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VAPOR-LIQUID EQUILIBRIA FOR NITRIC ACID-WATER AND
PLUTONIUM NITRATE-NITRIC ACID-WATER SOLUTIONS

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VAPOR-LIQUID EQUILIBRIA, FOR NITRIC ACID-WATER AND PLUTONIUM NITRATE-NITRIC ACID - WATER SOLUTIONS

ABSTRACT

The liquid-vapor equilibrium data for nitric acid and nitric acid-plutonium nitrate-water solutions were examined to develop correlations covering the range of conditions encountered in nuclear fuel reprocessing. The scanty available data for plutonium nitrate solutions are of poor quality but allow an order of magnitude estimate to be made. A formal thermodynamic analysis was attempted initially but was not successful due to the poor quality of the data as well as to the complex chemical equilibria involved in the nitric acid and in the plutonium nitrate solutions. Thus, while there was no difficulty in correlating activity coefficients for nitric acid solutions over relatively narrow temperature ranges, attempts to extend the correlations over the range 25 C to the boiling point were not successful. The available data were then analyzed using empirical correlations from which normal boiling points and relative volatilities can be obtained over the concentration ranges 0 to 700 g/l Pu, 0 to 13 M nitric acid. Activity coefficients are required, however, if estimates of individual component vapor pressures are needed. The required ternary activity coefficients can be approximated from the correlations.

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FOREWORD

William Harrison assisted in the early portion of this work by applying the GNLS code to the correlation of activity coefficients for pure nitric acid.

NOMENCLATURE

a_{ij}, A_i, A_{ij}	coefficients
B	one of the electrolytes in the mixture
b	coefficient to various equations
C	concentration
C_i, C^c	coefficients for various least square fits
E	deviation function
I	mean ionic strength
K	equilibrium constant
k	constant for Furtner's equation [Eq. (50)]
ln	logarithm base e
log	logarithm base 10
N_i	number of moles of component i in solution
N	number of points used in least squares fit
P	pressure, torr.
Q	a function of the excess free energy
R	universal gas constant

S	standard deviation
T	temperature, °K
t	temperature, °C
X_i	mole fractions
Z_{i+} or Z_{i-}	charge of positive (or negative) ion of species i
α	relative volatility for a binary system $\alpha = y(1-X)/(1-y)X$
α_s	relative volatility of salt containing solution
β	Hala's separation function
γ_i	activity coefficient of component i, mole fraction scale
Δ	difference between experimental and calculated boiling temperature; average value of Δ
ΔF	excess free energy
ΔT_b	calculated increase in boiling point
v_{i+}, v_{i-}	number of positive (or negative) ions obtained by ionization of component i
v_i	total number of ions of species i, $v_i = v_{i+} + v_{i-}$

Subscripts

+ or -	apply to positive or negative ions
$\pm$	mean ionic
s	applies to salt solution

- 1 applies to nitric acid
- 2 applies to plutonium (IV) nitrate
- 3 applies to water

Superscript

- ° value at the reference state

I. INTRODUCTION

The feasibility of using process control measurements as a part of the Material Control and Material Accounting measurements required for safeguarding nuclear material depends on the development of proper process models, which range from simple closure equations¹ to complex dynamic estimation^{2,3} techniques, and a firm data base of physical properties and thermodynamic data for the various process streams.

While a considerable body of data exists, most of it consists of compilations made when the basic separation processes in the nuclear fuel cycle were initially developed. These data were "good enough" for the job at hand but leave much to be desired when used with the models required for safeguards material estimation/material loss detection..

Knowledge of the vaporization behavior of plutonium nitrate solutions is required for modeling the dynamics of evaporation from a plutonium nitrate solution storage tank² and for predicting the boiling points and vapor compositions for the modeling of a plutonium nitrate concentrator.³ Initially a formal thermodynamic analysis was attempted, which would have allowed the use of the two independent sets of data available for plutonium nitrate solutions: vapor-liquid equilibria at various temperatures and normal boiling points. The formal thermodynamic analysis was not successful and the liquid-vapor compositions data were correlated using empirical fits; however, the results of the formal analysis are useful to approximate the value of the activity coefficients needed to estimate individual component vapor pressures at temperatures other than the normal boiling point.

The correlation of the few available data for plutonium nitrate requires as an input the behavior of the binary system nitric acid-water. Thus, the nitric acid-water system will be discussed first.

II. ANALYSIS OF NITRIC ACID LIQUID-VAPOR EQUILIBRIUM DATA

The most detailed currently available treatment of electrolyte solutions was initiated by Pitzer⁴⁻⁶ and extended by Cruz and Renon⁷; however, the simpler theoretical treatment of Hala et al.⁸ was used, because it initially appeared simpler to use and more easily extended to multicomponent systems and nonisothermal data. Hala⁹ has shown that his system of equations can be used to produce very good fits to the experimental data of electrolyte solutions over wide concentration ranges, including isobaric as well as isothermal data. Also, the author's initial attempt at correlating¹⁰ plutonium nitrate solution data from the Reactor Handbook¹¹ gave apparently satisfactory results. The correlation seemed to be limited by the intrinsic quality of the data.

A. HALA'S TREATMENT OF VAPOR-LIQUID EQUILIBRIUM FOR ELECTROLYTE SOLUTIONS

The main aspects of Hala's approach will be reviewed in the context of a three-component mixture of two strong electrolytes, B and C, and a non-ionizing volatile solvent, K. The individual ionizations are

If we define

$$v_1 = v_{1+} + v_{1-} \quad (3)$$

$$v_2 = v_{2+} + v_{2-} \quad (4)$$

where the values of v are chosen for the appropriate ionization equilibrium, the (analytical) mole fractions in terms of the number of moles of each component are given by

$$X_1 = \frac{N_1}{N_1 + N_2 + N_3} \quad (5)$$

$$X_2 = \frac{N_2}{N_1 + N_2 + N_3} \quad (6)$$

$$X_3 = \frac{N_3}{N_1 + N_2 + N_3} \quad (7)$$

and the concentrations of the individual ions (assuming complete ionization for the appropriate equilibria, Eqs. (1) and (2)), are

$$X_{1+} = \frac{v_{1+} N_1}{v_1 N_1 + v_2 N_2 + N_3} \quad (8)$$

$$X_{2+} = \frac{v_{2+} N_2}{v_1 N_1 + v_2 N_2 + N_3} \quad (9)$$

$$X_{1-} = \frac{v_{1-} N_1}{v_1 N_1 + v_2 N_2 + N_3} \quad (10)$$

$$X_{2-} = \frac{v_{2-} N_2}{v_1 N_1 + v_2 N_2 + N_3} \quad (11)$$

In our case, components 1 and 2 have a common anion (NO_3^-) and Eqs. (10) and (11) become

$$x_{1-} = x_{2-} = \frac{v_{1-} N_1 + v_{2-} N_2}{v_1 N_1 + v_2 N_2 + N_3} \quad (12)$$

The mean mole fractions are given by

$$x_{1+} = \left(x_{1+}^{v_{1+}} x_{1-}^{v_{1-}} \right)^{1/v_1} \quad (13)$$

$$x_{2+} = \left(x_{2+}^{v_{2+}} x_{2-}^{v_{2-}} \right)^{1/v_2} \quad (14)$$

$$x_3 = \frac{N_3}{v_1 N_1 + v_2 N_2 + N_3} \quad (15)$$

The ionic strength I is defined by

$$I = \frac{1}{2} \left[\left(v_{1+} z_{1+}^2 + v_{1-} z_{1-}^2 \right) x_1 + \left(v_{2+} z_{2+}^2 + v_{2-} z_{2-}^2 \right) x_2 \right] \quad (16)$$

The basis for Hala's approach is his assumption that the excess free energy of mixing can be expressed as a function of a term which handles the electrostatic interaction of the ions and another term which handles the non-Coulombic interactions. The first term, $Q_{\pm}$, can be related to the ionic strength by using the series expansion:

$$Q_{\pm} = \frac{-\Delta F_{\pm}^E}{\left[\left(\sum_{i=1}^3 N_i \right) 2.303 RT \right]} = bI + cI^{3/2} + dI^2 + \dots \quad (17)$$

while the second term, Q_b , is directly related to concentrations. For a ternary system,

$$Q_b = \frac{(-\Delta F_b^E)}{\left[2.303 RT \left(\sum_{i=1}^3 N_i \right) \right]} = X_1 A_1 + X_2 A_2 + X_1 X_2 A_{12} + X_1 X_3 A_{13} \quad (18)$$

$$+ X_2 X_3 A_{23}$$

The electrostatic interaction term predominates and Hala refers to treatments using only the electrostatic term, Eq. (17), as the first approximation, whereas both terms are used in the second approximation.

The individual mean activity coefficients can be formally derived from Eqs. (17) and (18):

$$v_i \log \gamma_{i\pm} = \left[\frac{\partial}{\partial N_i} \left(\sum_{j=1}^k N_j \right) Q \right]_{T_1, P_1, i \neq j} \quad (19)$$

to obtain, for a binary system ($\text{HNO}_3 - \text{H}_2\text{O}$), using the first and second approximations:

$$\log \gamma_{1\pm}^2 = A - \frac{1}{2} C X_1^{1/2} (X_1 - X_3) + B(1 - X_1) \quad (20)$$

$$\log \gamma_3 = -\frac{1}{2} C X_1^{3/2} + B X_1 \quad (21)$$

$$\log \gamma_{1\pm}^2 / \gamma_3 = A + \frac{3}{2} C X_1^{1/2} + (1 - 2 X_1) B \quad (22)$$

Similar, but more complex equations can be derived for ternary systems.

Hala defines a separation function β , similar to the relative volatility:

$$\beta_{ik} = \frac{y_i}{y_k} \cdot \frac{X_{k\pm}}{X_{i\pm}} = \frac{\gamma_{1\pm}^{v_i} P_1^o}{\gamma_k P_k^o} \quad (23)$$

which becomes, for $\text{HNO}_3 - \text{H}_2\text{O}$ solutions,

$$\beta_{1,3} = \frac{y_1}{(1-y_1)} \cdot \left(\frac{1}{X_1^2} - 1 \right) \quad (24)$$

and, for a ternary system, such as the $\text{HNO}_3 - \text{Pu}(\text{NO}_3)_4 - \text{H}_2\text{O}$ solutions (component 2 is nonvolatile).

$$\beta_{13} = \frac{y_1 X_{3\pm}}{y_3 X_{1\pm}^{v_1}} \quad (25)$$

If plutonium nitrate is assumed to be singly ionized³ in the range of concentrations of HNO_3 of interest to us, 2.1 to 3.8 molar,*

The ionic strength is given by

$$I = X_1 + X_2 \quad (27)$$

and

$$\beta_{13} = \frac{y_1 (1-I) (1+I)}{(1-y_1) X_1 I} \quad (28)$$

*The nominal concentrations at the outlet of the plutonium nitrate solution concentrator and in the storage tanks at the Allied General Nuclear Services reprocessing plant at Barnwell, So. Carolina, were going to be 250 g/l or 0.02159 mole fraction of $\text{Pu}(\text{NO}_3)_4$ and 3.0 M. or 0.06214 mole fraction of HNO_3 .

The dependence of the separation function on the composition of the liquid phase are given by the following:

first-order terms only:

$$\log \beta_{13} = a_{13} + b_{13} I^{1/2} + D X_2 \quad (29)$$

first- and second-order terms:

$$\log \beta_{13} = a_{13} + b_{13} I^{1/2} + c_{13} (X_3 - X_1) + D X_2 \quad (30)$$

where the values of a_{13} , b_{13} , and c_{13} are obtained from fitting the binary system ($X_2 = 0$) and the value of D is obtained from ternary data. The constants in Eqs. (29) and (30) are related to those in Eqs. (20) through (22) by the definition of β_{13} , Eq. (21), i.e.,

$$\log \beta_{13} = \log \frac{v_1^2}{\gamma_3} + \log \frac{p_1^o}{p_3} \quad (31)$$

Since the temperature range of the available data for plutonium nitrate solutions is about 30 to 130 C, there was a need to correlate the properties of the nitric acid water system over a relatively large temperature range.

B. EXTENSION OF HALA'S TREATMENT TO NONISOTHERMAL CONDITIONS

The approach described below was developed in the context of fitting the vaporization equilibrium data for the $\text{HNO}_3 - \text{H}_2\text{O}$ system, using the information available initially to the author (Hala's compilation⁹ and the tables in Perry's Chemical Engineering Handbook¹³). Since then a more complete set of data has been collected.¹³⁻²⁵ The least squares

fits were performed using the GNLS code²⁶ and/or standard polynomial fit routines.

The vapor pressures of the pure components were taken to be, for nitric acid,

$$\log P_1^\circ = 8.25225 - \frac{1918.3}{T} \quad (32)$$

which was obtained by fitting the pure HNO_3 vapor pressure values²⁷ for the range 30 to 100 C. (Mean error in P is 0.31 percent; however, the fit is poorer below 30 C. At 20 C, the predicted pressure is about 7 percent high). Antoine's equation was used for water:

$$\log P_3^\circ = 7.96681 - \frac{1668.21}{t + 228} \quad (33)$$

which fits the water data with a mean error of 0.1 percent.

For each of the nineteen sets of data (Table 1) the $\log (\gamma_{1+}^2 / \gamma_3)$ was calculated and fit using Eq. (22) and the GNLS code. Figure 1 shows the fit to the 50 C data of Yakimov and Mishin.²⁰ At this point we found that

TABLE 1. Liquid-vapor data used in the correlations of the $\text{HNO}_3 - \text{H}_2\text{O}$ system.

Ref. no.	Authors	Data used
23	Wilson and Miles	15, 20 C
17	Vandoni and Landy	20 C
20	Yakimov and Mishin	25, 35, 50 C
21	Boublik and Kuchinka	50, 100, 200, 400, 760 Torr
24	Potier	450, 600, 760 Torr
22	Prosek	740 Torr
13	Perry (Table 3-65)	60, 80, 100, 110 C

FIG. 1 $\log(\gamma_{1\pm}^2/\gamma_3)$ versus nitric acid mole fraction (Ref. 20).

the data of Wilson and Miles²³ and Potier²⁴ scattered excessively and did not show the same trends as the rest of the data.

We found that if the $\log \left(\gamma_{1+}^2 / \gamma_3 \right)$ calculated from the above individual fits was plotted versus $1/T$ at constant composition (Fig. 2), the data could be approximated by a linear fit, such that at constant composition

$$\log \left(\gamma_{1+}^2 / \gamma_3 \right) = A + \frac{B}{T} \quad (34)$$

The lack of fit of the data of Wilson and Miles²³ and Potier²⁴ was even more pronounced in this correlation and these data were eliminated from all subsequent manipulations. The equilibrium values tabulated in Perry¹³ fit smoothly into the data of Boublik and Kuchinka and of Prosek²² and were used, particularly to provide additional points at low acid concentration. We also found that the values of A and B [Eq. (34)] gave a smooth curve when plotted versus concentration and the general shape of the curves was such that it seemed reasonable to express Eqs. (20) through (22) as a function of temperature in the form

$$\log \left(\gamma_{1+}^2 / \gamma_3 \right) = \left(A_0 + A_1 x_1 + A_2 x_1^{1/2} \right) + \left(B_0 + B_1 x_1 + B_2 x_1^{1/2} \right) / T \quad (35)$$

$$\log \gamma_{1+}^2 =$$

$$\left(A_0 + \frac{B_0}{T} \right) + \frac{1}{2} \left(A_1 + \frac{B_1}{T} \right) x_1 + \left(A_2 + \frac{B_2}{T} \right) x_1^{1/2} - \frac{1}{3} \left(A_2 + \frac{B_2}{T} \right) x_1^{3/2} \quad (36)$$

$$\log \left(\gamma_3 \right) = - \frac{1}{2} \left(A_1 + \frac{B_1}{T} \right) x_1 - \frac{1}{3} \left(A_2 + \frac{B_2}{T} \right) x_1^{3/2} \quad (37)$$

The data were then fit to obtain the coefficients to Eqs. (35) through (37). Unfortunately, the fit was not good, as can be seen in Fig. 3, where the

FIG. 2 $\log(\gamma_{1\pm}^2/\gamma_3)$ versus $1/T$ at constant liquid composition.

FIG. 3 Comparison of experimental 0.5 calculated $\log(\gamma_{1\pm}^2/\gamma_3)$.

calculated vs. experimental value of $\log (\gamma_{1+}^2 \gamma_3)$ is plotted. The corresponding vapor compositions were also calculated and compared to the experimental ones. Figure 4 shows that most of the scatter takes place for liquid mole fractions below 0.32.

Since a major source of uncertainty in the values of $\log (\gamma_{1+}^2 / \gamma_3)$ arises from the errors in measurement of vapor composition, the formulation for γ_{1+}^2 and γ_3 was used to yield an expression for the total pressure from which a fit of total pressure versus temperature and liquid composition²⁸ could be obtained. The total pressure is given by

$$P = \gamma_{1+}^2 x_{1+}^2 P_1^0 + \gamma_3 x_{3+} P_3^0 \quad (38)$$

where the values of the activity coefficients can be obtained from Eqs. (36) and (37), and

$$x_{1+} = \frac{x_1}{1 + x_1} \quad (39)$$

$$x_{3+} = \frac{1 - x_1}{1 + x_1} \quad (40)$$

to obtain

$$P = \left(10^{\left(\log \gamma_{1+}^2 \right)} \right) \frac{x_1^2 P_1^0}{(1 + x_1)^2} + \left(10^{\left(\log \gamma_3 \right)} \right) \frac{(1 - x_1) P_3^0}{(1 + x_1)} \quad (41)$$

The best fit parameters were as follows:

$A_0 = -1.4295$	$B_0 = 0.9986$
$A_1 = 0.9521$	$B_1 = 3.1429$
$A_2 = -0.2422$	$B_2 = 0.9858$

FIG. 4 Comparison of calculated with experimental vapor composition,
 $\log (\gamma_{1\pm}^2/\gamma_3)$ fit.

A comparison of the calculated versus experimental pressure is shown in Fig. 5 and the vapor compositions are compared in Fig. 6; again, most of the scatter seems to originate with liquid compositions below about 0.32 mole fraction.

Clearly, there is something wrong either with the data or with the correlation techniques being used. However, since Hala and co-workers have been successful in correlating the properties of a number of binary and multicomponents systems, and, as mentioned earlier, the problems only arise when correlation is attempted over a large temperature range, it is likely that the problem originates elsewhere.

C. CORRELATION OF RELATIVE VOLATILITIES

Since the above approach did not yield satisfactory results and our main interest was to be able to extrapolate the few available data on plutonium nitrate solutions, the more empirical approach of Furter²⁹⁻³¹ was tried. The first step in the process is to obtain a consistent set of relative volatilities for pure nitric acid. The same set of data used above was manipulated to obtain the relative volatilities correlations.

The relative volatility, α , is defined by

$$\alpha = \frac{y_1(1 - X_1)}{(1 - y_1)X_1} \quad (42)$$

There was reasonably good agreement in the relative volatilities calculated from data from various investigators, provided the temperature range spanned was restricted. The data were fit using standard polynomial fit routines, forced to an assumed value of $\alpha = 0.001$ at $X_1 = 0$:

FIG. 5 Comparison of calculated and experimental pressures (total pressure fit).

FIG. 6 Comparison of calculated versus experimental vapor compositions (total pressure fit approach).

$$\alpha = B_0 + B_1 X_1 + B_2 X_1^2 + B_3 X_1^3 \quad (43)$$

The results for data around 60 C are compared in Fig. 7, and for data around 100 C in Fig. 8. As was the case in the activity coefficient correlations, there is good fit if the temperature range of the data is restricted but excessive scatter when the temperature range is extended, even when an attempt is made to compensate for the effects of temperature by using

$$\alpha = (A_0 + A_1 t) (B_0 + B_1 X_1 + B_2 X_1^2 + B_3 X_1^3) \quad (44)$$

The ratio of the experimental to the calculated relative volatility using Eq. (44) is plotted versus liquid composition in Fig. 9. The data used to calculate Fig. 9 are given in Table 2 and the coefficients for the polynomial fit equations in Table 3.

D. POSSIBLE REASONS FOR THE LACK OF FIT

Most of the work described above was finished before a more thorough literature search was completed that adds not only additional liquid vapor equilibrium data, but most importantly, illustrates the complexity of the $\text{HNO}_3\text{-H}_2\text{O}$ system.

The calculations of activity coefficients using compositions derived from Eq. 5-16 assume that HNO_3 is a strong (i.e., completely dissociated) electrolyte and that the only species present in the liquid phase are H^+ , NO_3^- , and H_2O . In fact, these assumptions are not correct. HNO_3 is only partially dissociated in aqueous solutions and there are a number of complexes in the $\text{HNO}_3\text{-H}_2\text{O}$ system.

FIG. 7 Nitric acid-water relative volatility at about 60 C.

FIG. 8. Nitric acid relative volatility at about 100 C.

FIG. 9 Ratio of experimental to calculated relative volatilities over an extended temperature range. See Eq. (44).

TABLE 2. Data used in the correlation of relative volatility over an extended temperature range.

Reference no.	Authors	Data used
20	Yakimov and Mishin	50 C
21	Boublik and Kuchinka	50, 100, 200, 400, 760 torr
22	Prosek	740 torr
13	Perry, Table 3-65	60, 80, 100, 110 C

TABLE 3. Coefficients for the polynomial fits to relative volatility, Eqs. (43) and (44).^a

Temperature range, °C	B ₀	B ₁	B ₂	B ₃	A ₀	A ₁	Coefficient of determination, r ²
50-72	0.0037	0.0309	-0.8872	24.05	--	--	0.997
90-110	0.0006	0.7061	0.7406	11.626	--	--	0.996
40-110	0.0625	-0.873	6.9029	6.4028	0.4915	0.0069	--
Reactor Handbook	-0.0026	0.3383	2.2947	12.7554	--	--	0.998

^a Range of X_1 : $0 < X_1 < 0.38$.

The degree of dissociation of HNO_3 , α , is a function of concentration and temperature^{32,33}

and varies between 0.985 at 25 C for 1 molar acid ($X_1 = 0.0183$) and 0.081 at 70 C and 17.2 molar acid ($X_1 = 0.4625$). Figure 10 illustrates the difference in concentration of NO_3^- that obtains between the fully and partially ionized acid. C is the stoichiometric concentration, and the concentration of the individual species is given by

The second reason for the lack of fit is the existence of $\text{HNO}_3\text{-H}_2\text{O}$ complexes. The thermodynamic properties of the solid mono- and tri-hydrates have been measured³⁴ and thermodynamic analysis of $\text{HNO}_3\text{-H}_2\text{O}$ solutions data,³⁵⁻³⁷ indicates that the mono- and trihydrate species are stable and should be considered in the analysis of thermodynamic data for nitric acid. The relative concentrations of the various species changes as the total acid concentration is increased (Fig. 11).

From Fig. 11 it can be seen that the trihydrate complex is an important species at concentrations below 16 M (about 0.4 mole fraction), which is where most of the scatter in the correlations occurs. It is likely that the trihydrate complex decomposes in the temperature range 60 to 100 C and the thermodynamic analysis should include it.

FIG. 10 Molarity of nitrate ion versus stoichiometric concentration of nitric acid (solid lines). The dashed portions of these lines show relative values of this quantity for concentrated solutions. OC represents complete dissociation. From Ref. 33.

FIG. 11 $C(1 - \alpha)$ plotted against the stoichiometric molarity of nitric acid. From Ref. 2.

A full thermodynamic analysis and correlation of all available data is, however, considerably beyond the scope of our program.

III. ANALYSIS OF PLUTONIUM NITRATE SOLUTIONS LIQUID-VAPOR EQUILIBRIUM DATA

The range of compositions of plutonium nitrate solutions of interest in the nuclear fuel cycle range from those at the outlet of the 3B extraction columns in the Purex process (approx. 50 g/l of Pu*) to those at the outlet of the Pu concentrator, which were to be in the range of 250 to 500 g/l. The free nitric acid content ranges from about 0.5 to 7 molar. The chemistry of plutonium (IV) nitrate complexes can be summarized as follows, taken from Cleveland³⁸:

Nitrate ions complex tetravalent plutonium to form all ions from $\text{Pu}(\text{NO}_3)_3^{3+}$ to $\text{Pu}(\text{NO}_3)_6^{2-}$; in concentrated HNO_3 solutions, the latter is the predominant complex.

Studies of the variation of the extinction coefficient of Pu (IV) nitrate in various solvents have led to the conclusion that Pu (IV) is associated with an average of 2.6 nitrate ions in aqueous solutions containing 2 to 4 M nitrate. There is conflicting information about the range of stability of the $\text{Pu}(\text{NO}_3)_3^+$ complex, but it is likely to be the dominant species in the range of 1.5 to 4.0 M free HNO_3 . $\text{Pu}(\text{NO}_3)_4$ is stable in the region 3.8 to 5.6 M, $\text{Pu}(\text{NO}_3)_5^-$ from 5.6 to 7.1 M and $\text{Pu}(\text{NO}_3)_6^{2-}$ for concentrations greater than 7.1 M. The abundance of the hexanitrate complex is given in Table 4.

*Nominal compositions, Allied General Nuclear Services (AGNS) reprocessing plant.

TABLE 4: Abundance of Pu(IV) hexanitrate complex in HNO₃ solutions.³⁸

HNO ₃ , M	Abundance of Pu(NO ₃) ₆ ²⁻ , %
5	4
6	10
7	29
8	50
9	75
10	91
11	95
13	100

Vaporization equilibrium data obtained at the time the Purex process was being designed are summarized in the Reactor Handbook, Vol. II¹¹ and the Purex Technical Manual³⁹; more recently, Swanson¹² performed a number of measurements on concentrated plutonium solutions. Swanson's data were made available to us by Allied General Nuclear Services, of Barnwell, S.C. The information in the Reactor Handbook and the Purex Technical Manual was in the form of smooth graphs, and even the source documents⁴² did not contain the raw experimental data. It was assumed that all the above data was obtained at--or near to--the normal boiling point of the solutions at 760 torr. The information in the various figures, such as Figs. 12 and 13 was digitized and manipulated using a 9830 Hewlett-Packard computer, thus it may appear as many individual "data" points in some of the computer plots of polynomial least squares fits. The size of the original Fig. 13 in the Reactor Handbook is only 2-1/2 inches square, thus appreciable reading errors could obtain during the digitizing process, particularly at low plutonium concentrations.

FIG. 12 Boiling points and region of polymer formation for plutonium-HNO₃ solutions (Ref. 42).

FIG. 13 Equilibrium diagram (Ref. 39).

The lack of good activity coefficients for nitric acid and the complex chemistry of plutonium solutions prevented a thorough analysis of the data, in particular, the data on boiling point versus liquid composition of Pugh⁴⁰ and Swanson¹² were not analyzed; the analysis was confined to the available liquid-vapor equilibrium data. The data were examined using the approach of Hala et al., Eqs. (29) and (30), as well as other, more empirical approaches.

A. ESTIMATION OF THE TERNARY INTERACTION CONSTANT, D

The ionic strength and mean mole fractions to be used in Eqs. (23), (25), (29), and (30) depend on the ionization equilibria of the particular species involved. In our case, the multiple equilibria of plutonium nitrate make the problem quite complex:

In addition, the regions of stability for each of the complexes, as indicated previously, are not very well known. Thus, one approach is to consider only the dominant equilibria in the region of interest, 1.5 to 4M nitric acid and observe the trends of the data in other concentration regions. Thus, the ternary interaction constant D, Eqs. (29) and (30), was calculated from the digitized "data," assuming that the applicable ionization equilibrium for Pu (IV) is

using values of the binary interaction constants a_{13} , b_{13} , and c_{13} listed by Hala⁹ as best fit to the 760 torr data of Boublik.

Figure 14 shows the value of D calculated using the first-order equation (29); Fig. 15 includes the second-order term, Eq. (30). There are two groups of

FIG. 14 First-order model of D versus X_1 for various plutonium concentrations.

FIG. 15 Second-order model of D versus X_1 for various plutonium concentrations (Boublik's binary constants).

"data": the 50 and 75 g/l information⁴⁰ and the 100, 200, 300, and 400 g/l information.³⁹ The latter is probably more dependable since it was included in the Reactor Handbook.

Also shown in Fig. 14 are the values of D calculated from Swanson's data (Table 8) at about 60 C. Since Swanson's data show a great deal of scatter, they were "adjusted", as follows: Within each group of (constant composition) data, only those in the range of 50 to 70 C were analyzed. The individual vapor pressures were adjusted to a common 60 C mean value by assuming that

$$P_i = \gamma_i X_i P_i^o$$

and that in the range 50 to 70 C the value of γ_i would stay relatively constant. Thus, the adjusted value of P_i at 60 C is obtained from

$$(P_i)_{60} = (P_i^o)_{60} \left(\frac{P_i}{P_i^o} \right)_t$$

Figure 14 shows the values of D calculated from the average of each of the data groups and the range of values within each group. The values of the binary constants used [Eq. (29)] were derived from the polynomial fit to the relative volatility of pure HNO_3 at about 60 C (Fig. 7 and Table 3).

From Figs. 14 and 15, it can be concluded that the fit to the data using the second-order model is not better than what is obtained with the simpler first-order model and that there is a significant correlation in the results for $X_1 > 0.18$ for solutions of 100 to 400 g/l.

At lower nitric acid concentrations, D shows a very large range of values (3.2 to 40+) and no obvious correlation with plutonium concentration. Not much weight should be given to the trends because of the

large inherent error in digitizing the curves at low nitric acid concentrations. Since the values of D calculated from Swanson's data are not very significantly different from the values obtaining at high acid concentrations, one can take a "mean" value of D to be 18 using the binary constants given in Table 5.

At this point it became apparent that the use of a rigorous thermodynamic approach was not justified and that perhaps more empirical techniques might be used to analyze the data. The boiling points and the vaporization equilibria were fit as follows:

B. ESTIMATION OF BOILING POINTS

Two sources of data are available: the curves in the Reactor Handbook¹¹ which were originally developed by Pugh,⁴⁰ (Fig. 12) and the data obtained by Swanson.¹² As will be seen later, these two sources are not in full agreement with one another, the discrepancy is, typically, about 3 deg C.

The data reduction was done somewhat differently for the two sources of data. The individual isotherms given by Pugh were digitized and then fitted with third-degree polynomials.

$$X_2 = A(T) + B(T)X_1 + C(T)X_1^2 + D(T)X_1^3 = X_2(X_1, T) \quad (47)$$

TABLE 5. Plutonium nitrate-nitric acid-water solutions values of constants to be used with Eqs. (28) and (29).

Temperature	a_{13}	b_{13}	D
about 100 C	-0.7252	2.1221	18
about 60 C	-1.2409	2.469	18

Likewise, the boiling point of nitric acid solutions²¹ data was fitted with a similar polynomial

$$T_1 = A' + B'X_1^2 + C'X_1 + D'X_1^3 = T_1(X_1) \quad (48)$$

it was observed that the deviation function

$$E = \frac{T - T_1(X_1)}{X_2(X_1, T)} \quad (49)$$

could be fitted with a polynomial

$$E = A'' + B''X_2 + C''X_2^2 + D''X_2^3 = E(X_2) \quad (50)$$

Thus, given the composition of the solution (X_1 and X_2) one can obtain E and from it, the boiling point

$$T_C = E(X_2) X_2 + T_1(X_1) \quad (51)$$

The correlation fits reasonably well, particularly given that the available curves had been "smoothed" from raw data of unknown accuracy and that "the boiling points were determined in a closed hood under negative pressure and are several degrees lower than would be expected for standard conditions".⁴² The mean error and standard deviations of the estimate were computed, i.e.,

$$\Delta = T - T_C \quad (52)$$

$$\bar{\Delta} = \frac{(T - T_C)}{N} \quad (53)$$

$$S = \frac{(T - T_C)^2}{N - 1} \quad (54)$$

For all the points digitized $\bar{A} = 0.2$ deg C, $S = 0.83$ deg C, the individual deviations being, in general, lower than 1 deg C. The poorest fit is to the 120 C isotherm, with individual deviations as high as 2 deg C. For the conditions of most interest to us, i.e., $2 < H^+ < 6$ moles/liter and $Pu < 300$ grams/liter, the fit is much better. Thus, if we consider only the 105, 110 and 115°C isotherms $\bar{A} = 0.07$ deg C; $S = 0.62$ deg C.

Values for the coefficients to the polynomials are given in Table 6, together with their range of applicability.

The boiling point data of Swanson, given in Table 7 and also shown in Fig. 12, were correlated in the same manner. However, he had, on some samples, up to 50 percent of Pu(VI) in solution. It was assumed that the stoichiometry had no effect on solution density and the density correlations previously developed apply.⁴¹ The mole fractions were found by assuming the Pu(VI) to be in the form of $PuO_2(NO_3)_2$, and the plutonium nitrate mole fraction is the sum of the Pu(IV) and Pu(VI) mole fractions.

Figure 16 shows the fit to the values of $E(X_2)$ versus X_2 , the individual numbers on the points show the fraction of Pu(VI), in the solution; there appear to be no systematic deviations due to stoichiometry. The fit to

TABLE 6. Values for the coefficients used in the estimating equations.

	Equation	A	B	C	D	Fit limits
	$Tl(X_1)$	100.004	66.5656	98.624	-346.018	$0 \leq x_1 \leq 0.4$
Pugh	$E(X_2)$	555.391	-17891	300277	-1.6732×10^6	$0 \leq x_2 \leq 0.0895$
Swanson	$E(X_2)$	220.66	-3619.4	25662	0	$0 \leq x_2 < 0.110$

TABLE 7. Swanson's boiling point data.

Pu, g/l	HNO ₃ , M	Pu(VI), % of total	Mole fractions		Boiling point, °C
			Acid, X_1	Pu ^a , X_2	
470	3.7	9	0.0887	0.0470	111
495	3.7	8	0.0909	0.0507	112
495	4.9	9	0.1235	0.0520	115
735	3.7	15	0.1186	0.0983	120
800	4.5	35	0.1473	0.1093	125
215	12.	50	0.2777	0.0207	122
420	11.	50	0.2728	0.0434	123

^aCorrected for Pu(VI) content.

the data with a quadratic is fairly good, the deviation between experimental and calculated boiling point temperatures $\bar{\Delta} = 0$, $S = 0.37$ deg C. However, there is appreciable difference between the two sets of data. In Fig. 17, the values of boiling point difference between the solution and pure nitric acid

$$\Delta T_b = E(X_2) X_2 \quad (49)$$

obtained using the two correlations are compared. The differences are about 2.8 deg C in our main area of interest (Pu concentration about 250 g/l), with Swanson's data showing a smaller effect of plutonium concentration on boiling point.

C. ESTIMATE OF RELATIVE VOLATILITY USING FURTER'S²⁹⁻³¹ METHOD

Starting from the effects of a dissolved salt on the chemical potentials of the two volatile components, and with a number of simplifying

FIG. 16 Deviation function E for Swanson's data.

FIG. 17 Comparison of Pugh's and Swanson's boiling point data.

assumptions, Furter derived Eq. (50):

$$\ln \left(\frac{\alpha_s}{\alpha} \right) = kX_2 \quad (55)$$

which³⁰

defines an improvement factor, which consists of the ratio of relative volatility with salt present (calculated using liquid composition on a salt-free basis for direct comparison purposes) to relative volatility at the same liquid composition but without salt present. It relates the logarithm of this improvement factor in a direct proportionality with X_2 the mole fraction of salt present in the liquid on a ternary basis.

"The constancy of k with changing salt concentration is predicted only when the ratio of volatile components in the liquid is held constant.*

While the above expression cannot be expected to hold over large ranges in composition, it has been used by a number of investigators. For example, there is good fit to the nitric acid-lanthanum nitrate-water system.⁴²

The relative volatility ratio was calculated for each plutonium data point as follows:

The relative volatilities for pure nitric acid were calculated using Eq. (43) with the coefficients given in Table 3. The 60 C fit was used

* k can be shown to be directly related to D Eqs. [(29) and (30)] by the definitions of α and β [Eqs. (42) and (23)].

to calculate Swanson's data, the fit to the pure nitric acid curve in the Reactor Handbook was used to calculate the Reactor Handbook and Purex Manual data.

Swanson's data (Table 8) scatter widely, however, some estimates can be made by averaging his data as previously indicated.

For pure nitric acid his relative volatilities are about 77 percent of the values calculated using Eq. (43), indicating that perhaps equilibrium was not being reached in his transpiration experiments. If this is the case for pure nitric acid, his data for plutonium nitrate solutions--which are more viscous--are likely to be even further from having attained equilibrium. The data in each of the four groups of plutonium nitrate results were averaged and are plotted in Fig. 18. Also show in Fig. 18 are the results using the earlier Purex process data. As was the case previously, the Reactor Handbook data present a self-consistent set of data at high acid concentrations.

IV. CONCLUSIONS

While the inherent quality of the data and the thermodynamic complexity of the systems precluded obtaining definitive correlations, a number of useful results was obtained:

1. For the nitric acid-water system, meaningful correlations of either activity coefficients or relative volatility vs. concentration can be obtained over limited temperature ranges. A correlation over the extended temperature range of 25 to 110 C will likely require obtaining additional data as well as

TABLE 8. Swanson's transpiration Results

Temp., °C	1000 °K	Avg air flow rate (mL/min)	Air	Millimoles				Vapor pressure, mm Hg		HNO ₃ in condensed vapor, M
				Ini- tial	Trap- ped	Ini- tial	Trap- ped			
				NaOH	HNO ₃	H ₂ O	H ₂ O	H ₂ O	HNO ₃	
12 M HNO ₃ :										
77	2.86	3.9	30.3	2.61	0.83	10.99	7.76	152	16	5.0
78	2.85	6.5	48.8	2.68	0.83	12.03	8.33	109	11	4.8
10 M HNO ₃ :										
69	2.92	3.8	36.9	1.48	0.30	6.17	6.51	135	6.2	2.4
78	2.85	3.7	29.9	1.48	0.17	9.84	7.86	157	3.4	1.2
~500 g/L Pu in 4 M HNO ₃ :										
32	3.28	1.1	15.6	0.52	0.24	2.30	0.81	37	11	10.7 ^a
33	3.27	0.24	13.1	0.49	0.13	2.20	1.68	86	6.6	3.8
54	3.06	3.0	36.9	1.05	0.42	5.34	16.1	229	6.0	
60	3.00	2.9	36.5	1.25	0.24	7.43	2.53	49	4.6	4.6
61	2.99	0.28	10.2	0.53	0.48	2.62	2.93	164	27	7.0
61	2.99	3.0	30.3	0.75	0.98	3.66	5.54	114	≥20	≥ 7.5
70	2.92	3.0	37.7	1.56	0.64	7.01	5.26	92	11	5.6
70	2.92	3.6	36.5	1.56	0.55	9.31	6.09	107	10	4.4
~500 g/L in 5M HNO ₃ :										
52	3.08	3.5	37.7	1.55	0.90	7.33	3.15	57	16	10.4
57	3.03	3.5	35.7	1.90	0.45	8.58	2.35	46	8.9	7.9
64	2.97	3.5	36.1	1.57	1.32	7.43	5.31	94	23	9.6
67	2.94	3.6	36.1	2.60	0.41	10.99	5.04	92	7.5	4.0
~700 g/L in 4M HNO ₃ :										
53	3.07	3.6	37.7	1.56	0.79	7.01	2.33	43	15	11.5
58	3.02	4.1	42.6	2.07	0.92	8.80	3.80	61	15	9.4
68	2.93	3.2	32.4	2.56	0.91	12.04	4.72	94	18	7.9
~700 g/L 5M HNO ₃ :										
35	3.25	0.22	10.2	0.37	0.071	1.99	0.25	18	5.1	10.4
60	3.00	0.20	8.6	0.54	0.36	2.51	0.61	48	28	15.2
60	3.00	2.8	28.7	1.24	0.84	7.01	0.90	22	21	17.6
59	3.01	2.9	28.7	0.00	--	0.00	3.00	72	--	--

^aThis point was not included.

FIG. 18 log alpha ratio versus X_1 .

inclusion of the effects of partial dissociation and the thermal decomposition of the mono- and trihydrate complexes.

2. For the plutonium nitrate-nitric acid water system, the vapor liquid equilibrium data were correlated over the range 0 to 700 g/l Pu and 0 to 13 M nitric acid using formal thermodynamic analysis as well as empirical correlations. The correlations are useful to illustrate the poor quality of available data and can be used to make estimates.
3. The normal boiling point data for plutonium nitrate solutions over the concentration range 0 to 700 g/l Pu and 0 to 14 M nitric acid were correlated using an empirical procedure. The correlation indicates that the two available data sets are inconsistent and can be used to obtain estimates.
4. The estimation of vapor pressures at temperatures other than the normal boiling point can be made from the approximate value of activity coefficient of water obtained from the correlations and a relative volatility from item 2, above.

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APPENDIX 1: ESTIMATE OF VAPOR COMPOSITION AND VAPOR PRESSURES
OVER THE PLUTONIUM NITRATE STORAGE TANKS AT THE REPROCESSING
PLANT AT BARNWELL, S.C.

(a) Nominal storage conditions

The nominal operating conditions were to be as follows:

Temperature: 60 C

Plutonium concentration: 250 g/l or $X_2 = 0.02159$

Nitric acid concentration: 3.0 M or $X_1 = 0.06214$

(b) Vapor composition

From Eq. (43) and the constants in Table 3, the relative volatility
for pure HNO_3 is

$$\alpha = 0.00796$$

If Furter's method is used, the value of k is obtained from Fig. 18
and

$$\alpha_s = \alpha_e^{kx_2}$$

However, there is a large uncertainty in the value of k , perhaps a
value of $k = 60$ is appropriate; a sensitivity analysis follows:

k	α_s	y
30	0.0152	0.0010
60	0.0291	0.0019
120	0.1062	0.0070

If Hala's method is used [Eqs. (28) and 29)] with the values
of the constants given in Table 5,

$$\beta_{13} = 0.728$$

and

$$y_1 = 0.0038$$

Thus, y is likely to range between 0.001 and 0.007 and a value of about 0.003 is reasonable.

(c) Total and partial pressures over the solution

The total pressure over the solution can be estimated for the dilute solution ($X_3 = 0.9162$) by assuming that the activity coefficient of water at 60 C can be estimated from Eq. (37) using the ionic strength, Eq. (27), instead of the nitric acid mole fraction, obtaining

$$\gamma_3 = 0.9406$$

From Eq. (33)

$$P_3^{\circ} = 149.42 \text{ torr}$$

and since

$$P_3 = \gamma_3 X_3 P_3^{\circ}$$

$$P_3 = 128.8 \text{ torr}$$

and the corresponding values of P_{TOTAL} and P_{HNO_3} are

y	P_{TOT}	P_{HNO_3}
0.001	128.9	0.13
0.003	129.2	0.39
0.007	129.7	0.91