{(Pu(NO_3)_4 \cdot 2TBP)_o}{(Pu^{4+})_a} = K_{Pu}^S (TBP)_o^2, \quad (2-28)$$

$$D_{H1}^S = \frac{(\text{HNO}_3 \cdot \text{TBP})_o}{(\text{H}^+)_a} = K_{H1}^S (\text{TBP})_o, \quad (2-29)$$

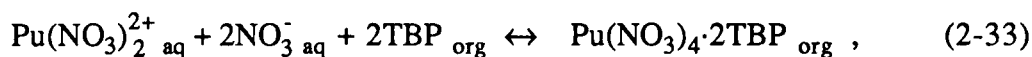
$$D_{H2}^S = \frac{(\text{HNO}_3 \cdot 2\text{TBP})_o}{(\text{H}^+)_a} = K_{H2}^S (\text{TBP})_o^2, \quad (2-30)$$

$$D_H^S = D_{H1}^S + D_{H2}^S. \quad (2-31)$$

The pseudo-thermodynamic equilibrium constants, K^S s, were correlated with the aqueous total nitrate concentrations, n_a , in the solute-free concentrations.

$$n_a = 2(\text{UO}_2^{2+})_a + 4(\text{Pu}^{4+})_a + (\text{H}^+)_a. \quad (2-32)$$

It has been known that the plutonium(IV) in the aqueous phase is virtually all complexed with various amounts of nitrates, even at low nitrate concentrations. When assumed that the predominant plutonium(IV) complex was associated with two nitrate ions, say $\text{Pu}(\text{NO}_3)_2^{2+}$, and that the major plutonium(IV) extraction reaction was, instead of Eq. (2-2),



the correlation for plutonium(IV) was better. Later, the number of nitrate ions contributed from plutonium(IV) was changed from 4 to 2.

The basic empirical equilibrium expressions were correlated using smoothed equilibrium data for 100 volume percent TBP equilibrated at 25 °C to give the following equations:

$$K_U^* = 3.7n_a^{1.57} + 1.4n_a^{3.9} + 0.011n_a^{7.3}, \quad (2-34)$$

$$K_{\text{Pu}}^* = K_U^* (0.20 + 0.55F^{1.25} + 0.0074n_a^{2.0}), \quad (2-35)$$

$$K_{H1}^* = 0.135n_a^{0.82} + 0.0052n_a^{3.44}, \quad (2-36)$$

$$K_{H2}^* \cong K_{H1}^*. \quad (2-37)$$

The plutonium constant, K_{Pu}^* , at 100 volume percent TBP and 25 °C was expressed as a function of the uranium constant at the same conditions and incorporated minor correction for TBP and the total aqueous nitrate concentrations. The first term in Eqs. (2-34) and (2-36) was determined in the low total nitrate concentration region where plutonium(IV) is hydrolyzed and disproportionated to both plutonium(III) and plutonium(VI), thus affecting the extraction of plutonium(IV). Actually, there is no confident plutonium data at either 100 volume percent TBP or zero nitric acid concentration. Also, the nitric acid data were artificially treated to produce reasonable results, i.e., K_{H2}^* would not be equal to K_{H1}^* .

The correction factors for other TBP concentrations and temperatures were included as follows:

$$K_U^S = K_U^* (4F^{-0.17} - 3) e^{2500\tau}, \quad (2-38)$$

$$K_{Pu}^S = K_{Pu}^* (4F^{-0.17} - 3) e^{-200\tau}, \quad (2-39)$$

$$K_{H1}^S = K_{H2}^S = K_{H1}^* (1.0 - 0.54 e^{-15F}) e^{340\tau}, \quad (2-40)$$

$$\text{where } \tau = \frac{1}{t + 273.16} - \frac{1}{298.16}. \quad (2-41)$$

The uncomplexed, free TBP concentration, $(TBP)_o$, is calculated by material balance as follows:

$$(TBP)_o = T_S - 2(UO_2(NO_3)_2 \cdot 2TBP)_o - 2(Pu(NO_3)_4 \cdot 2TBP)_o - (HNO_3 \cdot TBP)_o - 2(HNO_3 \cdot 2TBP)_o \quad (2-42)$$

Here T_S is the solute-free concentration (i.e., molar concentration) of total TBP in dry, solute-free solvent. T_S is calculated by the relation given in Eq. (2-11) and needs the density equation for TBP as a function of temperature because TBP density changes

with temperature. The equation for $(TBP)_o$ was obtained by substituting Eqs. (2-27)-(2-30) into Eq. (2-42) and solving the resulting quadratic equation for $(TBP)_o$.

Richardson's model accurately predicts the uranium distribution coefficients, but needs improvement for the plutonium and nitric acid distribution coefficients. The model was adapted to the SEPHIS computer code[6,15], and slight modifications have been made[79].

Jubin[80] compared Richardson's model with data taken from the German compilation[81] of data taken from the literature between 1952 and 1977. It covers only 30 volume percent TBP. The compilation provided 2013 data points for uranium(VI), plutonium(IV) and nitric acid, of which 796 data points were for uranium, 753 data points for plutonium, and 464 data points for nitric acid. Plutonium data points at nitric acid concentrations less than 0.3 M were discarded because of possible occurrence of plutonium(IV) hydrolysis and disproportionation and their effects on the experimental data, leaving 675 plutonium data points. As a result of this work, a correction factor for the calculated plutonium distribution coefficient was found to be

$$\text{Factor} = 0.56778 + 0.0131175 t + 0.743578 (UO_2^{2+})_a - 0.175829 (UO_2^{2+})_a (H^+)_a, \quad (2-43)$$

where the plutonium distribution coefficient and the uranium and nitric acid concentrations are in solute-free units, and t is the equilibrium temperature in °C. The plutonium distribution coefficients should be modified by dividing the present plutonium distribution coefficient by this factor.

Richardson's model, with Jubin's correction factor, still did not correctly describe temperature effects on the plutonium distribution. It turned out that the factor improved prediction of the model for plutonium distribution at 25 °C, but caused the model to calculate the wrong plutonium distribution coefficients at temperatures other

than 25 °C. Whatley[82] deleted the factor from the model and corrected the four parameters in the model using different approach. Data were taken from a new edition of the German compilation[83] which included new data but still only covered the use of 30 volume percent TBP. The new compilation included a total number of 4285 data points, of which 1492 data points were for uranium(VI), 986 data points for plutonium(IV), and 1240 data points for nitric acid. Plutonium(IV) data points were accepted only when the acidity of the aqueous phase was greater than 0.29 M and only when the plutonium(IV) concentration was greater than 0.014 g/l. If the uranium(VI) concentration was less than 10 g/l, the plutonium(IV) points with concentrations less than 0.14 g/l were also discarded. A final number of acceptable data points was 1860, consisting of 1222 uranium points and 603 plutonium points. The data set was then grouped into four subsets:

- (1) subset 1 included all accepted uranium and plutonium points;
- (2) subset 2 included only good plutonium points;
- (3) subset 3 included only good uranium points where plutonium concentration is of no importance, i.e. points having uranium concentrations greater than 0.1 g/l and plutonium concentrations less than 5 g/l;
- (4) subset 4 included good plutonium points taken at temperatures other than 25 °C.

The variance was used for estimating errors between experimental and calculated distribution coefficients. The variance was defined as follows:

$$\text{Variance} = \frac{1}{N} \sum_{i=1}^N \left[\frac{\text{Exp}(i) - \text{Cal}(i)}{\text{Exp}(i)} \right]^2, \quad (2-44)$$

where N is a total number of data points of uranium or plutonium in a subset, Cal(i) is the distribution coefficient calculated by the model from the ith data point in the subset, and Exp(i) is the corresponding experimental distribution coefficient. Four parameters were used to correct for temperature effects of the model on the plutonium distribution coefficients. The parameters were:

$$K_U^* = \theta_1 (3.7 n_a^{1.57} + 1.4 n_a^{3.9} + 0.011 n_a^{7.3}) , \quad (2-45)$$

$$K_{Pu}^* = K_U^* (\theta_2 + 0.55 F^{1.25} + \theta_3 n_a^{2.0}) , \quad (2-46)$$

$$K_{Pu}^S = K_{Pu}^* (4 F^{-0.17} - 3) e^{\theta_4 \tau} , \quad (2-47)$$

where θ 's represent the four parameters. Parameter for the temperature correction factor, θ_4 , for the plutonium distribution coefficients, was the target parameter, and the others were required to correct the shifts of the uranium and plutonium distribution coefficients caused by changing θ_4 value. Each parameter value was varied independently, while keeping other parameters constant, and for each value of a candidate parameter, variances for both uranium and plutonium distribution coefficients of each subset were calculated. Optimal value of a parameter was determined by locating the parameter value for minimum variance for the distribution coefficients of the corresponding component, say, uranium or plutonium, of the subset which includes data that most affect the parameter value. For instance, the optimal value of param4 in Eq. (2-47) would be one giving minimum variance for the plutonium distribution coefficients of subset 4. It was also shown that varying the values of a parameter affected the variances for both uranium and plutonium distribution coefficients, therefore, a particular parameter value for minimum variance for the plutonium distribution coefficients was not necessarily the one for the uranium distribution

coefficients. The corrected values and old values for the parameters are given in Table 1.

Whatley's approach[82] was successful, and with the corrected parameters, the model greatly improved its prediction for the plutonium distribution coefficients. Predictions for the uranium and nitric acid distribution coefficients were also improved but not as much as that for plutonium.

Table 1. New and Old Values for Four Parameters Corrected for the Better Description of Temperature Effect on the Plutonium Distribution Coefficients.

Parameters	New Values	Old Values
θ_1	1.13	1.0
θ_2	0.135	0.2
θ_3	0.01	0.0074
θ_4	-800.0	-200.0

2.3 Density Equations for Concentration Conversions

Since most experimental data are reported in molar concentrations, and Richardson's model performs the equilibrium calculations on a solute-free basis, accurate density equations for conversions between molar and solute-free concentrations are needed.

Conversions between molar and molal concentrations may be calculated either from solution density and solute concentrations or from solute molecular volumes, solvent density and solute concentrations. The latter is more flexible.

Equations for the conversions between molar and molal concentrations are given in terms of solute molecular volumes as follows:

$$m_i = \frac{C_i}{\rho_z (1.0 - \sum_{i=1}^n V_i C_i)}, \quad (2-48)$$

$$C_i = \frac{m_i \rho_z}{1.0 + \rho_z \sum_{i=1}^n V_i m_i}. \quad (2-49)$$

Without the density term the above equations calculate the conversions between molar and solute-free concentrations as follows:

$$S_i = \frac{C_i}{1.0 - \sum_{i=1}^n V_i C_i}, \quad (2-50)$$

$$C_i = \frac{S_i}{1.0 + \sum_{i=1}^n V_i S_i}, \quad (2-51)$$

where S_i is the solute-free concentration of solute i .

The molecular volumes of the solutes, i.e. uranium, plutonium and nitric acid, in both the organic and aqueous phases have been determined to be used in the density equations. In the aqueous phase[84],

$$V_{U,a} = 0.07669 + 4.189 \times 10^{-5} t, \quad (2-52)$$

$$V_{Pu,a} = 0.130 \text{ at } 25^\circ \text{C}, \quad (2-53)$$

$$V_{H,a} = 0.03070 + 6.646 \times 10^{-5} t, \quad (2-54)$$

and, in the organic phase,

$$V_{U,o} = 0.09154 \text{ at } 25^\circ\text{C} , \quad (2-55)$$

$$V_{Pu,o} = 0.139 \text{ at } 25^\circ\text{C} , \quad (2-56)$$

$$V_{H,o} = 0.04326 \text{ at } 25^\circ\text{C} , \quad (2-57)$$

$$V_{W,o} = 0.018 \text{ at } 25^\circ\text{C} , \quad (2-58)$$

where $V_{W,o}$ is the molecular volume of water in the organic phase. A certain amount of water is extracted into the organic phase during the extraction processes. Therefore, water concentration in the organic phase should be included in the density equations. Equations for the water concentrations in the organic phase on the molar and solute-free units have been determined as follows[79,85]:

$$C_{W,o} = (3.95 - 0.0144 t) \left(1.0 - \frac{C_{U,o}}{C_{U,os}} - \frac{C_{Pu,o}}{C_{Pu,os}} - \frac{0.65C_{H,o}}{C_{H,os}} \right) F^{1.65} , \quad (2-59)$$

$$S_{W,o} = (4.2 - 0.015 t) \left(1.0 - \frac{2S_{U,o}}{T_S} - \frac{2S_{Pu,o}}{T_S} - \frac{0.6S_{H,o}}{T_S} \right) F^{1.69} . \quad (2-60)$$

$C_{U,os}$, $C_{Pu,os}$ and $C_{H,os}$ are molar concentrations of uranium, plutonium and nitric acid, respectively, required to saturate the TBP. They are calculated by:

$$C_{U,os} = \frac{0.5 T_S}{1.0 + 0.046 T_S} , \quad (2-61)$$

$$C_{Pu,os} = \frac{0.5 T_S}{1.0 + 0.09 T_S} , \quad (2-62)$$

$$C_{H,os} = \frac{T_S [1.0 - 0.00609 (3.95 - 0.0144 t) F^{1.65}]}{(1.0 + 0.043 T_S)} . \quad (2-63)$$

The density equations for the use in the Purex solvent extraction processes, including uranium, plutonium and nitric acid as the solutes, can be expressed as follows for the aqueous phase:

$$\begin{aligned} \frac{S_{i,a}}{C_{i,a}} &= \frac{1.0}{1.0 - V_{U,a}C_{U,a} - V_{Pu,a}C_{Pu,a} - V_{H,a}C_{H,a}} \\ &= 1.0 + V_{U,a}S_{U,a} + V_{Pu,a}S_{Pu,a} + V_{H,a}S_{H,a} , \end{aligned} \quad (2-64)$$

and for the organic phase:

$$\frac{S_{i,o}}{C_{i,o}} = \frac{1.0}{1.0 - V_{U,o}C_{U,o} - V_{Pu,o}C_{Pu,o} - V_{H,o}C_{H,o} - V_{W,o}C_{W,o}}$$

$$= 1.0 + V_{U,o}S_{U,o} + V_{Pu,o}S_{Pu,o} + V_{H,o}S_{H,o} + V_{W,o}S_{W,o} . \quad (2-65)$$

The density equation for TBP, used for calculating total TBP concentrations in the organic phase in Eq. (2-11), was correlated as a function of temperature as follows:

$$\rho_{TBP} = 0.992486 - 7.6489 \times 10^{-4} t - 1.05 \times 10^{-6} t^2 . \quad (2-66)$$

CHAPTER 3

CORRECTION TO RICHARDSON'S MODEL FOR A BETTER DESCRIPTION OF NITRIC ACID DISTRIBUTION COEFFICIENTS

Whatley's correction[82] to Richardson's model parameters greatly improved the prediction of the plutonium(IV) distribution coefficients. However, the model for nitric acid distribution is still poor and needs improvement. It is known that at low concentrations that nitric acid in the aqueous phase promotes the extraction of uranium(VI) and plutonium(IV) by its salting-out effect, but as the nitric acid concentration is increased, it begins to compete with the uranium and plutonium for complexing with TBP, thus decreasing uncomplexed, free TBP concentrations. Since nitric acid as a salting agent is present in large concentrations in the aqueous phase in the Purex solvent extraction processes, accurate description of the nitric acid extraction with TBP is important in determining the free TBP concentration. This is needed for a model to calculate the uranium and plutonium distribution coefficients.

3.1 Data Collection and Screening

Most equilibrium distribution data for uranium(VI), plutonium(IV) and nitric acid were taken from the German compilation[83], discussed in Section 2.2. Since the compilation provides distribution data only for 30 volume percent TBP, the available literature was reviewed to collect distribution data for these components at TBP concentrations other than 30 volume percent. Through this work it was seen that published distribution data are largely clustered at 20 volume percent TBP, which is favored for the reprocessing of high plutonium-content fuels such as LMFBR fuels. Moiseenko and Rozen[55] reported 240 plutonium(IV) distribution data with 20 volume percent TBP at 0.2 g/l aqueous plutonium equilibrium concentration in the presence and

absence of uranium(VI) at various temperatures. Unfortunately all the data were discarded because it was pointed out that plutonium was partially oxidized by nitric acid at elevated temperatures[86].

Among the data collected at various TBP concentrations, only data sets for 20 volume percent TBP had enough data to be included in this study. The study included 137 uranium(VI) data points, 8 plutonium(IV) data points and 206 nitric acid data points from 6 sources. Before the data were used, they were screened to detect wild observations. The data inspection procedures are described elsewhere[81]. Since each uranium(VI), plutonium(IV) and nitric acid distribution coefficient at constant TBP concentration is a function of 4 independent variables, i.e., concentrations of the three components in the aqueous phase and temperature, the resulting 5 dimensional space does not lend itself to simple graphical inspection. Furthermore, the distribution data are not homogeneously distributed over the data space but are in fact clustered in concentration ranges that have been traditionally of most interest to the experimenter. One approach useful for inspecting such multidimensional data is to group the data in narrow concentration and temperature ranges by slicing the space of 4 independent variables into thin segments in which 3 independent variables are considered as practically constant, leaving only 1 independent variable for inspection of each dependent variable. To keep 3 of the 4 independent variables practically constant, the segments have to be as thin as practicable for a reasonable density of data points. On the other hand the segment width should not be less than at least the experimental error of the determination of the corresponding variables. This procedure can crudely detect wild observations. Further inspection is done through regression analysis for the 2 dimensional data space which contains one independent and one dependent variable.

The distribution data collected for 20 volume percent TBP were screened by the procedure described above, and 22 uranium data points and 40 nitric acid data points were detected as wild observations. The wild observations were designated by negative signs. The data are listed in Appendix B by source number, and sources of the data are also listed in Appendix B. In Appendix C the data are first grouped according to temperatures, then the data at constant temperature are grouped again by the presence and absence of uranium. The nitric acid distribution coefficients in the absence of uranium are now a function of one independent variable, the aqueous nitric acid concentrations. The nitric acid distribution coefficients are then sorted by increasing aqueous nitric acid concentrations and inspected by regression analysis. The data with the presence of uranium are further segmented according to aqueous nitric acid concentrations, and the data at constant aqueous nitric acid concentration are sorted by increasing aqueous uranium concentrations for regression analysis. Since the plutonium distribution data have only 8 points and are from one source, they were compared with plutonium data for 30 volume percent TBP. The plutonium data are listed at the end of Appendix C.

The total number of data points used in this study was 4096, of which 1629 were uranium(VI), 994 plutonium(IV) and 1446 nitric acid data points.

3.2 Correction for Nitric Acid Distribution Coefficients

As described in Section 2.2, the nitric acid distribution model was constructed by an artificial treatment with assumption that the pseudo-thermodynamic constants (Eqs. (2-37) and (2-40)) for nitric acid mono- and di-solvate reactions with TBP were equal. It has been shown that water is involved in the nitric acid di-solvate reaction[60] and the "extraction constant", which is another form of pseudo-thermodynamic constant that has been used by Russian researchers, for the nitric acid di-solvate reaction is

greater than that for the nitric acid mono-solvate reaction[87]. It has also been proposed that two molecules of nitric acid form solvates, possibly hydrated, with one molecule of TBP[20,53,67,68] at high nitric acid concentrations. However, this reaction mechanism has not been considered in constructing a mathematical model because it is not practical in the Purex solvent extraction processes which are operated at smaller nitric acid concentrations.

In order to include the hydrated nitric acid solvate in a mathematical model a knowledge of the activity of water in the aqueous phase, concentrations of water dissolved in free TBP, as well as the hydrate water in the di-solvate are needed. Since these were not available, the work assumed that the pseudo-thermodynamic constants, K_{H1}^S and K_{H2}^S , in Eq. (2-40) would not be equal and temperature effects on one constant would be different from the other. Parameters to be studied were designated as follows:

$$K_{H1}^* = A_{H1,1} n_a^{A_{H1,2}} + A_{H1,3} n_a^{A_{H1,4}}, \quad (3-1)$$

$$K_{H2}^* = A_{H2,1} n_a^{A_{H2,2}} + A_{H2,3} n_a^{A_{H2,4}}, \quad (3-2)$$

$$K_{H1}^S = K_{H1}^* (1.0 - 0.54 e^{-15F}) e^{A_{H1,T}\tau}, \quad (3-3)$$

$$K_{H2}^S = K_{H2}^* (1.0 - 0.54 e^{-15F}) e^{A_{H2,T}\tau}, \quad (3-4)$$

where A's represent the parameters. The variance defined in Eq. (2-44) was used to locate optimal values of candidate parameters in the same way as described in Section 2.2.

Four data subsets were needed to find the parameters for description of nitric acid distribution coefficients. The wild observations designated as negative signs in the German compilation[83] and in the data set collected in this study were discarded. Plutonium data points were included only when the aqueous acidity was greater than

0.29 M because of plutonium(IV) disproportionation and polymerization at lower acidity and their distorting effects on the plutonium(IV) data. Also, only data with plutonium concentration greater than 0.014 g/l were included. If the uranium concentration was less than 10.0 g/l, the plutonium concentration was required to exceed 0.14 g/l.

Since the changes of uranium and plutonium variances caused by the changes of the parameters must be considered as well, the data subset that included only good uranium data points was designated as population 1, and the data subset that included only good plutonium data points was designated as population 2. Acceptable uranium data points for population 1 had uranium concentrations greater than 0.1 g/l. In population 1, 1283 data points contributed to the uranium variance, 320 data points to the plutonium variance and 583 data points to the nitric acid variance. Plutonium data points for population 2 were screened to the same criteria described above. In this subset, 331 data points contributed to the uranium variance, 645 data points to the plutonium variance and 190 data points to the nitric acid variance. The subset that included all nitric acid data was designated as population 3. This subset contributed 620 data points to the uranium variance, 190 data points to the plutonium variance and 997 data points to the nitric acid variance.

Since it was supposed that the temperature effect on one nitric acid extraction reaction would be greater than the other, the subset designated as population 4 included nitric acid data taken at temperatures other than 25 °C. This subset contributed 449 data points to the uranium variance, 148 data points to the plutonium variance and 707 data points to the nitric acid variance.

First, the 10 parameters in Eqs. (3-1)-(3-4) were varied independently, and the variances for uranium, plutonium and nitric acid data in each subset at each value of each candidate parameter were calculated. Optimal values of the parameters $A_{H1,1}$ -

$A_{H1,4}$ and $A_{H2,1} - A_{H2,4}$ would be determined largely by the nitric acid variance from population 3, and those of the parameters $A_{H1,T}$ and $A_{H2,T}$ by the nitric acid variance from population 4, taking account of the uranium and plutonium variances from both populations. The lowest nitric acid variance for populations 3 and 4 was found by varying $A_{H1,1}$. The minimum nitric acid variance for population 3, which is of the greatest importance in selecting the optimal value of $A_{H1,1}$, was for $A_{H1,1}$ between 0.107 and 0.111 rather than the present value of 0.135 shown in Figure 2. The minimum nitric acid variance from population 4, which is less important than population 3, is found between 0.116 and 0.119. $A_{H1,1}$ has little effect on the plutonium variances from populations 3 and 4 while the uranium variances from populations 3 and 4 are decreasing with an increase of the parameter. Since the variances for uranium, plutonium and nitric acid from populations 1 and 2 do not have influence on selecting values of the parameter $A_{H1,1}$, these are not shown in Figure 2. Taking account of the nitric acid variances for populations 3 and 4, selected value of $A_{H1,1}$ was 0.115. Though the uranium variances for populations 3 and 4 at the selected parameter value are greater than those at the present parameter value, the selection of the parameter value is justified by the correction to the second candidate parameter $A_{H2,3}$.

With this value of $A_{H1,1}$, uranium variances from population 1 and plutonium variances from population 2 were examined by varying parameters in the equations for uranium and plutonium distribution coefficients (Eqs. (2-34)-(2-35) and (2-38)-(2-39)). The minima of the variances from the both populations were not affected by the new value of $A_{H1,1}$ and were near the present parameter values. Whenever a new parameter value was selected, uranium variances for population 1 and plutonium variances for population 2 were examined for possible shifts of the minima of the variances.

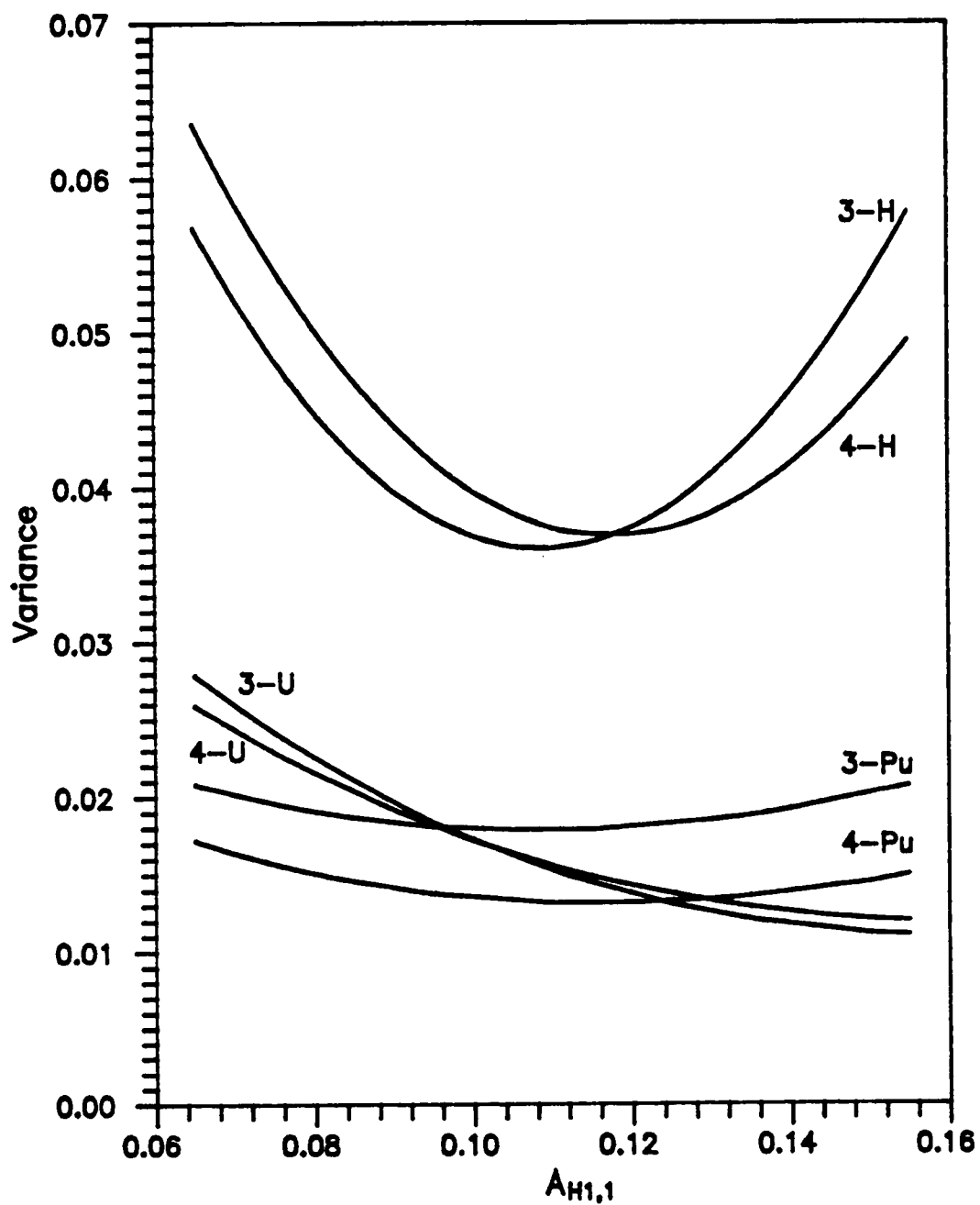


Figure 2. Variance Between Experimental and Calculated Distribution Coefficients of Uranium, Plutonium and Nitric Acid for Populations 3 and 4 as a Function of $A_{H1,1}$.

With the new value of $A_{H1,1}$, the uranium, plutonium and nitric acid variances for populations 3 and 4 were examined by varying values of the remaining 9 parameters. $A_{H2,3}$, which is a parameter for the pseudo-thermodynamic equilibrium constant for the nitric acid di-solvate extraction reaction, reduced the uranium variances for populations 3 and 4, but it had little effect on the nitric acid variances. These are shown in Figure 3. The plutonium variance for population 3 has a minimum between $A_{H2,3}$ values of 0.0046 and 0.0054, and for population 4, between 0.0054 and 0.0064. Reflecting the uranium and plutonium variances, 0.007 was selected as a new value for $A_{H2,3}$. With the new parameter value, the uranium variance for population 1 and the plutonium variance for population 2 were calculated, and there were no shifts of the minima for the variances.

The next parameter to be corrected was $A_{H2,4}$. As shown in Figure 4, it, like $A_{H2,3}$, had little effect on the nitric acid variances for populations 3 and 4. The minima for the uranium variances for both populations fall near 3.9, while the plutonium variances for both populations began to rise steeply at about 3.65. Taking account of the influence of $A_{H2,4}$ on the uranium and plutonium variances, 3.61 was selected as new value for $A_{H2,4}$.

Variances for uranium, plutonium and nitric acid in populations 3 and 4 were calculated as a function of the remaining 7 parameters, and $A_{H2,T}$, the coefficient of temperature effect on the nitric acid di-solvate extraction reaction, was chosen as the next parameter to be corrected. Figure 5 shows the effect of $A_{H2,T}$ on the variances of the three components in populations 3 and 4. It had no effect on the plutonium variances. The nitric acid and uranium variances have broad, poorly defined minima, and the minima for the nitric acid variances were between 0.8 and 1.3, while the minima for the uranium variances lie between 1.4 and 1.7. The present value of 0.34 for the

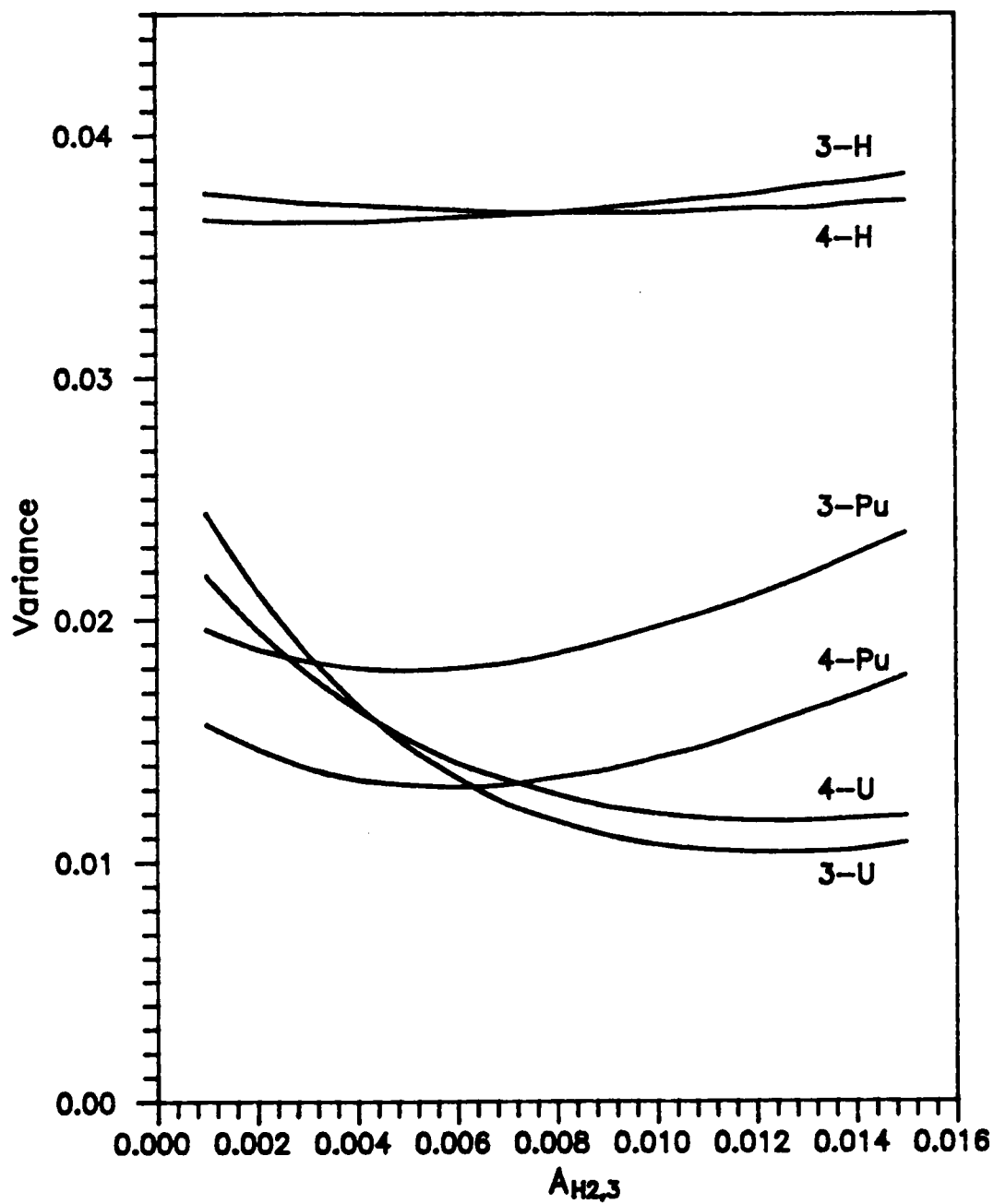


Figure 3. Variance Between Experimental and Calculated Distribution Coefficients of Uranium, Plutonium and Nitric Acid for Populations 3 and 4 as a Function of $A_{H2,3}$.

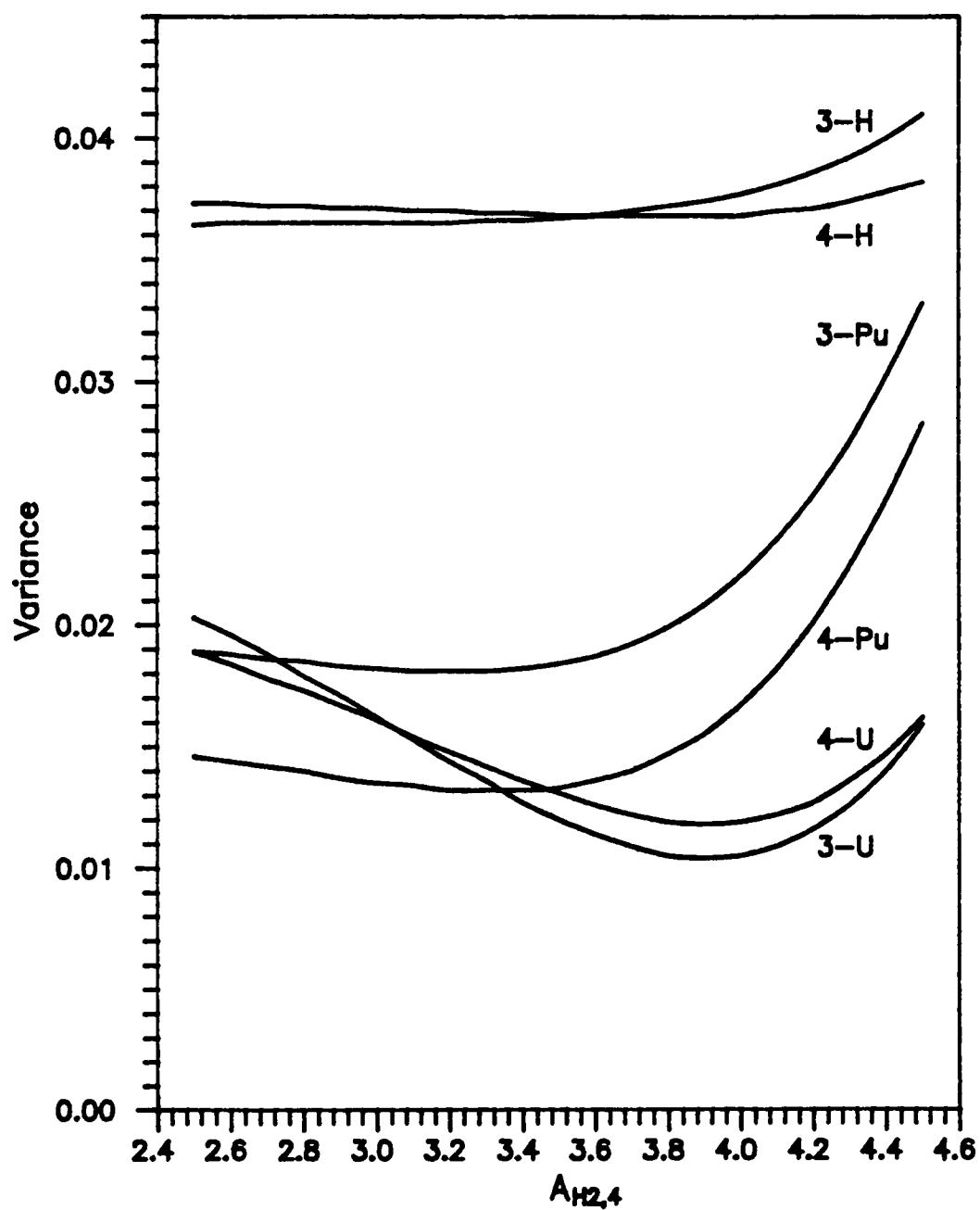


Figure 4. Variance Between Experimental and Calculated Distribution Coefficients of Uranium, Plutonium and Nitric Acid for Populations 3 and 4 as a Function of $A_{H2,4}$.

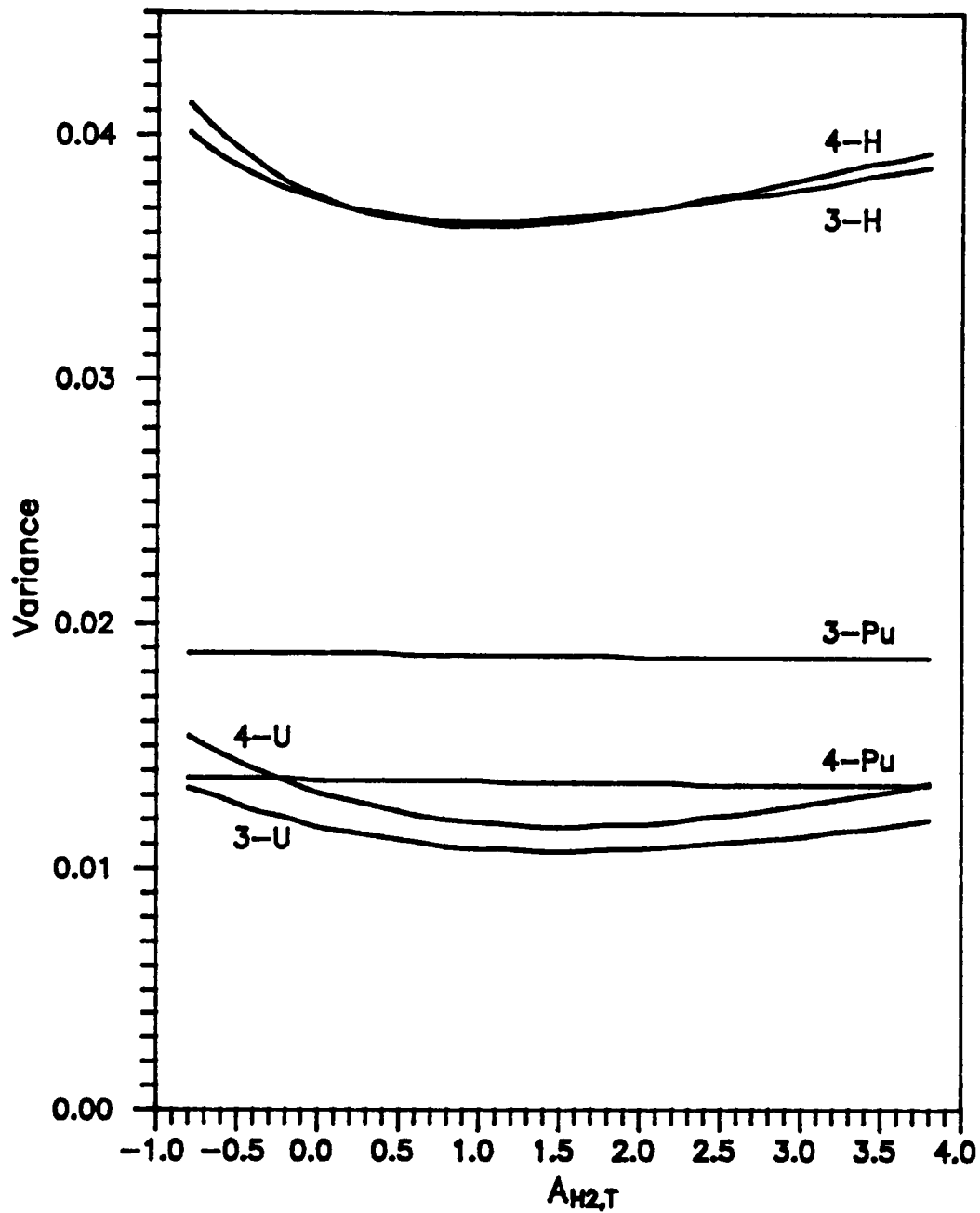


Figure 5. Variance Between Experimental and Calculated Distribution Coefficients of Uranium, Plutonium and Nitric Acid for Populations 3 and 4 as a Function of $A_{H_2,T}$.

parameter is out of range. Considering the effect of the parameter on the uranium variances, 1.29 was selected for $A_{H2,T}$.

The next candidate parameter was $A_{H1,T}$, the coefficient for the temperature effect on the nitric acid mono-solvate extraction reaction. Variances for uranium, plutonium and nitric acid distribution coefficients in populations 3 and 4 as a function of the parameter are shown in Figure 6. As before, the plutonium variances are not affected by the parameter values. The nitric acid variance minima fall together at 0.12, while the minima of the uranium variances lie between 0.0 and 0.2, suggesting 0.12 as new value for $A_{H1,T}$.

With the corrected parameter values, the variances for populations 3 and 4 were calculated by independently varying values of the remaining parameters. It was found that $A_{H1,2}$ lowered the nitric acid variance for population 3, while it had little effect on the nitric acid variance for population 4. As seen in Figure 7, the nitric acid variance minimum for population 3, which is most important, falls at about 0.69, and that for population 4, which is less important, falls about at 0.76. The uranium variances are steadily decreasing with an increase of $A_{H1,2}$, while the plutonium variances are slightly affected by the parameter. 0.73 was selected for $A_{H1,2}$, and the selection was influenced by the effect of $A_{H1,2}$ on the nitric acid variance for population 4 and the uranium variances.

The last parameter to be included in this study was $A_{H1,4}$ with an effect on the variances of uranium, plutonium and nitric acid shown in Figure 8. The uranium and plutonium variances show flat and poorly defined minima. The uranium variance for population 3 has a minimum between the $A_{H1,4}$ values of 3.48 and 3.53, and for population 4 between 3.47 and 3.5. The minimum of the plutonium variance for population 3 is found between 3.42 and 3.44, and that for population 4 between 3.43

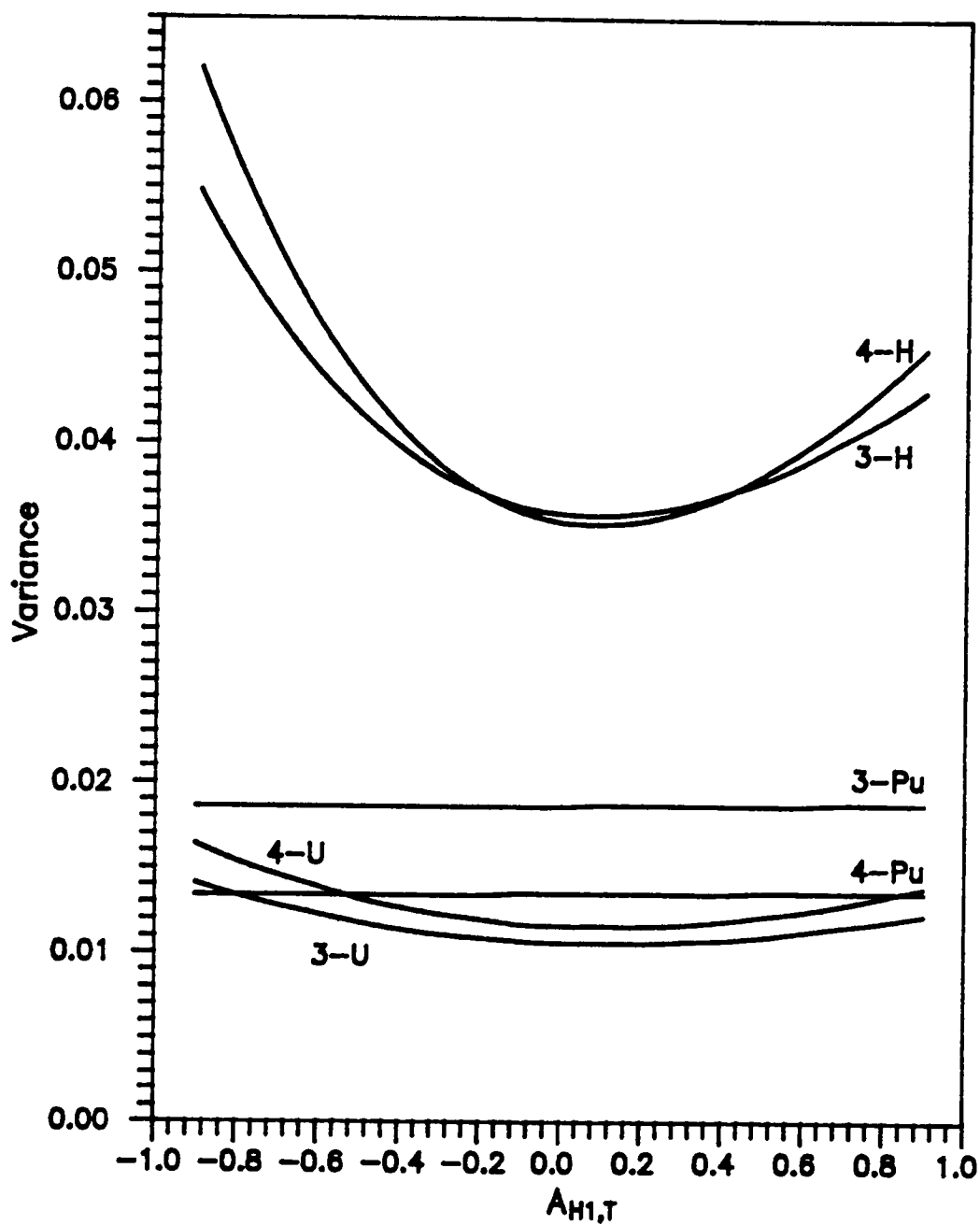


Figure 6. Variance Between Experimental and Calculated Distribution Coefficients of Uranium, Plutonium and Nitric Acid for Populations 3 and 4 as a Function of $A_{H1,T}$.

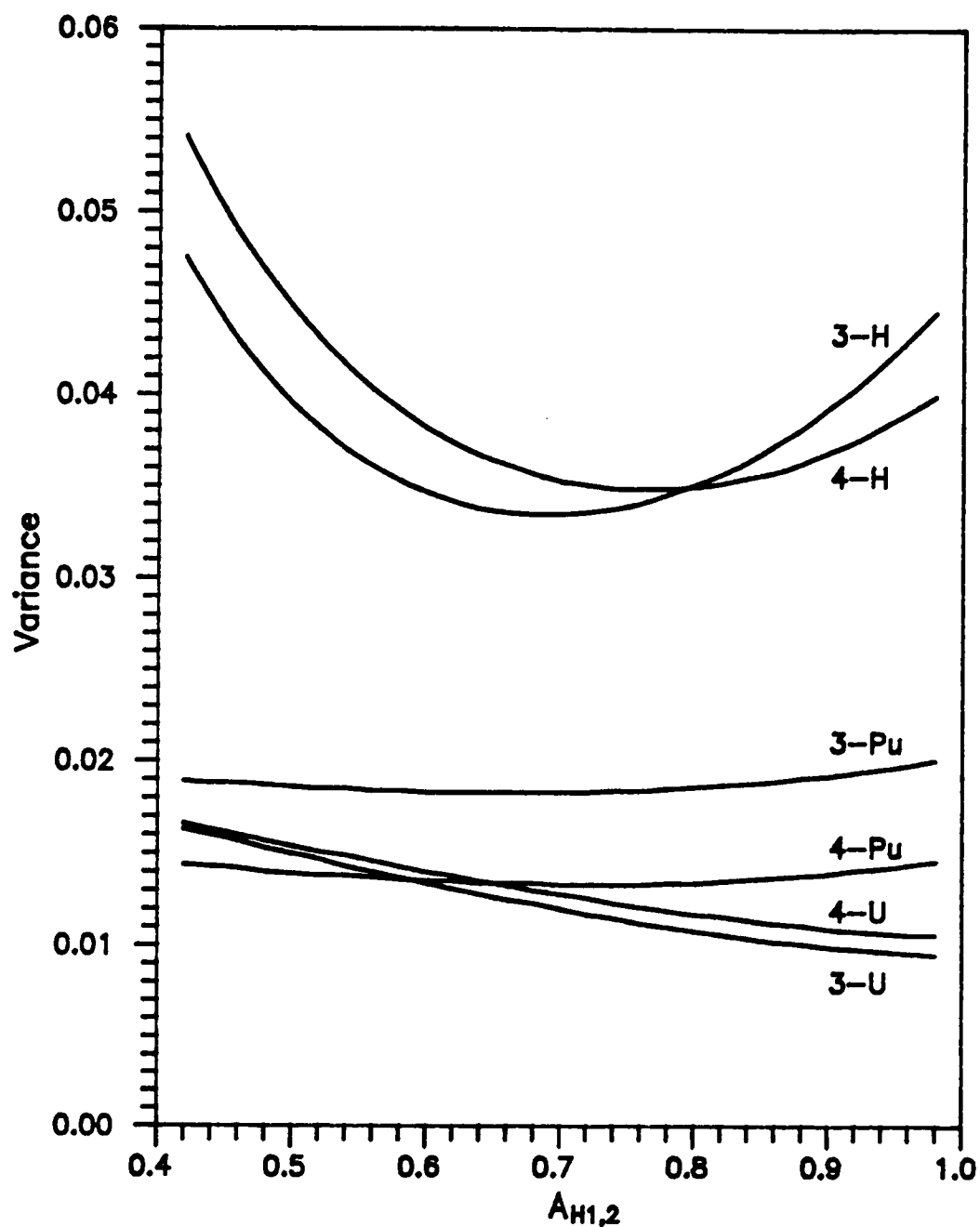


Figure 7. Variance Between Experimental and Calculated Distribution Coefficients of Uranium, Plutonium and Nitric Acid for Populations 3 and 4 as a Function of $A_{H1,2}$.

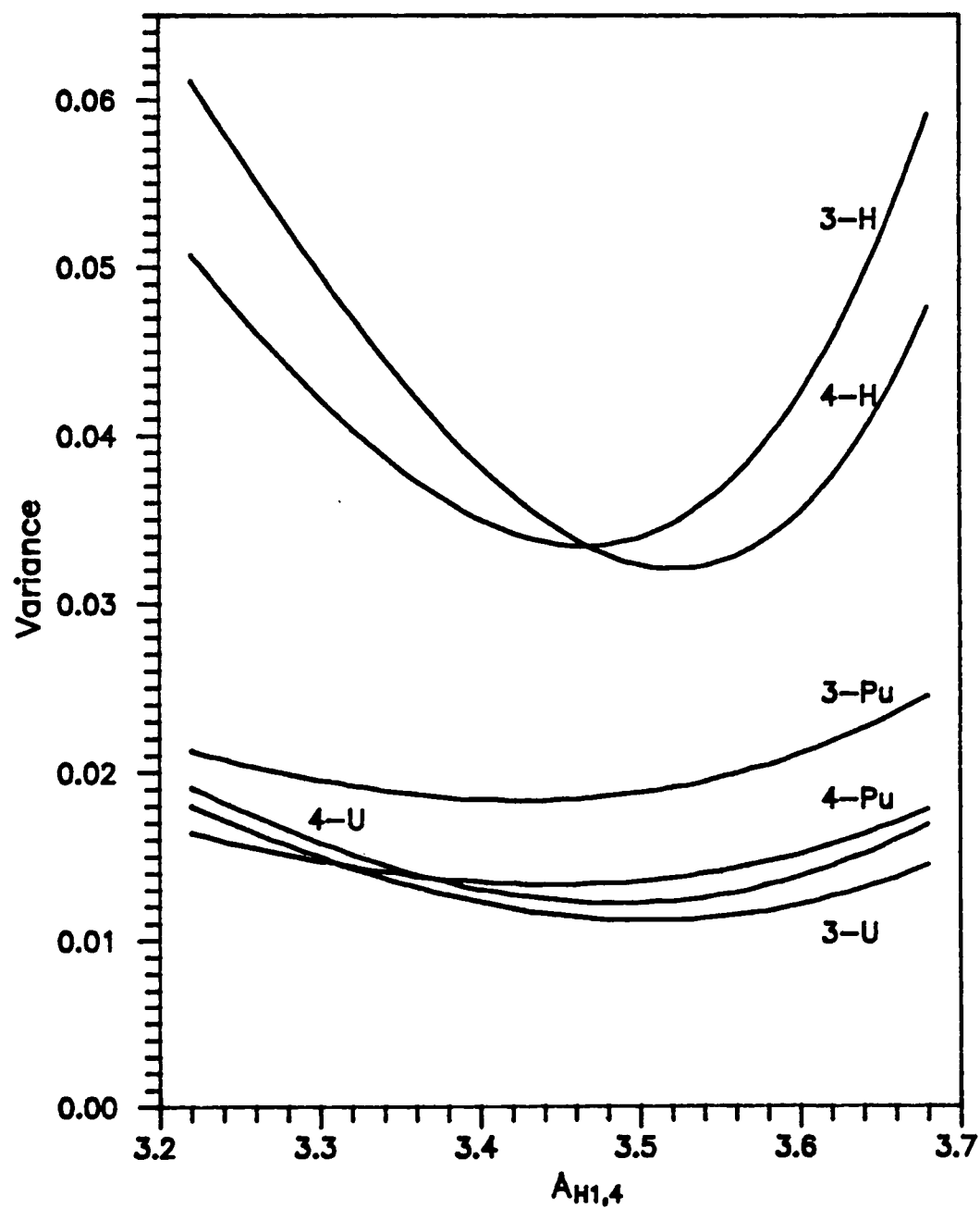


Figure 8. Variance Between Experimental and Calculated Distribution Coefficients of Uranium, Plutonium and Nitric Acid for Populations 3 and 4 as a Function of $A_{H1,4}$.

and 3.46. The minimum of the nitric acid variance for population 3, which is most strongly affected by $A_{H1,4}$ values, falls at about 3.47, and that for population 4, which is less affected, falls at about 5.1. Taking account of the effect of $A_{H1,4}$ on the uranium and plutonium variances as well as the nitric acid variance for population 4, selected value for $A_{H1,4}$ was 3.49 rather than the present value of 3.44.

With all the corrected parameter values the uranium and plutonium variances for population 1 and population 2 respectively were calculated, and there were no shifts of the minima. It was concluded that the present parameter values for the uranium and plutonium distribution coefficients have well-defined minima for the uranium and plutonium variances.

The new values of the seven parameters corrected in this study are listed with old values in Table 2. In Table 3 the variances of errors for uranium, plutonium and nitric acid distribution coefficients for each of four populations which was calculated with new parameter values are compared with those calculated by Whatley's correction, Jubin's correction and Richardson's original model. It is seen that the nitric acid variances for populations 1, 3 and 4 calculated with the new parameter values are much less than those calculated with Whatley's correction, Jubin's correction and Richardson's model. The most effect is noted unexpectedly in population 1, which includes only good uranium data, rather than in population 3 or 4. The least effect is seen in population 2 which includes only good plutonium data. The uranium variances for populations 3 and 4 were only slightly reduced, and there is no change in the uranium variance for population 1.

Though it has been known that nitric acid distribution data are not as accurate as those of uranium and plutonium because of the presence of various nitric acid complexes with TBP, the nitric acid variances were reduced less than expected. It was

Table 2. New and Old Values of Seven Parameters Corrected for the Better Description of Nitric Acid Distribution Coefficients.

Parameters	New Values	Old Values
$A_{H1,1}$	0.115	0.135
$A_{H1,2}$	0.73	0.82
$A_{H1,4}$	3.49	3.44
$A_{H2,3}$	0.007	0.0052
$A_{H2,4}$	3.61	3.44
$A_{H1,T}$	0.12	0.34
$A_{H2,T}$	1.29	0.34

Table 3. Comparison of Variances of Errors of Uranium, Plutonium and Nitric Acid Distribution Coefficients.

Populations	Components	New Parameters	Whatley's Correction	Jubin's Correction	Richardson's Model
Population 1	U	0.0082	0.0083	0.0097	0.0097
	Pu	0.0238	0.0237	0.0574	0.0477
	HNO ₃	0.0439	0.0599	0.0728	0.0728
Population 2	U	0.0127	0.0121	0.0095	0.0095
	Pu	0.0234	0.0240	0.0501	0.0362
	HNO ₃	0.0428	0.0430	0.0468	0.0468
Population 3	U	0.0112	0.0121	0.0130	0.0130
	Pu	0.0187	0.0188	0.0289	0.0214
	HNO ₃	0.0337	0.0432	0.0516	0.0516
Population 4	U	0.0122	0.0129	0.0133	0.0133
	Pu	0.0134	0.0136	0.0240	0.0150
	HNO ₃	0.0325	0.0397	0.0433	0.0433

also expected that decreasing the nitric acid variances would appreciably reduce uranium and plutonium variances because, with better description for the nitric acid distribution, the mathematical model can perform better calculations for the free TBP concentration which is then used to calculate uranium and plutonium distribution coefficients.

It can be concluded that the nitric acid distribution model is incomplete and, as suggested by Russian researchers[86,87], water dissolved in TBP, partly in free TBP and partly in nitric acid di-solvate, should be included to calculate the nitric acid distribution accurately. Presumably, the nitric acid distribution may not be adequately described as a function of aqueous total nitrate concentrations.

CHAPTER 4

STUDY OF A MATHEMATICAL MODEL FOR EQUILIBRIUM DISTRIBUTION OF URANIUM(VI), PLUTONIUM(IV) AND NITRIC ACID USING REGRESSION ANALYSIS

The optimal parameter value estimation using the minimum variance location procedure described in Section 3.2 is quite subjective to personal judgement. To avoid such sometimes biased determination of a parameter value the use of a statistical tool is beneficial.

SAS (Statistical Analysis System) provides various useful statistical procedures. Because of the nonlinear simultaneous nature of Richardson's model, a simple GLM (General Linear Model) procedure can not be used to the model. SYSNLIN procedure[88], which estimates parameters in a simultaneous system of nonlinear equations using iterative minimization methods for nonlinear regression, was the best available for this work.

In this chapter parameters in Richardson's model are re-evaluated using the procedure. In addition, another way to construct a model for equilibrium distribution of uranium(VI), plutonium(IV) and nitric acid between aqueous nitric acid solutions of the components and organic TBP solutions is demonstrated.

4.1 Evaluation of Parameters in Richardson's Model Using Regression Analysis

Since SYSNLIN procedure excludes observations having missing values, such observations were discarded from the data set used to correct the parameters for nitric acid distribution coefficients in Chapter 3. Observations having plutonium data at an acidity less than 0.29 M were also discarded. The data screening process retained 957

observations. The total number of data points were 1750, of which 646 data points were for uranium, 183 data points for plutonium and 921 data points for nitric acid.

To reduce computing time the data were converted to the solute-free unit using the linear density equations, Eqs. (2-64)-(2-65). Richardson's model gives a certain value to the distribution coefficients of uranium, plutonium and nitric acid even when the corresponding component is not present because the pseudo-thermodynamic constants of the components are calculated as a function of aqueous total nitrate concentrations and since the constant for the plutonium is determined from the uranium constant. For instance, the constant for uranium is not zero when uranium is not present and when nitric acid or plutonium or both are present because the aqueous total nitrate concentration is not zero. Even when concentrations of uranium and plutonium are zero and nitric acid is the only solute present, the constants for the uranium and plutonium are still calculated as non-zero values. Because of that, the organic concentrations of the components, rather than distribution coefficients, were used as dependent variables in SYSNLIN procedure. As in Chapter 3, it was assumed that the pseudo-thermodynamic constant for nitric acid di-solvate extraction reaction with TBP would not equal to that for nitric acid mono-solvate extraction reaction. The parameters to be estimated were designated as follows:

$$K_U^* = B_{U,1} n_a^{B_{U,2}} + B_{U,3} n_a^{B_{U,4}} + B_{U,5} n_a^{B_{U,6}}, \quad (4-1)$$

$$K_{Pu}^* = K_U^* (B_{Pu,1} + 0.55 F^{1.25} + B_{Pu,2} n_a^{B_{Pu,3}}), \quad (4-2)$$

$$K_{H1}^* = B_{H1,1} n_a^{B_{H1,2}} + B_{H1,3} n_a^{B_{H1,4}}, \quad (4-3)$$

$$K_{H2}^* = B_{H2,1} n_a^{B_{H2,2}} + B_{H2,3} n_a^{B_{H2,4}}, \quad (4-4)$$

$$(UO_2(NO_3)_2 \cdot 2TBP)_o = K_U^* (UO_2^{2+})_a (TBP)_o^2 (4 F^{-0.17} - 3) e^{B_{U,T} T}, \quad (4-5)$$

$$(\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP})_o = K_{\text{Pu}}^* (\text{Pu}^{4+})_a (\text{TBP})_o^2 (4 F^{-0.17} - 3) e^{B_{\text{Pu},T}\tau}, \quad (4-6)$$

$$(\text{HNO}_3 \cdot \text{TBP})_o = K_{\text{H1}}^* (\text{H}^+)_a (\text{TBP})_o (1.0 - 0.54 e^{-15F}) e^{B_{\text{H1},T}\tau}, \quad (4-7)$$

$$(\text{HNO}_3 \cdot 2\text{TBP})_o = K_{\text{H2}}^* (\text{H}^+)_a (\text{TBP})_o^2 (1.0 - 0.54 e^{-15F}) e^{B_{\text{H2},T}\tau}, \quad (4-8)$$

$$(\text{H}^+)_o = (\text{HNO}_3 \cdot \text{TBP})_o + (\text{HNO}_3 \cdot 2\text{TBP})_o, \quad (4-9)$$

where B's are the parameters to be estimated. Since most of the data were for 30 volume percent TBP, parameters for TBP concentration effects in Eqs. (4-2) and (4-5)-(4-8) were not included in the study.

The present parameter values were used as the initial values for SYSNLIN procedure. The ITOLS (iterated ordinary least squares) option was requested as the parameter estimation method, and the GAUSS option, which is the default, was requested as the method to minimize the sum of squares of errors. The convergence criterion used was 0.0001.

The procedure converged at 56 iterations, and the coefficients of determination (r^2) for the organic uranium, plutonium and nitric acid concentrations were 0.9949, 0.9921 and 0.9788 respectively. In Table 4 the new values of the parameters estimated by SYSNLIN procedure are listed with old parameter values from Whatley's correction and Richardson's model. Since plutonium distribution coefficients increase with increasing temperatures, it was expected that, considering the definition of τ in Eq. (2-41), $B_{\text{Pu},T}$, which is the coefficient for the temperature effect, would have negative value. However, its estimated value is unexpectedly large and positive. This is because 173 data points out of 183 plutonium data points were at 25 and 26 °C. Therefore, the use of the parameter value should be restricted to 25 °C, and more plutonium data at temperatures other than 25 °C are needed to re-estimate the parameter value.

Table 4. New Parameter Values Estimated by the SYSNLIN Procedure and Old Parameter Values from Whatley's Correction and Richardson's Model.

Parameters	New Values	Whatley's Correction	Richardson's Model
$B_{U,1}$	5.669	4.181	3.7
$B_{U,2}$	1.880	1.57	1.57
$B_{U,3}$	0.198	1.582	1.4
$B_{U,4}$	5.681	3.9	3.9
$B_{U,5}$	0.00004	0.01243	0.011
$B_{U,6}$	11.242	7.3	7.3
$B_{U,T}$	2104.92	2500.0	2500.0
$B_{Pu,1}$	0.179	0.135	0.2
$B_{Pu,2}$	0.015	0.010	0.0074
$B_{Pu,3}$	1.858	2.0	2.0
$B_{Pu,T}$	5507.07	-800.0	-200.0
$B_{H1,1}$	0.160	0.135	0.135
$B_{H1,2}$	0.712	0.82	0.82
$B_{H1,3}$	0.0003	0.0052	0.0052
$B_{H1,4}$	5.361	3.44	3.44
$B_{H2,1}$	0.071	0.135	0.135
$B_{H2,2}$	0.496	0.82	0.82
$B_{H2,3}$	0.0024	0.0052	0.0052
$B_{H2,4}$	4.885	3.44	3.44
$B_{H1,T}$	-660.559	340.0	340.0
$B_{H2,T}$	8793.32	340.0	340.0

The coefficient for temperature effects on two nitric acid extractions, $B_{H1,T}$ and $B_{H2,T}$, show their opposite effects on the nitric acid extraction and a stronger effect of temperature on the nitric acid di-solvate extraction. A report by Eschrich[69], who studied the distribution of 0-14 M nitric acid between aqueous and 100 volume percent TBP phase at 4, 23, 37 and 75 °C, found the distribution coefficient of nitric acid

decreased with an increase in temperature at equilibrium aqueous acidities up to 2 M. At higher acidities, the distribution coefficient increased with temperature. It was also shown that temperature has strong effect on the nitric acid distribution up to an equilibrium aqueous nitric acid concentration of 1.5 M, and beyond this concentration the distribution of nitric acid is only slightly influenced by temperature variations.

It has been known that at low nitric acid concentrations in the organic phase, i.e., at high free TBP concentrations, hydrated higher solvates of nitric acid with TBP as well as unhydrated nitric acid mono-solvate are formed, and, as the acidity increases, the higher solvates, which reach a maximum concentration at equilibrium aqueous nitric acid concentrations of 2-3 M, are replaced by the mono-solvate[60].

r^2 s for the organic uranium, plutonium and nitric acid concentrations calculated with the new parameter values are compared with those calculated with Whatley's correction and Richardson's model in Table 5. r^2 s for the organic plutonium and nitric acid concentrations from the model with the new parameter values are better, but there are little differences in r^2 s for the organic uranium concentrations. It was shown in Table 3 that Whatley's model better described the distribution of uranium, plutonium and nitric acid than Richardson's model. However, it is seen in Table 5 that there is slight improvement of Whatley's corrected model over Richardson's model in terms of r^2 .

4.2 Construction of a New Mathematical Model Using Regression Analysis

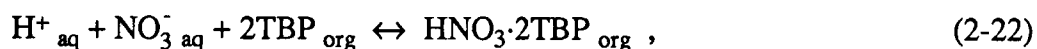
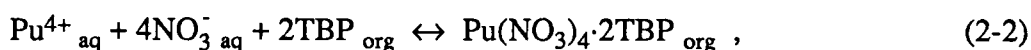
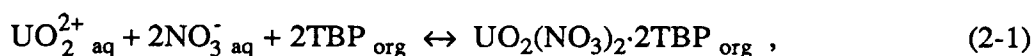
As discussed in Section 4.1, Richardson's model calculates non-zero distribution coefficients of uranium, plutonium and nitric acid even when the corresponding component is not present in the system. A study was initiated to construct an empirical mathematical model without such contradictions and to demonstrate the use of the SYSNLIN procedure for model construction.

Table 5. Comparison of the Coefficients of Determination (r^2) for the Organic Uranium, Plutonium and Nitric Acid Concentrations.

Components	New Parameters	Whatley's Correction	Richardson's Model
U	0.9949	0.9945	0.9934
Pu	0.9921	0.9829	0.9810
HNO ₃	0.9788	0.9697	0.9686

Since most of the data usable for the SYSNLIN procedure were for 30 volume percent TBP, model construction was based on the only 30 volume percent TBP. Then, the effect of TBP concentrations could be implemented by adding terms for TBP volume fraction. The total number of usable observations for 30 volume percent TBP was 801, and the total number of data points used was 1512, of which 564 data points were for uranium, 183 data points for plutonium and 765 data points for nitric acid.

The derivation of the model was exactly as Horner[73] except for the use of a solute-free concentration unit. From the following assumed reactions for the Purex solvent extraction processes,



the pseudo-thermodynamic equilibrium constants in solute-free concentration unit are defined by:

$$K_U^{S'} = \frac{(UO_2(NO_3)_2 \cdot 2TBP)_o}{(UO_2^{2+})_a (NO_3^-)_a^2 (TBP)_o^2}, \quad (4-10)$$

$$K_{Pu}^{S'} = \frac{(Pu(NO_3)_4 \cdot 2TBP)_o}{(Pu^{4+})_a (NO_3^-)_a^4 (TBP)_o^2}, \quad (4-11)$$

$$K_{H1}^{S'} = \frac{(HNO_3 \cdot TBP)_o}{(H^+)_a (NO_3^-)_a (TBP)_o}, \quad (4-12)$$

$$K_{H2}^{S'} = \frac{(HNO_3 \cdot 2TBP)_o}{(H^+)_a (NO_3^-)_a (TBP)_o^2}, \quad (4-13)$$

where the quantities in parentheses represent the solute-free concentrations of the reacting species, superscripts *s* means the solute-free base, and the prime is used to distinguish the constants from those used by Richardson.

The organic phase concentrations of the components, rather than the distribution coefficients of the components, were used as dependent variables for the SYSNLIN procedure as follows:

$$(UO_2(NO_3)_2 \cdot 2TBP)_o = K_U^{S'} (UO_2^{2+})_a (NO_3^-)_a^2 (TBP)_o^2, \quad (4-14)$$

$$(Pu(NO_3)_4 \cdot 2TBP)_o = K_{Pu}^{S'} (Pu^{4+})_a (NO_3^-)_a^4 (TBP)_o^2, \quad (4-15)$$

$$\begin{aligned} (H^+)_o &= (HNO_3 \cdot TBP)_o + (HNO_3 \cdot 2TBP)_o \\ &= [K_{H1}^{S'} + K_{H2}^{S'} (TBP)_o] (NO_3^-)_a (TBP)_o, \end{aligned} \quad (4-16)$$

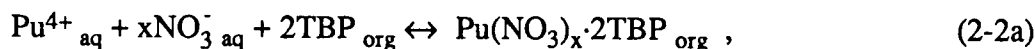
where aqueous total nitrate concentrations, $(NO_3^-)_a$, is calculated by:

$$(NO_3^-)_a = 2(UO_2^{2+})_a + 4(Pu^{4+})_a + (H^+)_a. \quad (4-17)$$

The coefficient 4 was reduced to 2 as discussed in Section 2.2. Later, a new coefficient was proposed, which was defined as follows[90]:

$$x = 4.0 - 2.0 \frac{(Pu^{4+})_a}{(Pu^{4+})_a - (UO_2^{2+})_a}. \quad (4-18)$$

Both coefficients, 2 and x, were tested for the SYSNLIN procedure. Since using x resulted in better fitting and faster convergence, x was adopted. This required modifications as follows:



$$K_{\text{Pu}}^{\text{S}'} = \frac{(\text{Pu}(\text{NO}_3)_x \cdot 2\text{TBP})_{\text{o}}}{(\text{Pu}^{4+})_{\text{a}} (\text{NO}_3^{-})_{\text{a}}^x (\text{TBP})_{\text{o}}^2} , \quad (4-11a)$$

$$(\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP})_{\text{o}} = K_{\text{Pu}}^{\text{S}'} (\text{Pu}^{4+})_{\text{a}} (\text{NO}_3^{-})_{\text{a}}^x (\text{TBP})_{\text{o}}^2 . \quad (4-15a)$$

The uncomplexed, free TBP concentrations, $(\text{TBP})_{\text{o}}$, is calculated by material balance, as before. Thus,

$$(\text{TBP})_{\text{o}} = T_{\text{S}} - 2(\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP})_{\text{o}} - 2(\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBP})_{\text{o}} - (\text{HNO}_3 \cdot \text{TBP})_{\text{o}} - 2(\text{HNO}_3 \cdot 2\text{TBP})_{\text{o}} . \quad (2-42)$$

Substituting Eqs. (4-14)-(4-16) into Eq. (2-42) results in quadratic equation for $(\text{TBP})_{\text{o}}$ as follows:

$$(\text{TBP})_{\text{o}} = T_{\text{S}} - 2K_{\text{U}}^{\text{S}'} (\text{UO}_2^{2+})_{\text{a}} (\text{NO}_3^{-})_{\text{a}}^2 (\text{TBP})_{\text{o}}^2 - 2K_{\text{Pu}}^{\text{S}'} (\text{Pu}^{4+})_{\text{a}} (\text{NO}_3^{-})_{\text{a}}^x (\text{TBP})_{\text{o}}^2 - K_{\text{H1}}^{\text{S}'} (\text{H}^+)_{\text{a}} (\text{NO}_3^{-})_{\text{a}} (\text{TBP})_{\text{o}} - 2K_{\text{H2}}^{\text{S}'} (\text{H}^+)_{\text{a}} (\text{NO}_3^{-})_{\text{a}} (\text{TBP})_{\text{o}}^2 . \quad (4-19)$$

Solving the quadratic equation produces

$$(\text{TBP})_{\text{o}} = \frac{-B + \sqrt{B^2 - 4AC}}{2A} , \quad (4-20)$$

$$\text{where } A = 2[K_{\text{U}}^{\text{S}'} (\text{UO}_2^{2+})_{\text{a}} (\text{NO}_3^{-})_{\text{a}}^2 + K_{\text{Pu}}^{\text{S}'} (\text{Pu}^{4+})_{\text{a}} (\text{NO}_3^{-})_{\text{a}}^x + K_{\text{H2}}^{\text{S}'} (\text{H}^+)_{\text{a}} (\text{NO}_3^{-})_{\text{a}}] , \quad (4-21)$$

$$B = 1 + K_{\text{H1}}^{\text{S}'} (\text{H}^+)_{\text{a}} (\text{NO}_3^{-})_{\text{a}} , \quad (4-22)$$

$$C = -T_{\text{S}} . \quad (4-23)$$

The pseudo-thermodynamic constant for each component was fitted to the data as a function of the concentrations of the components, temperature, aqueous total nitrate

concentration and their cross products. Terms up to third-order were needed to describe the distribution of the components as follows:

$$\begin{aligned}
 K_U^S = & [\beta_1 (UO_2^{2+})_a + \beta_{11} (UO_2^{2+})_a^2 + \beta_{12} (UO_2^{2+})_a (Pu^{4+})_a + \beta_{13} (UO_2^{2+})_a (H^+)_a \\
 & + \beta_{111} (UO_2^{2+})_a^3 + \beta_{122} (UO_2^{2+})_a (Pu^{4+})_a^2 + \beta_{133} (UO_2^{2+})_a (H^+)_a^2 \\
 & + \beta_{112} (UO_2^{2+})_a^2 (Pu^{4+})_a + \beta_{113} (UO_2^{2+})_a^2 (H^+)_a + \beta_{123} (UO_2^{2+})_a (Pu^{4+})_a \\
 & (H^+)_a] \text{Exp}[\beta_{UT} t + \beta_{UTN} (NO_3^-)_a t], \quad (4-24)
 \end{aligned}$$

$$\begin{aligned}
 K_{Pu}^S = & [\beta_2 (Pu^{4+})_a + \beta_{22} (Pu^{4+})_a^2 + \beta_{21} (Pu^{4+})_a (UO_2^{2+})_a + \beta_{23} (Pu^{4+})_a (H^+)_a \\
 & + \beta_{222} (Pu^{4+})_a^3 + \beta_{211} (Pu^{4+})_a (UO_2^{2+})_a^2 + \beta_{233} (Pu^{4+})_a (H^+)_a^2 \\
 & + \beta_{221} (Pu^{4+})_a^2 (UO_2^{2+})_a + \beta_{223} (Pu^{4+})_a^2 (H^+)_a + \beta_{213} (Pu^{4+})_a (UO_2^{2+})_a \\
 & (H^+)_a] \text{Exp}[\beta_{PT} t + \beta_{PTN} (NO_3^-)_a t], \quad (4-25)
 \end{aligned}$$

$$\begin{aligned}
 K_{H1}^S = & [\alpha_3 (H^+)_a + \alpha_{33} (H^+)_a^2 + \alpha_{31} (H^+)_a (UO_2^{2+})_a + \alpha_{32} (H^+)_a (Pu^{4+})_a \\
 & + \alpha_{333} (H^+)_a^3 + \alpha_{311} (H^+)_a (UO_2^{2+})_a^2 + \alpha_{322} (H^+)_a (Pu^{4+})_a^2 \\
 & + \alpha_{331} (H^+)_a^2 (UO_2^{2+})_a + \alpha_{332} (H^+)_a^2 (Pu^{4+})_a + \alpha_{312} (H^+)_a (UO_2^{2+})_a \\
 & (Pu^{4+})_a] \text{Exp}[\alpha_{H1T} t + \alpha_{H1TN} (NO_3^-)_a t], \quad (4-26)
 \end{aligned}$$

$$\begin{aligned}
 K_{H2}^S = & [\beta_3 (H^+)_a + \beta_{33} (H^+)_a^2 + \beta_{31} (H^+)_a (UO_2^{2+})_a + \beta_{32} (H^+)_a (Pu^{4+})_a \\
 & + \beta_{333} (H^+)_a^3 + \beta_{311} (H^+)_a (UO_2^{2+})_a^2 + \beta_{322} (H^+)_a (Pu^{4+})_a^2 \\
 & + \beta_{331} (H^+)_a^2 (UO_2^{2+})_a + \beta_{332} (H^+)_a^2 (Pu^{4+})_a + \beta_{312} (H^+)_a (UO_2^{2+})_a \\
 & (Pu^{4+})_a] \text{Exp}[\beta_{H2T} t + \beta_{H2TN} (NO_3^-)_a t], \quad (4-27)
 \end{aligned}$$

where β 's and α 's are parameters to be estimated, Exp is exponential, and numbers 1,2 and 3 in subscripts refer to uranium, plutonium and nitric acid respectively.

The total number of the parameters was 48. As in Section 4.1, the ITOLS and GAUSS options were requested, and the convergence criterion used was 0.01.

The procedure converged at 97 iterations. Six parameters out of 48 were statistically insignificant, and, after excluding these terms, r^2 s for the organic uranium, plutonium and nitric acid concentrations were 0.9918, 0.9931 and 0.9630 respectively. r^2 for the organic plutonium concentration was unexpectedly better than that for the organic uranium concentration. Presumably, this was because 173 plutonium data points out of 183 were at 25 and 26 °C, i.e., r^2 for the organic plutonium concentration would be lower if the plutonium data well-distributed over the temperature ranges. This model does not fully describe the temperature effect on the plutonium distribution. Therefore, the use of the model to calculate the plutonium distribution coefficients at temperatures other than 25 °C requires careful considerations. Without the statistically insignificant terms, the equations, with estimated parameter values, for K_U^S , K_{Pu}^S , K_{H1}^S and K_{H2}^S are

$$\begin{aligned}
 K_U^S = & [248.778 (UO_2^{2+})_a - 801.58 (UO_2^{2+})_a^2 - 7109.3 (UO_2^{2+})_a (Pu^{4+})_a \\
 & + 784.102 (UO_2^{2+})_a^3 + 13214.44 (UO_2^{2+})_a (Pu^{4+})_a^2 + 1384.9 (UO_2^{2+})_a (H^+)_a^2 \\
 & + 706.336 (UO_2^{2+})_a^2 (H^+)_a + 8645.63 (UO_2^{2+})_a (Pu^{4+})_a (H^+)_a] \\
 & \text{Exp}[-0.0269 t] , \quad (4-28)
 \end{aligned}$$

$$\begin{aligned}
 K_{Pu}^S = & [210.381 (Pu^{4+})_a - 3250.9 (Pu^{4+})_a^2 + 2122.97 (Pu^{4+})_a (UO_2^{2+})_a \\
 & + 292.719 (Pu^{4+})_a (H^+)_a + 11720.6 (Pu^{4+})_a^3 + 417.083 (Pu^{4+})_a (UO_2^{2+})_a^2 \\
 & - 5159.1 (Pu^{4+})_a^2 (UO_2^{2+})_a + 416.762 (Pu^{4+})_a^2 (H^+)_a - 403.59 (Pu^{4+})_a \\
 & (UO_2^{2+})_a (H^+)_a] \text{Exp}[-0.0311 t + 0.01 (NO_3^-)_a t] , \quad (4-29)
 \end{aligned}$$

$$\begin{aligned}
K_{H1}^{S'} = & [0.056 (H^+)_a - 0.0097 (H^+)_a^2 + 0.447 (H^+)_a (UO_2^{2+})_a \\
& + 0.38 (H^+)_a (Pu^{4+})_a + 0.00062 (H^+)_a^3 - 0.284 (H^+)_a (UO_2^{2+})_a^2 \\
& + 1.596 (H^+)_a (Pu^{4+})_a^2 + 0.0181 (H^+)_a^2 (UO_2^{2+})_a - 0.0363 (H^+)_a^2 (Pu^{4+})_a] \\
& \text{Exp}[0.00763 t + 0.0014 (NO_3^-)_a t] , \quad (4-30)
\end{aligned}$$

$$\begin{aligned}
K_{H2}^{S'} = & [0.343 (H^+)_a - 0.141 (H^+)_a^2 - 20.922 (H^+)_a (UO_2^{2+})_a \\
& + 8.171 (H^+)_a (Pu^{4+})_a + 0.0132 (H^+)_a^3 + 403.139 (H^+)_a (UO_2^{2+})_a^2 \\
& + 381.906 (H^+)_a (Pu^{4+})_a^2 + 27.733 (H^+)_a^2 (UO_2^{2+})_a - 1.814 (H^+)_a^2 (Pu^{4+})_a \\
& + 1289.63 (H^+)_a (UO_2^{2+})_a (Pu^{4+})_a] \text{Exp}[-0.0084 (NO_3^-)_a t] . \quad (4-31)
\end{aligned}$$

With these equations the organic uranium, plutonium and nitric acid concentrations can be calculated. Though the model needed more refinements for the nitric acid distribution and TBP concentration effects, this study could not be completed because, with 42 plus additional parameters to be included for the refinements and 801 observations with a total number of data points of 1512, the SYSNLIN procedure required unacceptable amounts of computer times.

CHAPTER 5

SUMMARY AND RECOMMENDATION

Two approaches have been made to improve Richardson's model which calculates equilibrium distribution coefficients of uranium(VI), plutonium(IV) and nitric acid between aqueous nitric acid solutions of these components and organic solutions of TBP diluted in normal paraffin hydrocarbon as a function of aqueous total nitrate concentrations, TBP volume fraction and a temperature correction factor. First, assuming that the pseudo-thermodynamic equilibrium constant for nitric acid di-solvate extraction with TBP would not be equal to that for nitric acid mono-solvate extraction, 7 parameters in nitric acid distribution model were re-evaluated using the minimum variance location procedure. The assumption was based on previous work[60,87]. With the new values of the parameters, the variance of the errors of the nitric acid distribution coefficients was reduced.

Only a slight reduction of the variances for uranium and plutonium distribution coefficients was achieved by reducing the nitric acid variance. Failure to reduce the uranium and plutonium variances could be due to the incompleteness of the nitric acid distribution model.

It has been known that the nitric acid di-solvate in TBP is hydrated and that other types of hydrated higher solvates are formed, depending on the acidity and concentrations of uranium and plutonium in organic phase. Therefore, water in the organic phase, partly dissolved in uncomplexed, free TBP, and partly in the solvates, should be included in the nitric acid distribution model.

It can be concluded that the nitric acid distribution model is incomplete and needs to be re-constructed to include water in order to correctly describe the nitric acid

distribution and to improve predictions of Richardson's model for uranium and plutonium distribution coefficients as well.

Another approach to improving Richardson's model was made by re-estimating parameters in the model with a nonlinear simultaneous regression procedure in SAS, the SYSNLIN procedure. In this procedure organic phase concentrations of uranium, plutonium and nitric acid were used as independent variables instead of the distribution coefficients of the components. As a result of this work, 21 parameters were estimated, and, with the new parameter values, coefficients of determination (r^2) for uranium, plutonium and nitric acid were 0.9949, 0.9921 and 0.9788 respectively. r^2 for plutonium and nitric acid were improved, but there was little difference in r^2 for uranium.

Caution should be given to the use of the new value for the plutonium temperature coefficient at temperatures other than 25 °C because 173 out of 183 plutonium data points used to estimate the coefficient were at 25 and 26 °C.

Further corrections should be done to the coefficients for the temperature correction factors. It has been shown that temperature effects on the distribution of uranium, plutonium and nitric acid are diminished as TBP "loading" with the components is increased and becomes nearly zero as TBP is saturated [29,52,53,57,69]. Thus, a single coefficient for temperature effect would not properly describe the distribution of uranium, plutonium and nitric acid when TBP loading is high.

The SYSNLIN procedure has been used to demonstrate one way to construct an empirical model for equilibrium distribution of uranium(VI), plutonium(IV) and nitric acid. The pseudo-thermodynamic equilibrium constant for each component was fitted to the data screened for the procedure as a function of aqueous concentrations of the

components, temperature, aqueous total nitrate concentrations and their cross products up to third-order.

Since most of the data usable for the SYSNLIN procedure were at 30 volume percent TBP, the fitting procedure was limited to 30 volume percent TBP. The r^2 of uranium, plutonium and nitric acid were 0.9918, 0.9931 and 0.9630 respectively. The results showed that the pseudo-thermodynamic constants could be fitted as a function of the component concentrations in a system.

Further refinements to the model could not be done because of large computing time requirements for the procedure.

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APPENDIXES

APPENDIX A

NOMENCLATURE

APPENDIX A

NOMENCLATURE

A = parameter, Eqs. (3-1)-(3-4)

B = parameter, Eqs. (4-1)-(4-9)

C = molar concentration of a solute, Eqs. (2-48)-(2-51)

D^C = distribution coefficient in molar concentration, Eqs. (2-7)-(2-9)

D^S = distribution coefficient in solute-free concentration, Eqs. (2-27)-(2-31)

F = volume fraction of TBP in dry, solute-free solvent

I = ionic strength in aqueous phase, Eq. (2-14)

K^C = pseudo-thermodynamic equilibrium constant in molar concentration,
Eqs. (2-4)-(2-6)

K^S = pseudo-thermodynamic equilibrium constant in solute-free concentration,
Eqs. (2-23)-(2-26)

$K^{S'}$ = pseudo-thermodynamic equilibrium constant in solute-free concentration,
Eqs. (4-10)-(4-13)

K^* = pseudo-thermodynamic equilibrium constant in solute-free concentration at 100
volume percent TBP and 25 °C, Eqs. (2-34)-(2-37)

m = molal concentration of a solute, Eqs. (2-48)-(2-49)

N = total number of data points of a components in a subset, Eq. (2-44)

n_a = aqueous total nitrate concentration in solute-free concentration unit, Eq. (2-32)

S = solute-free concentration of a solute, Eqs. (2-50)-(2-51)

t = temperature, °C

T_C = equilibrium molar concentration of total amount of TBP in organic phase

T_S = solute-free concentration of TBP in dry, solute-free solvent, Eq. (2-11)

V = molecular volume of a solute

() = solute-free concentration

[] = molar concentration

Greek Letters

α = parameter

β = parameter

θ = parameter, Eqs. (2-45)-(2-47)

ρ_{TBP} = density of TBP, Eqs. (2-11) and (2-66)

ρ_z = density of a solvent, Eqs. (2-48)-(2-49)

τ = quantity defined in Eq. (2-41)

Subscripts

a = aqueous phase

aq = aqueous phase

C = molar concentration

H = nitric acid

H1 = nitric acid solvated with 1 molecule of TBP

H2 = nitric acid solvated with 2 molecules of TBP

i = ith component

o = organic phase

org = organic phase

os = concentration of a solute required to saturate the TBP, Eqs. (2-59)-(2-63)

Pu = plutonium

S = solute-free concentration

U = uranium

W = water

1 = uranium, Eqs. (4-24)-(4-27)

2 = plutonium, Eqs. (4-24)-(4-27)

3 = nitric acid, Eqs. (4-24)-(4-27)

Superscripts

C = molar concentration

S = solute-free concentration

* = equilibrium at 100 percent TBP and 25 °C, Eqs. (2-34)-(2-37)

APPENDIX B

DISTRIBUTION COEFFICIENTS OF URANIUM(VI), PLUTONIUM(IV) AND
NITRIC ACID WITH 20 VOLUME PERCENT TBP - PART I

APPENDIX B

DISTRIBUTION COEFFICIENTS OF URANIUM(VI), PLUTONIUM(IV) AND NITRIC ACID WITH 20 VOLUME PERCENT TBP - PART I

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
1	3.000	0.713	0.000	25.0	16.700	0.000	
2	2.998	0.952	0.000	25.0	15.000	0.000	
3	2.995	1.997	0.000	25.0	12.000	0.000	
4	3.000	2.380	0.000	25.0	11.000	0.000	
5	2.998	4.964	0.000	25.0	7.200	0.000	
6	2.999	9.605	0.000	25.0	4.700	0.000	
7	2.998	11.306	0.000	25.0	4.200	0.000	
8	2.853	0.000	0.398	25.0	0.000	8.000	
9	2.645	0.000	0.116	25.0	0.000	5.198	
10	1.565	0.000	1.554	25.0	0.000	3.000	
11	2.708	0.000	8.170	25.0	0.000	3.300	
12	1.495	0.000	0.126	25.0	0.000	2.802	
13	1.461	0.000	5.228	25.0	0.000	2.200	
14	1.611	0.000	13.351	25.0	0.000	1.900	
15	0.285	0.000	14.938	25.0	0.000	0.200	
16	0.102	0.000	0.000	25.0	0.000	0.000	0.020
17	0.208	0.000	0.000	25.0	0.000	0.000	0.038
18	0.487	0.000	0.000	25.0	0.000	0.000	0.081
19	0.950	0.000	0.000	25.0	0.000	0.000	0.115
20	1.370	0.000	0.000	25.0	0.000	0.000	-0.140
21	1.740	0.000	0.000	25.0	0.000	0.000	0.144
22	1.870	0.000	0.000	25.0	0.000	0.000	0.144
23	2.620	0.000	0.000	25.0	0.000	0.000	-0.146
24	3.530	0.000	0.000	25.0	0.000	0.000	0.139
25	4.760	0.000	0.000	25.0	0.000	0.000	0.124
26	5.980	0.000	0.000	25.0	0.000	0.000	0.108
27	7.620	0.000	0.000	25.0	0.000	0.000	-0.091
28	9.310	0.000	0.000	25.0	0.000	0.000	0.080
29	10.900	0.000	0.000	25.0	0.000	0.000	0.074
30	12.600	0.000	0.000	25.0	0.000	0.000	0.072
31	13.800	0.000	0.000	25.0	0.000	0.000	0.076
32	15.300	0.000	0.000	25.0	0.000	0.000	0.083
33	0.280	0.000	0.000	20.0	0.000	0.000	-0.068
34	0.550	0.000	0.000	20.0	0.000	0.000	0.097
35	0.800	0.000	0.000	20.0	0.000	0.000	0.127

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (°C)	D _U	D _{Pu}	D _H
36	1.060	0.000	0.000	20.0	0.000	0.000	0.140
37	1.300	0.000	0.000	20.0	0.000	0.000	0.148
38	1.520	0.000	0.000	20.0	0.000	0.000	0.152
39	1.810	0.000	0.000	20.0	0.000	0.000	0.153
40	2.050	0.000	0.000	20.0	0.000	0.000	0.155
41	2.300	0.000	0.000	20.0	0.000	0.000	0.155
42	2.550	0.000	0.000	20.0	0.000	0.000	0.155
43	2.930	0.000	0.000	20.0	0.000	0.000	0.150
44	3.310	0.000	0.000	20.0	0.000	0.000	-0.153
45	3.460	0.000	0.000	20.0	0.000	0.000	0.146
46	3.880	0.000	0.000	20.0	0.000	0.000	0.140
47	4.080	0.000	0.000	20.0	0.000	0.000	0.137
48	4.450	0.000	0.000	20.0	0.000	0.000	0.133
49	4.700	0.000	0.000	20.0	0.000	0.000	0.131
50	5.030	0.000	0.000	20.0	0.000	0.000	0.126
51	5.200	0.000	0.000	20.0	0.000	0.000	0.124
52	6.340	0.000	0.000	20.0	0.000	0.000	0.109
53	7.340	0.000	0.000	20.0	0.000	0.000	0.099
54	8.170	0.000	0.000	20.0	0.000	0.000	0.092
55	9.440	0.000	0.000	20.0	0.000	0.000	0.084
56	10.290	0.000	0.000	20.0	0.000	0.000	0.080
57	0.350	0.000	0.000	25.0	0.000	0.000	-0.014
58	0.720	0.000	0.000	25.0	0.000	0.000	0.096
59	1.180	0.000	0.000	25.0	0.000	0.000	0.123
60	1.280	0.000	0.000	25.0	0.000	0.000	-0.139
61	1.560	0.000	0.000	25.0	0.000	0.000	0.135
62	2.080	0.000	0.000	25.0	0.000	0.000	0.144
63	2.580	0.000	0.000	25.0	0.000	0.000	0.149
64	2.960	0.000	0.000	25.0	0.000	0.000	0.145
65	3.140	0.000	0.000	25.0	0.000	0.000	0.143
66	3.670	0.000	0.000	25.0	0.000	0.000	0.138
67	3.880	0.000	0.000	25.0	0.000	0.000	0.138
68	4.500	0.000	0.000	25.0	0.000	0.000	-0.131
69	5.140	0.000	0.000	25.0	0.000	0.000	0.123
70	5.350	0.000	0.000	25.0	0.000	0.000	0.120
71	6.420	0.000	0.000	25.0	0.000	0.000	0.107
72	7.400	0.000	0.000	25.0	0.000	0.000	0.097
73	8.610	0.000	0.000	25.0	0.000	0.000	0.087
74	9.700	0.000	0.000	25.0	0.000	0.000	0.083
75	0.500	1.430	0.000	20.0	-1.329	0.000	
76	0.500	2.620	0.000	20.0	1.450	0.000	
77	0.500	6.400	0.000	20.0	1.109	0.000	
78	0.500	14.500	0.000	20.0	-1.103	0.000	-0.052
79	0.500	42.000	0.000	20.0	-0.976	0.000	-0.062

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
80	0.500	80.800	0.000	20.0	0.705	0.000	-0.062
81	0.500	148.500	0.000	20.0	-0.492	0.000	-0.052
82	1.000	5.000	0.000	20.0	-2.320	0.000	
83	1.000	9.800	0.000	20.0	-2.643	0.000	-0.076
84	1.000	13.580	0.000	20.0	-2.551	0.000	0.078
85	1.000	22.680	0.000	20.0	-1.764	0.000	0.066
86	1.000	42.700	0.000	20.0	-1.264	0.000	0.040
87	1.000	50.600	0.000	20.0	1.107	0.000	0.038
88	1.000	104.000	0.000	20.0	0.673	0.000	0.034
89	1.000	133.000	0.000	20.0	0.553	0.000	0.026
90	1.000	164.200	0.000	20.0	0.463	0.000	0.022
91	2.000	1.440	0.000	20.0	-6.250	0.000	
92	2.000	4.700	0.000	20.0	5.957	0.000	0.099
93	2.000	8.800	0.000	20.0	4.030	0.000	0.076
94	2.000	13.300	0.000	20.0	-3.489	0.000	-0.054
95	2.000	18.000	0.000	20.0	-2.717	0.000	0.060
96	2.000	39.300	0.000	20.0	1.605	0.000	0.046
97	2.000	88.000	0.000	20.0	0.824	0.000	0.027
98	2.000	135.500	0.000	20.0	0.554	0.000	0.025
99	2.000	240.000	0.000	20.0	0.321	0.000	0.023
100	4.000	3.910	0.000	20.0	9.258	0.000	0.083
101	4.000	8.200	0.000	20.0	6.732	0.000	
102	4.000	17.660	0.000	20.0	3.570	0.000	
103	4.000	19.100	0.000	20.0	-3.382	0.000	-0.055
104	4.000	46.400	0.000	20.0	1.552	0.000	0.034
105	4.000	95.000	0.000	20.0	0.795	0.000	0.019
106	4.000	214.000	0.000	20.0	0.379	0.000	0.017
107	4.000	108.000	0.000	20.0	0.713	0.000	
108	4.000	173.600	0.000	20.0	0.450	0.000	
109	6.000	3.800	0.000	20.0	10.921	0.000	0.067
110	6.000	28.600	0.000	20.0	2.273	0.000	0.033
111	6.000	72.300	0.000	20.0	1.015	0.000	0.023
112	6.000	121.000	0.000	20.0	0.628	0.000	0.020
113	6.000	156.000	0.000	20.0	0.492	0.000	0.020
114	8.000	4.400	0.000	20.0	8.023	0.000	0.056
115	8.000	31.100	0.000	20.0	2.016	0.000	0.034
116	8.000	53.200	0.000	20.0	1.258	0.000	0.027
117	8.000	99.300	0.000	20.0	0.764	0.000	0.018
118	8.000	206.000	0.000	20.0	0.374	0.000	0.019
119	0.500	12.030	0.000	40.0	0.993	0.000	0.028
120	0.500	42.300	0.000	40.0	-0.849	0.000	-0.010
121	0.500	94.300	0.000	40.0	-0.651	0.000	0.010
122	0.500	178.700	0.000	40.0	-0.421	0.000	
123	1.000	24.200	0.000	40.0	1.446	0.000	0.040
124	1.000	50.300	0.000	40.0	1.034	0.000	0.033

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
125	1.000	100.500	0.000	40.0	0.672	0.000	-0.028
126	1.000	180.400	0.000	40.0	0.425	0.000	0.013
127	2.000	11.700	0.000	40.0	3.094	0.000	0.085
128	2.000	29.600	0.000	40.0	1.757	0.000	-0.040
129	2.000	38.900	0.000	40.0	1.503	0.000	0.041
130	2.000	52.800	0.000	40.0	1.193	0.000	0.042
131	2.000	101.200	0.000	40.0	0.707	0.000	-0.035
132	2.000	195.400	0.000	40.0	0.384	0.000	0.020
133	4.000	4.800	0.000	40.0	7.583	0.000	0.090
134	4.000	29.500	0.000	40.0	2.039	0.000	-0.066
135	4.000	53.660	0.000	40.0	1.258	0.000	-0.032
136	4.000	97.150	0.000	40.0	0.750	0.000	0.027
137	4.000	192.500	0.000	40.0	0.399	0.000	0.023
138	8.000	7.800	0.000	40.0	4.228	0.000	-0.062
139	8.000	28.700	0.000	40.0	1.742	0.000	0.050
140	8.000	30.500	0.000	40.0	1.679	0.000	0.045
141	8.000	46.100	0.000	40.0	1.291	0.000	0.043
142	8.000	49.000	0.000	40.0	1.243	0.000	0.043
143	8.000	60.000	0.000	40.0	1.067	0.000	0.040
144	8.000	105.000	0.000	40.0	0.682	0.000	0.026
145	8.000	122.500	0.000	40.0	0.588	0.000	0.024
146	8.000	198.200	0.000	40.0	0.404	0.000	0.023
147	0.500	20.000	0.000	40.0	-0.635	0.000	-0.040
148	0.500	47.000	0.000	70.0	0.702	0.000	0.038
149	0.500	97.500	0.000	70.0	-0.595	0.000	-0.040
150	0.500	195.000	0.000	70.0	0.364	0.000	0.024
151	1.000	32.500	0.000	70.0	1.025	0.000	-0.050
152	1.000	60.000	0.000	70.0	0.783	0.000	0.041
153	1.000	122.000	0.000	70.0	0.541	0.000	-0.020
154	1.000	210.000	0.000	70.0	0.360	0.000	-0.026
155	1.000	15.500	0.000	70.0	1.258	0.000	-0.100
156	2.000	11.100	0.000	70.0	2.324	0.000	0.116
157	2.000	15.500	0.000	70.0	2.065	0.000	0.092
158	2.000	36.070	0.000	70.0	1.309	0.000	0.086
159	2.000	45.200	0.000	70.0	1.150	0.000	-0.064
160	2.000	54.700	0.000	70.0	1.040	0.000	0.080
161	2.000	112.800	0.000	70.0	0.622	0.000	0.067
162	2.000	186.000	0.000	70.0	0.410	0.000	0.058
163	4.000	9.570	0.000	70.0	3.333	0.000	0.098
164	4.000	9.660	0.000	70.0	3.282	0.000	0.100
165	4.000	35.500	0.000	70.0	1.563	0.000	0.070
166	4.000	66.000	0.000	70.0	0.983	0.000	0.063
167	4.000	114.000	0.000	70.0	0.649	0.000	0.053
168	4.000	200.400	0.000	70.0	0.385	0.000	0.053
169	8.000	13.600	0.000	70.0	1.831	0.000	0.068

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
170	8.000	35.000	0.000	70.0	1.200	0.000	-0.071
171	8.000	70.500	0.000	70.0	0.767	0.000	0.056
172	8.000	74.800	0.000	70.0	0.745	0.000	0.053
173	8.000	111.270	0.000	70.0	0.588	0.000	0.050
174	8.000	150.000	0.000	70.0	0.467	0.000	0.048
175	8.000	211.100	0.000	70.0	0.357	0.000	0.044
176	0.237	0.000	0.000	23.0	0.000	0.000	0.042
177	0.466	0.000	0.000	23.0	0.000	0.000	0.075
178	0.869	0.000	0.000	23.0	0.000	0.000	0.113
179	1.730	0.000	0.000	23.0	0.000	0.000	0.143
180	2.700	0.000	0.000	23.0	0.000	0.000	0.143
181	3.570	0.000	0.000	23.0	0.000	0.000	0.136
182	5.480	0.000	0.000	23.0	0.000	0.000	0.115
183	7.280	0.000	0.000	23.0	0.000	0.000	0.097
184	11.040	0.000	0.000	23.0	0.000	0.000	0.077
185	0.277	0.000	0.000	40.0	0.000	0.000	0.036
186	0.490	0.000	0.000	40.0	0.000	0.000	0.061
187	0.905	0.000	0.000	40.0	0.000	0.000	0.102
188	1.780	0.000	0.000	40.0	0.000	0.000	0.136
189	2.570	0.000	0.000	40.0	0.000	0.000	-0.156
190	3.620	0.000	0.000	40.0	0.000	0.000	0.136
191	5.400	0.000	0.000	40.0	0.000	0.000	0.118
192	7.630	0.000	0.000	40.0	0.000	0.000	-0.092
193	10.820	0.000	0.000	40.0	0.000	0.000	0.079
194	0.228	0.000	0.000	70.0	0.000	0.000	0.031
195	0.472	0.000	0.000	70.0	0.000	0.000	0.055
196	0.862	0.000	0.000	70.0	0.000	0.000	0.092
197	1.630	0.000	0.000	70.0	0.000	0.000	-0.143
198	2.640	0.000	0.000	70.0	0.000	0.000	0.145
199	3.370	0.000	0.000	70.0	0.000	0.000	0.140
200	5.400	0.000	0.000	70.0	0.000	0.000	0.119
201	7.090	0.000	0.000	70.0	0.000	0.000	0.102
202	10.700	0.000	0.000	70.0	0.000	0.000	0.082
203	0.500	0.000	0.000	20.0	0.000	0.000	-0.063
204	0.500	5.000	0.000	20.0	-1.080	0.000	
205	0.500	20.000	0.000	20.0	-1.095	0.000	
206	0.500	50.000	0.000	20.0	-0.928	0.000	
207	0.500	100.000	0.000	20.0	0.624	0.000	
208	0.500	150.000	0.000	20.0	-0.500	0.000	
209	1.000	0.000	0.000	20.0	0.000	0.000	-0.113
210	1.000	5.000	0.000	20.0	3.020	0.000	-0.100
211	1.000	10.000	0.000	20.0	2.460	0.000	0.084
212	1.000	20.000	0.000	20.0	1.820	0.000	-0.072

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
213	1.000	50.000	0.000	20.0	1.120	0.000	-0.053
214	1.000	100.000	0.000	20.0	0.705	0.000	0.035
215	1.000	150.000	0.000	20.0	0.513	0.000	0.025
216	2.000	0.000	0.000	20.0	0.000	0.000	-0.148
217	2.000	5.000	0.000	20.0	5.560	0.000	0.103
218	2.000	10.000	0.000	20.0	3.890	0.000	-0.086
219	2.000	20.000	0.000	20.0	2.435	0.000	0.069
220	2.000	50.000	0.000	20.0	1.296	0.000	0.043
221	2.000	100.000	0.000	20.0	0.726	0.000	0.031
222	2.000	150.000	0.000	20.0	0.511	0.000	0.021
223	3.000	0.000	0.000	20.0	0.000	0.000	0.148
224	3.000	5.000	0.000	20.0	6.860	0.000	0.090
225	3.000	10.000	0.000	20.0	4.400	0.000	0.075
226	3.000	20.000	0.000	20.0	2.740	0.000	0.057
227	3.000	50.000	0.000	20.0	1.346	0.000	0.037
228	3.000	100.000	0.000	20.0	0.740	0.000	0.026
229	3.000	150.000	0.000	20.0	0.525	0.000	0.015
230	4.000	0.000	0.000	20.0	0.000	0.000	0.136
231	4.000	5.000	0.000	20.0	7.280	0.000	0.079
232	4.000	10.000	0.000	20.0	4.720	0.000	0.063
233	4.000	20.000	0.000	20.0	2.880	0.000	0.048
234	4.000	50.000	0.000	20.0	1.372	0.000	0.030
235	4.000	100.000	0.000	20.0	0.755	0.000	0.021
236	4.000	150.000	0.000	20.0	0.535	0.000	0.016

LIST OF SOURCES

<u>Data Number</u>	<u>Source</u>
1-15	W. Ochsenfeld, H. Schmieder and G. Baumgartel, "Distribution Characteristic of Pu(IV) and U(VI) and Their Mathematical Determination in Metal Nitrate-Nitric Acid and Tributylphosphate Systems," KFK-671 (EUR-3703d), Kernforschungszentrum, Karlsruhe, September 1967.
16-32	D. R. Olander, L. Donadieu and M. Benedict, "The Distribution of Nitric Acid Between Water and Tributyl Phosphate-Hexane Solvents," A.I.Ch.E. Journal, Vol. 7, No. 1, pp.152-159 (1961).
33-74	P. E. Burns, and C. Hanson, "Distribution of Nitric Acid Between Tri-n-Butyl Phosphate and Water," J. Applied Chemistry, Vol. 14, pp. 117-121 (1964).
75-175	A. M. Rozen, L. P. Khorkhorina and S. M. Karpacheva and G. D. Agashkina, "Effect of Temperature on Extraction with Tributyl Phosphate," Soviet Radiochemistry, Vol. 4, pp. 518-526 (1962).
176-202	N. M. Adamskii, S. M. Karpacheva, I. N. Mel'nikov and A. M. Rozen, "The Effect of Temperature on the Extraction of Nitric Acid with Tributylphosphate," Soviet Radiochemistry, Vol. 2, No. 1, pp. 12-18 (1960).
203-236	A. M. Rozen, and Yu. V. Reshet'ko, "Calculation of the Isotherms of Extraction Considering the Change in the Volumes of Phases," Soviet Radiochemistry, Vol. 12, pp. 1-8 (1970).

APPENDIX C

DISTRIBUTION COEFFICIENTS OF URANIUM(VI), PLUTONIUM(IV) AND
NITRIC ACID WITH 20 VOLUME PERCENT TBP - PART II

APPENDIX C

DISTRIBUTION COEFFICIENTS OF URANIUM(VI), PLUTONIUM(IV) AND NITRIC ACID WITH 20 VOLUME PERCENT TBP - PART II

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
33	0.280	0.000	0.000	20.0	0.000	0.000	-0.068
203	0.500	0.000	0.000	20.0	0.000	0.000	-0.063
34	0.550	0.000	0.000	20.0	0.000	0.000	0.097
35	0.800	0.000	0.000	20.0	0.000	0.000	0.127
209	1.000	0.000	0.000	20.0	0.000	0.000	-0.113
36	1.060	0.000	0.000	20.0	0.000	0.000	0.140
37	1.300	0.000	0.000	20.0	0.000	0.000	0.148
38	1.520	0.000	0.000	20.0	0.000	0.000	0.152
39	1.810	0.000	0.000	20.0	0.000	0.000	0.153
216	2.000	0.000	0.000	20.0	0.000	0.000	-0.148
40	2.050	0.000	0.000	20.0	0.000	0.000	0.155
41	2.300	0.000	0.000	20.0	0.000	0.000	0.155
42	2.550	0.000	0.000	20.0	0.000	0.000	0.155
43	2.930	0.000	0.000	20.0	0.000	0.000	0.150
223	3.000	0.000	0.000	20.0	0.000	0.000	0.148
44	3.310	0.000	0.000	20.0	0.000	0.000	-0.153
45	3.460	0.000	0.000	20.0	0.000	0.000	0.146
46	3.880	0.000	0.000	20.0	0.000	0.000	0.140
230	4.000	0.000	0.000	20.0	0.000	0.000	0.136
47	4.080	0.000	0.000	20.0	0.000	0.000	0.137
48	4.450	0.000	0.000	20.0	0.000	0.000	0.133
49	4.700	0.000	0.000	20.0	0.000	0.000	0.131
50	5.030	0.000	0.000	20.0	0.000	0.000	0.126
51	5.200	0.000	0.000	20.0	0.000	0.000	0.124
52	6.340	0.000	0.000	20.0	0.000	0.000	0.109
53	7.340	0.000	0.000	20.0	0.000	0.000	0.099
54	8.170	0.000	0.000	20.0	0.000	0.000	0.092
55	9.440	0.000	0.000	20.0	0.000	0.000	0.084
56	10.290	0.000	0.000	20.0	0.000	0.000	0.080
75	0.500	1.430	0.000	20.0	-1.329	0.000	
76	0.500	2.620	0.000	20.0	1.450	0.000	
204	0.500	5.000	0.000	20.0	-1.080	0.000	
77	0.500	6.400	0.000	20.0	1.109	0.000	
78	0.500	14.500	0.000	20.0	-1.103	0.000	-0.052
205	0.500	20.000	0.000	20.0	-1.095	0.000	
79	0.500	42.000	0.000	20.0	-0.976	0.000	-0.062

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
206	0.500	50.000	0.000	20.0	-0.928	0.000	
80	0.500	80.800	0.000	20.0	0.705	0.000	-0.062
207	0.500	100.000	0.000	20.0	0.624	0.000	
81	0.500	148.500	0.000	20.0	-0.492	0.000	-0.052
208	0.500	150.000	0.000	20.0	-0.500	0.000	
82	1.000	5.000	0.000	20.0	-2.320	0.000	
210	1.000	5.000	0.000	20.0	3.020	0.000	-0.100
83	1.000	9.800	0.000	20.0	-2.643	0.000	-0.076
211	1.000	10.000	0.000	20.0	2.460	0.000	0.084
84	1.000	13.580	0.000	20.0	-2.551	0.000	0.078
212	1.000	20.000	0.000	20.0	1.820	0.000	-0.072
85	1.000	22.680	0.000	20.0	-1.764	0.000	0.066
86	1.000	42.700	0.000	20.0	-1.264	0.000	0.040
213	1.000	50.000	0.000	20.0	1.120	0.000	-0.053
87	1.000	50.600	0.000	20.0	1.107	0.000	0.038
214	1.000	100.000	0.000	20.0	0.705	0.000	0.035
88	1.000	104.000	0.000	20.0	0.673	0.000	0.034
89	1.000	133.000	0.000	20.0	0.553	0.000	0.026
215	1.000	150.000	0.000	20.0	0.513	0.000	0.025
90	1.000	164.200	0.000	20.0	0.463	0.000	0.022
91	2.000	1.440	0.000	20.0	-6.250	0.000	
92	2.000	4.700	0.000	20.0	5.957	0.000	0.099
217	2.000	5.000	0.000	20.0	5.560	0.000	0.103
93	2.000	8.800	0.000	20.0	4.030	0.000	0.076
218	2.000	10.000	0.000	20.0	3.890	0.000	-0.086
94	2.000	13.300	0.000	20.0	-3.489	0.000	-0.054
95	2.000	18.000	0.000	20.0	-2.717	0.000	0.060
219	2.000	20.000	0.000	20.0	2.435	0.000	0.069
96	2.000	39.300	0.000	20.0	1.605	0.000	0.046
220	2.000	50.000	0.000	20.0	1.296	0.000	0.043
97	2.000	88.000	0.000	20.0	0.824	0.000	0.027
221	2.000	100.000	0.000	20.0	0.726	0.000	0.031
98	2.000	135.500	0.000	20.0	0.554	0.000	0.025
222	2.000	150.000	0.000	20.0	0.511	0.000	0.021
99	2.000	240.000	0.000	20.0	0.321	0.000	0.023
224	3.000	5.000	0.000	20.0	6.860	0.000	0.090
225	3.000	10.000	0.000	20.0	4.400	0.000	0.075
226	3.000	20.000	0.000	20.0	2.740	0.000	0.057
227	3.000	50.000	0.000	20.0	1.346	0.000	0.037
228	3.000	100.000	0.000	20.0	0.740	0.000	0.026
229	3.000	150.000	0.000	20.0	0.525	0.000	0.015

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
100	4.000	3.910	0.000	20.0	9.258	0.000	0.083
231	4.000	5.000	0.000	20.0	7.280	0.000	0.079
101	4.000	8.200	0.000	20.0	6.732	0.000	
232	4.000	10.000	0.000	20.0	4.720	0.000	0.063
102	4.000	17.660	0.000	20.0	3.570	0.000	
103	4.000	19.100	0.000	20.0	-3.382	0.000	-0.055
233	4.000	20.000	0.000	20.0	2.880	0.000	0.048
104	4.000	46.400	0.000	20.0	1.552	0.000	0.034
234	4.000	50.000	0.000	20.0	1.372	0.000	0.030
105	4.000	95.000	0.000	20.0	0.795	0.000	0.019
235	4.000	100.000	0.000	20.0	0.755	0.000	0.021
107	4.000	108.000	0.000	20.0	0.713	0.000	
236	4.000	150.000	0.000	20.0	0.535	0.000	0.016
108	4.000	173.600	0.000	20.0	0.450	0.000	
106	4.000	214.000	0.000	20.0	0.379	0.000	0.017
109	6.000	3.800	0.000	20.0	10.921	0.000	0.067
110	6.000	28.600	0.000	20.0	2.273	0.000	0.033
111	6.000	72.300	0.000	20.0	1.015	0.000	0.023
112	6.000	121.000	0.000	20.0	0.628	0.000	0.020
113	6.000	156.000	0.000	20.0	0.492	0.000	0.020
114	8.000	4.400	0.000	20.0	8.023	0.000	0.056
115	8.000	31.100	0.000	20.0	2.016	0.000	0.034
116	8.000	53.200	0.000	20.0	1.258	0.000	0.027
117	8.000	99.300	0.000	20.0	0.764	0.000	0.018
118	8.000	206.000	0.000	20.0	0.374	0.000	0.019
176	0.237	0.000	0.000	23.0	0.000	0.000	0.042
177	0.466	0.000	0.000	23.0	0.000	0.000	0.075
178	0.869	0.000	0.000	23.0	0.000	0.000	0.113
179	1.730	0.000	0.000	23.0	0.000	0.000	0.143
180	2.700	0.000	0.000	23.0	0.000	0.000	0.143
181	3.570	0.000	0.000	23.0	0.000	0.000	0.136
182	5.480	0.000	0.000	23.0	0.000	0.000	0.115
183	7.280	0.000	0.000	23.0	0.000	0.000	0.097
184	11.040	0.000	0.000	23.0	0.000	0.000	0.077
16	0.102	0.000	0.000	25.0	0.000	0.000	0.020
17	0.208	0.000	0.000	25.0	0.000	0.000	0.038
57	0.350	0.000	0.000	25.0	0.000	0.000	-0.014
18	0.487	0.000	0.000	25.0	0.000	0.000	0.081
58	0.720	0.000	0.000	25.0	0.000	0.000	0.096
19	0.950	0.000	0.000	25.0	0.000	0.000	0.115
59	1.180	0.000	0.000	25.0	0.000	0.000	0.123

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
60	1.280	0.000	0.000	25.0	0.000	0.000	-0.139
20	1.370	0.000	0.000	25.0	0.000	0.000	-0.140
61	1.560	0.000	0.000	25.0	0.000	0.000	0.135
21	1.740	0.000	0.000	25.0	0.000	0.000	0.144
22	1.870	0.000	0.000	25.0	0.000	0.000	0.144
62	2.080	0.000	0.000	25.0	0.000	0.000	0.144
63	2.580	0.000	0.000	25.0	0.000	0.000	0.149
23	2.620	0.000	0.000	25.0	0.000	0.000	-0.146
64	2.960	0.000	0.000	25.0	0.000	0.000	0.145
65	3.140	0.000	0.000	25.0	0.000	0.000	0.143
24	3.530	0.000	0.000	25.0	0.000	0.000	0.139
66	3.670	0.000	0.000	25.0	0.000	0.000	0.138
67	3.880	0.000	0.000	25.0	0.000	0.000	0.138
68	4.500	0.000	0.000	25.0	0.000	0.000	-0.131
25	4.760	0.000	0.000	25.0	0.000	0.000	0.124
69	5.140	0.000	0.000	25.0	0.000	0.000	0.123
70	5.350	0.000	0.000	25.0	0.000	0.000	0.120
26	5.980	0.000	0.000	25.0	0.000	0.000	0.108
71	6.420	0.000	0.000	25.0	0.000	0.000	0.107
72	7.400	0.000	0.000	25.0	0.000	0.000	0.097
27	7.620	0.000	0.000	25.0	0.000	0.000	-0.091
73	8.610	0.000	0.000	25.0	0.000	0.000	0.087
28	9.310	0.000	0.000	25.0	0.000	0.000	0.080
74	9.700	0.000	0.000	25.0	0.000	0.000	0.083
29	10.900	0.000	0.000	25.0	0.000	0.000	0.074
30	12.600	0.000	0.000	25.0	0.000	0.000	0.072
31	13.800	0.000	0.000	25.0	0.000	0.000	0.076
32	15.300	0.000	0.000	25.0	0.000	0.000	0.083
1	3.000	0.713	0.000	25.0	16.700	0.000	
2	2.998	0.952	0.000	25.0	15.000	0.000	
3	2.995	1.997	0.000	25.0	12.000	0.000	
4	3.000	2.380	0.000	25.0	11.000	0.000	
5	2.998	4.964	0.000	25.0	7.200	0.000	
6	2.999	9.605	0.000	25.0	4.700	0.000	
7	2.998	11.306	0.000	25.0	4.200	0.000	

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
185	0.277	0.000	0.000	40.0	0.000	0.000	0.036
186	0.490	0.000	0.000	40.0	0.000	0.000	0.061
187	0.905	0.000	0.000	40.0	0.000	0.000	0.102
188	1.780	0.000	0.000	40.0	0.000	0.000	0.136
189	2.570	0.000	0.000	40.0	0.000	0.000	-0.156
190	3.620	0.000	0.000	40.0	0.000	0.000	0.136
191	5.400	0.000	0.000	40.0	0.000	0.000	0.118
192	7.630	0.000	0.000	40.0	0.000	0.000	-0.092
193	10.820	0.000	0.000	40.0	0.000	0.000	0.079
119	0.500	12.030	0.000	40.0	0.993	0.000	0.028
147	0.500	20.000	0.000	40.0	-0.635	0.000	-0.040
120	0.500	42.300	0.000	40.0	-0.849	0.000	-0.010
121	0.500	94.300	0.000	40.0	-0.651	0.000	0.010
122	0.500	178.700	0.000	40.0	-0.421	0.000	
123	1.000	24.200	0.000	40.0	1.446	0.000	0.040
124	1.000	50.300	0.000	40.0	1.034	0.000	0.033
125	1.000	100.500	0.000	40.0	0.672	0.000	-0.028
126	1.000	180.400	0.000	40.0	0.425	0.000	0.013
127	2.000	11.700	0.000	40.0	3.094	0.000	0.085
128	2.000	29.600	0.000	40.0	1.757	0.000	-0.040
129	2.000	38.900	0.000	40.0	1.503	0.000	0.041
130	2.000	52.800	0.000	40.0	1.193	0.000	0.042
131	2.000	101.200	0.000	40.0	0.707	0.000	-0.035
132	2.000	195.400	0.000	40.0	0.384	0.000	0.020
133	4.000	4.800	0.000	40.0	7.583	0.000	0.090
134	4.000	29.500	0.000	40.0	2.039	0.000	-0.066
135	4.000	53.660	0.000	40.0	1.258	0.000	-0.032
136	4.000	97.150	0.000	40.0	0.750	0.000	0.027
137	4.000	192.500	0.000	40.0	0.399	0.000	0.023
138	8.000	7.800	0.000	40.0	4.228	0.000	-0.062
139	8.000	28.700	0.000	40.0	1.742	0.000	0.050
140	8.000	30.500	0.000	40.0	1.679	0.000	0.045
141	8.000	46.100	0.000	40.0	1.291	0.000	0.043
142	8.000	49.000	0.000	40.0	1.243	0.000	0.043
143	8.000	60.000	0.000	40.0	1.067	0.000	0.040
144	8.000	105.000	0.000	40.0	0.682	0.000	0.026
145	8.000	122.500	0.000	40.0	0.588	0.000	0.024
146	8.000	198.200	0.000	40.0	0.404	0.000	0.023

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
194	0.228	0.000	0.000	70.0	0.000	0.000	0.031
195	0.472	0.000	0.000	70.0	0.000	0.000	0.055
196	0.862	0.000	0.000	70.0	0.000	0.000	0.092
197	1.630	0.000	0.000	70.0	0.000	0.000	-0.143
198	2.640	0.000	0.000	70.0	0.000	0.000	0.145
199	3.370	0.000	0.000	70.0	0.000	0.000	0.140
200	5.400	0.000	0.000	70.0	0.000	0.000	0.119
201	7.090	0.000	0.000	70.0	0.000	0.000	0.102
202	10.700	0.000	0.000	70.0	0.000	0.000	0.082
148	0.500	47.000	0.000	70.0	0.702	0.000	0.038
149	0.500	97.500	0.000	70.0	-0.595	0.000	-0.040
150	0.500	195.000	0.000	70.0	0.364	0.000	0.024
155	1.000	15.500	0.000	70.0	1.258	0.000	-0.100
151	1.000	32.500	0.000	70.0	1.025	0.000	-0.050
152	1.000	60.000	0.000	70.0	0.783	0.000	0.041
153	1.000	122.000	0.000	70.0	0.541	0.000	-0.020
154	1.000	210.000	0.000	70.0	0.360	0.000	-0.026
156	2.000	11.100	0.000	70.0	2.324	0.000	0.116
157	2.000	15.500	0.000	70.0	2.065	0.000	0.092
158	2.000	36.070	0.000	70.0	1.309	0.000	0.086
159	2.000	45.200	0.000	70.0	1.150	0.000	-0.064
160	2.000	54.700	0.000	70.0	1.040	0.000	0.080
161	2.000	112.800	0.000	70.0	0.622	0.000	0.067
162	2.000	186.000	0.000	70.0	0.410	0.000	0.058
163	4.000	9.570	0.000	70.0	3.333	0.000	0.098
164	4.000	9.660	0.000	70.0	3.282	0.000	0.100
165	4.000	35.500	0.000	70.0	1.563	0.000	0.070
166	4.000	66.000	0.000	70.0	0.983	0.000	0.063
167	4.000	114.000	0.000	70.0	0.649	0.000	0.053
168	4.000	200.400	0.000	70.0	0.385	0.000	0.053
169	8.000	13.600	0.000	70.0	1.831	0.000	0.068
170	8.000	35.000	0.000	70.0	1.200	0.000	-0.071
171	8.000	70.500	0.000	70.0	0.767	0.000	0.056
172	8.000	74.800	0.000	70.0	0.745	0.000	0.053
173	8.000	111.270	0.000	70.0	0.588	0.000	0.050
174	8.000	150.000	0.000	70.0	0.467	0.000	0.048
175	8.000	211.100	0.000	70.0	0.357	0.000	0.044

DATA NO.	HNO ₃ (AQ) (M/L)	U (AQ) (G/L)	Pu (AQ) (G/L)	TEMP (° C)	D _U	D _{Pu}	D _H
15	0.285	0.000	14.938	25.0	0.000	0.200	
13	1.461	0.000	5.228	25.0	0.000	2.200	
12	1.495	0.000	0.126	25.0	0.000	2.802	
10	1.565	0.000	1.554	25.0	0.000	3.000	
14	1.611	0.000	13.351	25.0	0.000	1.900	
9	2.645	0.000	0.116	25.0	0.000	5.198	
11	2.708	0.000	8.170	25.0	0.000	3.300	
8	2.853	0.000	0.398	25.0	0.000	8.000	

VITA

Joon-Hyoun Lee was born in Seoul, Korea, on August 6, 1957. He attended elementary schools in that city and was graduated from the High School Attached to the College of Education, Chung-Ang University in Seoul in February 1976. The following March he entered Chung-Ang University, and in February 1981 he received a Bachelor of Engineering degree in Chemical Engineering.

He entered The Graduate School of the University of Tennessee, Knoxville, in September 1983. He received the Master of Science degree with a major in Chemical Engineering in December 1987.