**Idaho
National
Engineering
Laboratory**

INEL-96/0234

September 1996

RECEIVED

OCT 07 1996

OSTI

***Physical Property Parameter Set
for Modeling ICPP Aqueous Wastes
with ASPEN Electrolyte NRTL Model***

R. E. Schindler

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

LOCKHEED MARTIN

Physical Property Parameter Set for Modeling ICPP Aqueous Wastes with ASPEN Electrolyte NRTL Model

R. E. Schindler

Published September 1996

**Idaho National Engineering Laboratory
Nuclear Operations Department
Lockheed Martin Idaho Technologies Company
Idaho Falls, Idaho 83415**

**Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-94ID13223**

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

The aqueous waste evaporators at the Idaho Chemical Processing Plant (ICPP) are being modeled using ASPEN software leased from a vendor. The ASPEN software calculates chemical and vapor-liquid equilibria with activity coefficients calculated using the electrolyte Non-Random Two Liquid (NRTL) model for local excess Gibbs free energies of interactions between ions and molecules in solution. The use of the electrolyte NRTL model requires the determination of empirical parameters for the excess Gibbs free energies of the interactions between species in solution. This report covers the development of a set parameters, from literature data, for the use of the electrolyte NRTL model with the major solutes in the ICPP aqueous wastes.

The major solutes in the ICPP aqueous wastes are nitric acid, sodium nitrate, and aluminum nitrate. The wastes also contain low concentrations of chloride, fluoride, and a number of metal cations. The greatest concern in modeling the evaporation of the wastes is calculation of the volatilization of the nitric, hydrofluoric and hydrochloric acids into the condensate. The precipitation after cooling of sodium and aluminum nitrates is also of concern.

Property parameters for the electrolyte NRTL model were regressed or verified first for binary aqueous solutions of HNO_3 , HCl , and HF . Then the parameters were regressed for two-solute solutions of HNO_3 with HCl , NaNO_3 , KNO_3 , $\text{Al}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, $\text{Ca}(\text{NO}_3)_2$, and $\text{Cu}(\text{NO}_3)_2$. The complexing reactions of the Al^{+3} and F^- ions, and the Hg^{+2} and Cl^- ions were modeled; and the precipitation of NaNO_3 and $\text{Al}(\text{NO}_3)_3$ from HNO_3 solutions was also modeled.

The calculations using the resulting parameter sets were tested against the literature data and against laboratory simulations of ICPP waste evaporations. With the regressed parameter set, the electrolyte NRTL model calculates vapor-phase HNO_3 concentrations within 25 percent for NaNO_3 concentrations to 50 percent, and for concentrations of the polyvalent nitrate salts to about 20 percent. The calculations of vapor-phase concentrations of HCl and HF appear to be within 50 percent for HCl and within a factor of two for HF .

CONTENTS

ABSTRACT	iii
1. INTRODUCTION	1
1.1 ICPP Aqueous Wastes	1
1.2 Electrolyte NRTL Solution Model	1
2. REGRESSION OF ELEC NRTL MODEL PARAMETERS	2
2.1 Objectives and Evaluation Criteria	3
2.2 Nitric Acid Solutions	3
2.2.1 Evaluation of Parameter Set from ASPEN Plus™ Software	4
2.2.2 Preliminary Regressions of Data at 25°C	4
2.2.3 VLE Data Regressions	4
2.3 Solutions of Sodium Nitrate and Nitric Acid	11
2.4 Solutions of Aluminum Nitrate and Nitric Acid	15
2.5 Solutions of Sodium Nitrate and Aluminum Nitrate	16
2.6 Solutions of Potassium Nitrate and Nitric Acid	21
2.7 Solutions of Hydrochloric and Nitric Acids	21
2.8 Solutions of Hydrofluoric and Nitric Acids	28
2.9 Solutions of Calcium Nitrate and Nitric Acid	28
2.10 Solutions of Ferric Nitrate and Nitric Acid	35
2.11 Solutions of Minor Bivalent Nitrates and Nitric Acid	35
2.12 Mercury Chloride Solutions	36
2.12.1 Thermochemical Parameters for HgCl ₂	36
2.12.2 Activity Coefficients	38
2.12.3 Chemical Speciation Calculations	38

2.13	Boric Acid Solutions	41
2.14	Undissolved Solids	42
2.15	Zirconium Complexes	42
2.16	Parameters for Solution Density	42
2.16.1	Clarke Model for Aqueous Solutions	42
2.16.2	Density Parameter Regression	43
2.16.3	Test Calculations for HLLW Tanks	43
3.	TESTING AND ADJUSTMENTS BASED ON LABORATORY TESTS OF WASTE EVAPORATION	45
3.1	Test Operation	45
3.2	Simulation Models of Tests	46
3.3	Comparison of Calculations with Test Results	47
3.3.1	Temperature	47
3.3.2	Liquid Density	48
3.3.3	Nitric Acid in Condensate	48
3.3.4	Chloride in Condensate	50
3.3.5	Fluoride in Condensate	50
3.3.6	Mercury Chloride	55
4.	PROPERTIES FILE PROP-R9C	58
4.1	Properties File Usage	58
4.2	Parameter Set Verification	58
5.	SUMMARY EVALUATION	59
5.1	Nitric Acid Solutions	59
5.2	Solutions of Nitric Acid and Nitrate Salts	59
5.3	Solutions of Hydrochloric and Nitric Acids	61
5.4	Solutions of Hydrofluoric and Nitric Acids	61
5.5	Other Molecular Solutes	61

5.6	Calculated Local Excess Gibbs Free Energy Values	63
5.7	Chemical Equilibria Calculation Convergence	63
6.	CONCLUSIONS ON WASTE EVAPORATION CALCULATIONS	66
7.	REFERENCES	66

Appendix A—Property Parameters File PROP-R9C

FIGURES

1.	Comparison of measured partial pressures of HNO_3 at 25°C with those calculated using activity coefficient parameters regressed from 1) VLE data only, 2) VLE plus enthalphy of mixing (HLMX) data, and 3) VLE plus solution heat capacity (CPLMX) data (E96 0296)	5
2.	Comparison of calculated and measured vapor-phase concentrations of HNO_3 at 760 torr (E96 0297)	7
3.	Comparison of calculated and measured partial pressures of HNO_3 at 25 and 50°C (E96 0298)	8
4.	Comparison of calculated and measured vapor-phase concentrations of HNO_3 at 200 torr (E96 0299)	9
5.	Comparison of calculated and measured hydrolysis of HNO_3 at 25°C (E96 0300)	10
6.	Calculated activity coefficients at 25°C (E96 0301)	12
7.	Comparison of calculated and measured effect of NaNO_3 on vapor-phase concentrations of HNO_3 over HNO_3 solutions (E96 0302)	13
8.	Comparison of calculated and measured solubilities of NaNO_3 in aqueous nitric acid solutions at 15 and 20°C (E96 0303)	14
9.	Comparison of calculated and measured effect on vapor-phase HNO_3 concentrations of adding $\text{Al}(\text{NO}_3)_3$ to solutions initially containing 10 and 20% HNO_3 (E96 0304)	18
10.	Comparison of calculated and measured solubilities of $\text{Al}(\text{NO}_3)_3$ in aqueous nitric acid solutions at 20°C (E96 0305)	19
11.	Comparison of calculated and measured solubilities of NaNO_3 in aqueous $\text{Al}(\text{NO}_3)_3$ solutions at 20°C (E96 0306)	20
12.	Comparison of calculated and measured solubilities of potassium nitrate in nitric acid solutions at 20 and 30°C (E96 0307)	22

13. Comparison of calculated and measured partial pressures of HCl over sub-azeotropic HCl solutions (E96 0308)	25
14. Comparison of calculated and measured effect of HNO ₃ concentration on vapor-to-liquid mole fraction ratio (Y/X) for HCl at 200 torr (E96 0309)	26
15. Comparison of calculated and measured effect of HNO ₃ concentration on vapor-to-liquid mole fraction ratio (Y/X) for HCl at 760 torr (G96-0189)	27
16. Comparison of calculated and measured partial pressures of HF over aqueous solutions at 25, 40, 60 and 75°C (G96-0190)	29
17. Comparison of calculated and measured partial pressures of HF over aqueous solutions at 30, 50 and 70°C (G96-0191)	30
18. Comparison of calculated and measured vapor compositions over aqueous HF solutions at 760 torr (G96-0192)	31
19. Calculated activity coefficients (mole fraction basis) of HF and fluoride ion at 25°C (G96-0183)	32
20. Comparison of calculated and measured effect on vapor-phase HNO ₃ concentrations of adding Ca(NO ₃) ₂ to solutions initially containing 20% HNO ₃ (G96-0184)	34
21. Calculated activity coefficients of HgCl ₂ in aqueous solution (G96-0193)	39
22. Calculated partial pressure of HgCl ₂ over aqueous solutions (E96 0310)	40
23. Condensate nitric acid concentration during semi-batch HLLWE simulation (E96 0311) . . .	49
24. Condensate chloride concentration during semi-batch HLLWE simulation (G96-0185)	51
25. Condensate chloride concentration during batch waste simulant evaporation (G96-0186) . . .	52
26. Condensate fluoride concentration during semi-batch evaporations (E96 0312)	53
27. Comparison of calculated and measured concentrations of mercury as HgCl ₂ in condensate from the batch evaporation test (G96-0187)	57
28. Vapor compositions of boiling solutions made by adding various nitrate salts to a nitric acid solution initially containing 20 percent nitric acid (E96 0313)	60

29. Vapor compositions of boiling solutions made by adding various nitrate salts to a nitric acid solution initially containing 20 percent nitric acid (G96-0188)	62
30. Local excess Gibbs free energies (τ) for ion pair-molecule interactions calculated at 100°C (G96-0194)	65

TABLES

1. Activity coefficient parameters for nitric acid solutions	6
2. Activity coefficient parameters for aqueous mixtures of nitric acid and sodium nitrate	15
3. Activity coefficient parameters for aqueous mixtures of nitric acid and aluminum nitrate . . .	17
4. Activity coefficient parameters for aqueous mixtures of sodium and aluminum nitrates	17
5. Activity coefficient parameters for aqueous mixtures of potassium nitrate with nitric acid and sodium nitrate	23
6. Activity coefficient parameters for aqueous solutions of HCl and HNO ₃	24
7. Activity coefficient parameters for HF solutions	33
8. Activity coefficient parameters for aqueous mixtures of nitric acid and calcium nitrate	33
9. Activity coefficient parameters for aqueous mixtures of nitric acid and ferric nitrate	35
10. Activity coefficient parameters for aqueous mixtures of nitric acid and cupric nitrate	36
11. Calculated mercury species distributions as percentages at 100°C	41
12. Clarke density parameters in 1/kmole	44
13. Rackett density parameters (SI)	44
14. Differences between calculated and measured densities	45
15. Molar concentrations of solutes in feeds for semi-batch laboratory evaporations	46
16. Molar concentrations of solutes in feed for batch laboratory evaporation and its simulation .	47
17. Activity coefficient parameters for aqueous mixtures of nitric acid and AlF complexes	54

18. Activity coefficient parameters for aqueous HgCl_2 solutions containing dissolved nitrates . .	56
19. Local excess Gibbs free energies at 100°C calculated from GMELCC, GMELCD, and GMELCE parameters of this report	64

Physical Property Parameter Set for Modeling ICPP Aqueous Wastes with ASPEN Electrolyte NRTL Model

1. INTRODUCTION

The Idaho Chemical Processing Plant (ICPP) generates a variety of aqueous wastes that are concentrated by evaporation with the concentrate being solidified by fluidized-bed calcination. Process simulation models are being developed to model the ICPP waste treatment processes beginning with the evaporators. The process simulation models use the ASPEN PlusTM simulation software (leased from ASPEN Technology, Inc.) as the thermodynamic framework for the simulations. The vapor-liquid equilibria (VLE) and chemical equilibria calculations use its electrolyte NRTL model to calculate activity coefficients. This report documents the regression and verification of a set of physical and chemical property parameters for use by the simulation models in calculating VLE and chemical equilibria for the major chemical species in the ICPP wastes. The physical and chemical property parameter sets were developed in the format required for the electrolyte NRTL model.

1.1 ICPP Aqueous Wastes

The ICPP aqueous wastes are acid wastes, mostly dilute, in which the major chemical solutes are nitric acid, sodium nitrate and aluminum nitrate. They also contain lesser concentrations of chloride and fluoride, and low, variable concentrations of many other cations and anions. The evaporators concentrate the aqueous wastes to concentrations that approach the solubility of sodium nitrate. However, the acid concentrations remain sub-azeotropic.

A major concern in the evaporators is the vaporization of the corrosive acids: nitric, hydrochloric, and hydrofluoric. The chemical equilibria of greatest concern are: (1) the complexing of the fluoride with aluminum ions to reduce the volatility and corrosiveness of HF, and (2) the complexing of mercuric ion with chloride ions to form mercuric chloride which is slightly volatile at boiling temperatures.

1.2 Electrolyte NRTL Solution Model

The ASPEN PlusTM process simulation software provides a thermodynamic framework for the energy and mass balances, chemical equilibria calculations, and VLE calculations of the chemical process simulations. It offers a number of number of thermodynamic and activity-coefficient models of which the electrolyte non-random two-liquid model^{1,2} (abbreviated ELECNRTL) is the most developed for use in concentrated electrolyte solutions. (Electrolyte NRTL models are also offered with other process simulation software from different vendors.) The ELECNRTL model is an extension by Chen,² et. al., to multi-solvent electrolyte solutions of the Renon³ non-random two-liquid (NRTL) model³ for local excess Gibbs free energy in solution. It sums contributions to the local

excess Gibbs free energy of long-range ion-ion interactions, local ion-molecule interactions, and molecule-molecule interactions and then calculates the activity coefficients for each specie from the excess Gibbs free energies.

In application the ELECNRTL model generates (and provides a thermodynamic basis for) a large number of adjustable coefficients for the interactions between species. The values of the coefficients are determined for each specie in solution by data regression of their solution properties. The vendor provides physical and chemical property parameters for many of the more common chemicals. However, many of the parameters needed for the solutes in the ICPP wastes are missing. This report documents the regression and evaluation of the parameters needed for equilibrium and VLE calculations for the major species in the ICPP aqueous wastes.

Process chemistry calculations can be done on either an "apparent" (i.e., makeup) basis or on a "true" basis. For illustration consider a liter of solution to which 5 moles of nitric acid has been added. The apparent nitric acid concentration, based on its makeup, is 5 M. However, most of the nitric acid will hydrolyze to ions, and the true concentration of molecular nitric acid will be less than 1 M. The ASPEN ELECNRTL model does its internal chemical and vapor-liquid equilibria calculations using the true-basis mole fractions of each chemical specie. The ASPEN Plus™ program can take feed stream compositions on a number of apparent composition bases, but it converts them to true mole fractions and usually reports products on a calculated true basis. Hence, the activity coefficients are based on mole fractions and "true" species compositions.

There are a number of different activity coefficient conventions. A major difference is whether activity coefficients for molecular solutes (e.g., HNO_3 and HF) are on a "symmetric" or "asymmetric" convention. Both conventions define the activity coefficients of water and all ions as unity at infinite dilution. However, the symmetric convention assigns molecular solutes an activity coefficient of one at infinite dilution; whereas the asymmetric convention assigns an activity coefficient of one to the pure solvent. The ELECNRTL model uses the asymmetric convention in which the activity coefficients of molecular solutes can differ by orders of magnitude from one at infinite dilution -- greater than one for low-solubility solutes (e.g., hydrocarbons) and less than one for hydrophilic solutes (e.g., HNO_3 and HF). A conflict comes in the use of literature chemical equilibria constants which are usually determined in the symmetric convention because the activity coefficients all become one at infinite dilution. A conversion of equilibrium constants from one convention to the other involves multiplication or division by the activity coefficients at infinite dilution of the molecular solutes. Uncertainties in converting between the activity coefficient conventions can be avoided by calculating equilibrium constants from free energy of formation which remains the same under both conventions (and which ASPEN Plus can use).

2. REGRESSION OF ELECNRTL MODEL PARAMETERS

The data regression sequence centers on nitric acid because it is a major component in every mixture. The regressions begin with binary aqueous solutions of HNO_3 , NaNO_3 , $\text{Al}(\text{NO}_3)_3$, HCl , and HF , then progress to aqueous mixtures of HNO_3 with NaNO_3 , $\text{Al}(\text{NO}_3)_3$, HCl , and HF .

The ASPEN Plus software contains a data regression system (DRS) which will regress the ELECNRTL activity coefficient parameters and chemical equilibria constants from a variety of physical and chemical data. The parameters developed for this report were regressed using the DRS system to regress VLE, salt solubility, enthalpy of mixing, and osmotic coefficient data for two and three component mixtures of the major solutes in the ICPP wastes.

2.1 Objectives and Evaluation Criteria

Although a property parameter set that calculates all properties well is desirable, it is rarely achieved. Real activity coefficient models have inaccuracies and usually require weighing of objectives and evaluation criteria. The objectives given priority in this evaluation series are those of concern in modeling the waste evaporators:

1. Vapor-liquid equilibria at boiling

The first priority is given to vapor-liquid equilibria (VLE) at boiling for calculating condensate compositions. The composition range of interest is relatively-dilute (sub-azeotropic) acid concentrations and relatively-high concentrations of sodium and aluminum nitrates.

2. Nitrate ion activity at ambient temperatures

The calculation of the solubility of nitrate salts in nitric acid solutions at ambient temperature is needed to evaluate precipitation potential in the waste evaporators. An accurate calculation of the ionization equilibria between nitric acid and the nitrate and acid ions is desirable as an indication of accurate activity of the nitrate ion which is needed to calculate the solubility of the nitrate salts.

3. Vapor-liquid equilibria at other temperatures

Accurate VLE calculations at all temperatures would be useful for other applications (e.g., the NWCF scrub system). Errors on the high side would be preferable to errors on the low side for calculation of the partial pressure of nitric acid because many applications seek conservative calculations.

The regression sequence attempted to cover a range of properties and temperatures. However, when conflicts occurred in fitting data sets at different temperatures, the priority was given as listed above and primarily to the VLE at boiling.

2.2 Nitric Acid Solutions

Nitric acid is central to the overall regression plan because it is the most concentrated acid and the acid that most effects the other solutes. The regressions of the parameters for the interactions of nitric acid with the other solutes use the activity coefficient parameters for nitric acid and its ions.

2.2.1 Evaluation of Parameter Set from ASPEN Plus™ Software

The activity-coefficient parameter set for nitric acid provided with the ASPEN Plus™ software was tested against VLE^{4,5,6,7,8,9,10,11,12} and acid hydrolysis¹³ data and found inadequate primarily for dilute solutions. The VLE calculations at boiling provide vapor-phase nitric acid concentrations that are a factor of two-to-three low for dilute solutions. (The data fit is acceptable for concentrated solutions.) Also, the calculated dissociation of the nitric acid is way high (i.e., very little molecular nitric acid).

The basic physical property parameters (e.g., heat capacity, heat of vaporization, and vapor pressure) provided with the ASPEN Plus™ software appear reasonable and are used in the regressions. Also retained is the calculation of nitric acid dissociation using thermochemical parameters from the NBS tables.¹⁴

2.2.2 Preliminary Regressions of Data at 25°C

Some preliminary regressions were run on the regressible data at 25°C to check whether the ASPEN ELECNRTL model can reconcile VLE,^{5,6,7,8,9} enthalpy of mixing,¹⁴ solution heat capacity,¹⁵ and acid hydrolysis¹³ data for nitric acid. The activity coefficient parameters for nitric acid solutions were regressed using (1) VLE data only, (2) VLE plus enthalpy of mixing (HLMX) data, and (3) VLE plus solution heat capacity (CPLMX) data. Nitric acid partial pressures, calculated at 25°C using each of the regressed activity coefficient parameter sets, are shown on Figure 1. The calculations with the parameter set from VLE data only fit the data well, but the addition of the other data pulls the calculated curves high for dilute solutions. The addition of the CPLMX data also distorts the shape of the curve. A comparison of calculated and measured (direct measurement¹³ of nitrate ion concentrations by Raman spectroscopy) acid hydrolysis shows the cases with the HLMX and CPLMX data deviating further (high) from the data than the VLE data only case. Hence it is concluded that the VLE, enthalpy of mixing and solution heat capacity data for nitric acid cannot be reconciled by the ASPEN ELECNRTL model.

One possible explanation of the difficulty in reconciling different types of data is that the chemistry equations describing the reactions of nitric acid with water are simplified by ignoring the hydrated forms¹⁴ of nitric acid (e.g., $\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$) which exist at least at the lower temperatures. The hydrated form would have a different effect on the vapor composition than on other data. The ASPEN model attempts to cover the chemistry simplifications with an activity coefficient for nitric acid which is much less than one, but this is not entirely successful. Other explanations are that the ELECNRTL model may be inadequate and that some of the data may be in error (or misinterpreted).

2.2.3 VLE Data Regressions

Based on the results of the preliminary regressions, the regressions used VLE only. First, all of the available VLE data^{4,5,6,7,8,9,10,11,12,16,17} from 25°C to boiling was regressed. (Handbook¹⁷ VLE numbers were not used because they are extrapolations¹⁸ rather than actual data.) VLE calculations, with the parameters provided by the regression, fit the data in the middle of the temperature range but

Figure 1. Comparison of measured partial pressures of HNO_3 at 25°C with those calculated using activity coefficient parameters regressed from (1) VLE data^{5,6,7,8,9} only, (2) VLE plus enthalpy of mixing¹⁴ (HLMX) data, and (3) VLE plus solution heat capacity¹⁵ (CPLMX) data (E96 0296).

calculated low vapor-phase nitric acid concentrations for dilute solutions at 760 torr and at 25°C which are the most important conditions.

The regressions were then repeated using only the VLE data at 760 torr and 25°C to obtain the activity coefficient parameter set listed in Table 1. The vapor compositions calculated with the parameters of Table 1 are compared with data in Figures 2, 3, and 4. The nitric acid concentrations (or partial pressures) fit the data well at 760 torr (Figure 2), are a little low at the dilute end at 25°C (Figure 3), and are high at 50°C (Figure 3) and at 200 torr (Figure 4). The calculated nitric acid dissociation, shown on Figure 5, is high but closer than calculated with the base (ASPEN Plus) parameter set. (The calculated molecular nitric acid concentration, which is about a factor of two low, is compensated for by a nitric acid activity coefficient which is high.)

Table 1. Activity coefficient parameters for nitric acid solutions.

Parameter	Species Pair	Value
NRTL 1	HNO ₃ H ₂ O	90
NRTL 1	H ₂ O HNO ₃	-3.627717
NRTL 2	HNO ₃ H ₂ O	0
NRTL 2	H ₂ O HNO ₂	65.86466
NRTL 3	HNO ₃ H ₂ O	0.30
NRTL 3	H ₂ O HNO ₃	0.05
GMELCC	H ₂ O (H ₃ O ⁺ NO ₃ ⁻)	-3.411562
GMELCC	(H ₃ O ⁺ NO ₃ ⁻) H ₂ O	-1.379389
GMELCD	H ₂ O (H ₃ O ⁺ NO ₃ ⁻)	4021.066
GMELCD	(H ₃ O ⁺ NO ₃ ⁻) H ₂ O	-1005.608
GMELCC	HNO ₃ (H ₃ O ⁺ NO ₃ ⁻)	18.35049
GMELCC	(H ₃ O ⁺ NO ₃ ⁻) HNO ₃	28.03711
GMELCD	HNO ₃ (H ₃ O ⁺ NO ₃ ⁻)	-2595.605
GMELCD	(H ₃ O ⁺ NO ₃ ⁻) HNO ₃	-9671.993
GMELCE	HNO ₃ (H ₃ O ⁺ NO ₃ ⁻)	-82.78977
GMELCE	(H ₃ O ⁺ NO ₃ ⁻) HNO ₃	47.90918

Figure 2. Comparison of calculated and measured vapor-phase concentrations of HNO_3 at 760 torr (E96 0297).

E96 0298

Figure 3. Comparison of calculated and measured partial pressures of HNO₃ at 25 and 50°C (E96 0298).

Figure 4. Comparison of calculated and measured vapor-phase concentrations of HNO_3 at 200 torr (E96 0299).

Figure 5. Comparison of calculated and measured¹³ hydrolysis of HNO_3 at 25°C (E96 0300).

The calculated activity coefficients, shown on Figure 6, appear acceptable. The activity coefficient for nitric acid has a small (questionable) minimum but is otherwise reasonable. The activity coefficients for water and nitrate ion (which is identical to the coefficient for the acid ion) are of the expected¹⁹ shape.

Figure 4 illustrates the difficulty in regressing the full VLE data set. The shape of the VLE curves (i.e., slope vs. concentration) changes with temperature in a way that cannot be matched with the available activity coefficient parameters. (The previously discussed omission of hydrated acid forms may contribute to the difficulty.) Allowing the nitric acid vapor pressure to be regressed did not improve the data fit.

2.3 Solutions of Sodium Nitrate and Nitric Acid

The mixing of nitric acid and sodium nitrate in solution effects both the volatility of the nitric acid and the solubility of the sodium nitrate. The addition of sodium nitrate to nitric acid solutions increases the concentration of nitric acid in its vapor by (1) the increased nitrate shifting the hydrolysis equilibrium towards more nitric acid, and (2) the increased concentration of solutes increasing the activity coefficients. The addition of nitric acid to sodium nitrate solutions decreases the solubility of sodium nitrate by (1) the increased nitrate shifting the salt equilibrium towards more solid, and (2) the increased concentration of solutes increasing the activity coefficients of the ions. The calculation of these effects requires determination of the interactions of the ions of sodium nitrate with water, nitric acid and the ions of nitric acid.

The determination of the parameters needed for the $\text{NaNO}_3\text{-HNO}_3\text{-H}_2\text{O}$ system was done in three steps. First, VLE data^{20,21} for sodium nitrate solutions was regressed to obtain the activity coefficient parameters for water and the ions of NaNO_3 listed in Table 2. Next, solubility data²² for NaNO_3 in water was regressed, using the parameters obtained from the first regression, for a solubility product equation of the form

$$\text{K-SALT} = A + B/T + C \cdot \ln T$$

where T is temperature (K), and the coefficients for NaNO_3 are: $A = -26.15063$, $B = -179.9668$, and $C = 3.774540$. These solubility-product coefficients provide an excellent correlation of the solubility data.²² Finally, the VLE²⁰ and solubility²² data for aqueous mixtures of NaNO_3 and HNO_3 was regressed together, using the parameters obtained from the earlier two steps, to obtain the activity coefficient parameters, listed in Table 2, for the interactions of the ions of NaNO_3 with HNO_3 and its ions. Preliminary regressions could not correlate data sets at 760 and 400 torr (possibly because the nitric acid correlation is not accurate at 400 torr), so the regression included only VLE data²⁰ at 760 torr and solubility data at 15 and 20°C.

The data correlation provided by the parameters obtained (listed in Table 2) is shown on Figures 7 and 8. Figure 7, which compares calculated and measured²⁰ vapor compositions for aqueous solutions of NaNO_3 and HNO_3 , shows a good correlation (within 20%) of the vapor compositions at NaNO_3 concentrations up to about 0.2 mole fraction (10 $\underline{\text{M}}$). Figure 8, which compares calculated and measured solubilities of NaNO_3 in HNO_3 solutions at 15 and 20°C, shows

Figure 6. Calculated activity coefficients at 25°C (E96 0301).

Figure 7. Comparison of calculated and measured effect of NaNO_3 on vapor-phase concentrations of HNO_3 over HNO_3 solutions (E96 0302).

Figure 8. Comparison of calculated and measured solubilities of NaNO_3 in aqueous nitric acid solutions at 15 and 20°C (E96 0303).

Table 2. Activity coefficient parameters for aqueous mixtures of nitric acid and sodium nitrate.

Parameter	Species Pair	Value
GMELCC	H ₂ O (NA+ NO ₃ -)	8.509752
GMELCC	(NA+ NO ₃ -) H ₂ O	-4.460697
GMELCD	H ₂ O (NA+ NO ₃ -)	-505.2884
GMELCD	(NA+ NO ₃ -) H ₂ O	288.6656
GMELCC	HNO ₃ (NA+ NO ₃ -)	-29.90617
GMELCC	(NA+ NO ₃ -) HNO ₃	-33.52829
GMELCD	HNO ₃ (NA+ NO ₃ -)	17681.22
GMELCD	(NA+ NO ₃ -) HNO ₃	13131.20
GMELCC	(H ₃ O+ NO ₃ -) (NA+ NO ₃ -)	5.284384
GMELCC	(NA+ NO ₃ -) (H ₃ O+ NO ₃ -)	-0.6550303

good solubility data²² correlation for HNO₃ concentrations of over 0.3 mole fraction (13 M) which is an adequate range for the HLLW and PEW evaporators. Figure 8 shows only one line for the two temperatures because the temperatures and data are close (some of the measured solubilities at 20°C are lower than those at 15°C).

2.4 Solutions of Aluminum Nitrate and Nitric Acid

The addition of aluminum nitrate to nitric acid solutions increases the concentration of nitric acid in its vapor by (1) shifting the hydrolysis equilibrium towards more nitric acid with the increased nitrate, and (2) increasing the activity coefficients. The addition of nitric acid to aluminum nitrate solutions decreases the solubility of aluminum nitrate by (1) shifting the salt equilibrium towards more solid with the increased nitrate, and (2) increasing the activity coefficients of the ions. Aluminum nitrate has a stronger effect than sodium nitrate because of its higher charge.

The regression of activity coefficient parameters for aluminum nitrate solutions is inhibited by a shortage of data. Only solubility data²² and one set of osmotic pressure²³ coefficients (at 25°C) are available for Al(NO₃)₃-H₂O solutions. One set¹² of atmospheric pressure VLE data, an incomplete set²¹ (no temperature) of reduced pressure VLE data and solubility data²² are available for Al(NO₃)₃-HNO₃-H₂O solutions. The data regression worked best when done in two steps. First, the Al(NO₃)₃-H₂O solubility data, osmotic pressure²³ coefficients and VLE¹² data were regressed for the Al(NO₃)₃-H₂O activity coefficient parameters and the Al(NO₃)₃ solubility product coefficients. The second step used the results of the first step and regressed the Al(NO₃)₃-HNO₃ activity coefficient parameters using the Al(NO₃)₃-HNO₃-H₂O VLE¹² and solubility data.²²

The solubility product coefficients were regressed for $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ which is the least soluble aluminum nitrate salt at temperatures below 60°C :

The solubility coefficient equation is of the form,

$$\text{K-SOL} = A + B/T + C \cdot \ln T, \text{ with the values}$$

$$A = 316.3685, B = -12511.94, C = -50.$$

Note that the above K-SOL equation is influenced strongly by the activity coefficient of water because there are nine waters in the reaction. The solubilities calculated with these coefficients agree within 8% with the data over the temperature range from 0 to 60°C .

The activity coefficient parameters obtained from the regressions are listed in Table 3. The vapor compositions calculated with the parameters of Table 3, are compared with measured vapor compositions¹² in Figure 9. The experiment measured vapor composition and temperature obtained from adding increasing amounts of $\text{Al}(\text{NO}_3)_3$ to (initially) 10% and 20% solutions of HNO_3 (thereby diluting the HNO_3). The calculated vapor compositions agree within about 25% with the measured values for $\text{Al}(\text{NO}_3)_3$ concentrations up to 30% (about 1.8 M), which is adequate for most ICPP waste solutions, then show a negative error which increased with $\text{Al}(\text{NO}_3)_3$ concentration. The calculated $\text{Al}(\text{NO}_3)_3$ - HNO_3 - H_2O solubilities at 20°C agree well with the measured values as shown in Figure 10. The calculated solubilities at 0°C (not shown) also agree adequately (average deviation of 25%) with the measured values.

The data regression problem for the VLE is that the electrolyte NRTL model cannot fit both the temperature and composition data (with the given chemistry) at the higher $\text{Al}(\text{NO}_3)_3$ concentrations. It fits the temperatures closely and calculates low vapor nitric acid concentrations at $\text{Al}(\text{NO}_3)_3$ above 30%. The regression can be constrained to fit the vapor compositions, but it then calculates erroneous temperatures [way high at 50% $\text{Al}(\text{NO}_3)_3$].

2.5 Solutions of Sodium Nitrate and Aluminum Nitrate

The addition of aluminum nitrate to sodium nitrate solutions reduces the solubility of sodium nitrate by increasing the nitrate ion concentration and by increasing activity coefficients. Solubility data²² for $\text{Al}(\text{NO}_3)_3$ - NaNO_3 - H_2O solutions was regressed to obtain the activity coefficient parameters listed in Table 4. Figure 11 shows good agreement between solubilities calculated using the parameters of Table 4 and measured²² solubilities of NaNO_3 in $\text{Al}(\text{NO}_3)_3$ solutions at 20°C . Later tests showed that the parameters of Table 4, which were regressed with data at 20°C , cause erroneous HF volatility calculations at boiling. Hence, they are omitted unless solubility is the primary objective of the calculation.

Table 3. Activity coefficient parameters for aqueous mixtures of nitric acid and aluminum nitrate.

Parameter	Species Pair	Value
GMELCC	H2O (A1+ NO3-)	29.959114
GMELCC	(A1+3 NO3-) H2O	-10.1010
GMELCD	H2O (A1+ NO3-)	-5892.001
GMELCD	(A1+3 NO3-) H2O	1470.918
GMELCE	H2O (A1+3 NO3-)	-100
GMELCE	(A1+3 NO3-) H2O	33.16584
GMELCC	HNO3 (A1+3 NO3-)	2.192842
GMELCC	(A1+3 NO3-) HNO3	-8.52746
GMELCD	HNO3 (A1+3 NO3-)	1562.688
GMELCD	(A1+3 NO3-) HNO3	5736.824
GMELCE	HNO3 (A1+3 NO3-)	93.7309
GMELCE	(A1+3 NO3-) HNO3	-100
GMELCC	(H3O+ NO3-) (A1+3 NO3-)	12.68662
GMELCC	(A1+3 NO3-) (H3O+ NO3-)	6.911549
GMELCD	(H3O+ NO3-) (A1+3 NO3-)	6092.308
GMELCD	(A1+3 NO3-) (H3O+ NO3-)	-550.0901

Table 4. Activity coefficient parameters for aqueous mixtures of sodium and aluminum nitrates.

Parameter	Species Pair	Value
GMELCC	(A1+3 NO3-) (NA+ NO3-)	7.959875
GMELCC	(NA+ NO3-) (AL+3 NO3-)	-0.7859297

Figure 9. Comparison of calculated and measured effect on vapor-phase HNO_3 concentrations of adding $\text{Al}(\text{NO}_3)_3$ to solutions initially containing 10 and 20% HNO_3 (E96 0304).

Figure 10. Comparison of calculated and measured solubilities²² of $\text{Al}(\text{NO}_3)_3$ in aqueous nitric acid solutions at 20°C (E96 0305).

Figure 11. Comparison of calculated and measured solubilities²² of NaNO_3 in aqueous $\text{Al}(\text{NO}_3)_3$ solutions at 20°C (E96 0306).

2.6 Solutions of Potassium Nitrate and Nitric Acid

The regression of data for solutions of potassium nitrate and nitric acid was troublesome. The regressions were not able to correlate solubility data together with VLE data (25°C), or to correlate solubility data over a wide temperature range. So, the regression effort focused on providing a correlation of solubility data at ambient temperature. (There is no VLE data for boiling solutions.)

The regression was a four-step series:

1. First, vapor pressure depression data²⁴ for KNO_3 solutions was regressed to obtain the activity coefficient parameters, listed in Table 5, for water and the ions of KNO_3 . (These parameters are close to those provided with the ASPEN Plus software.) The data fit is excellent.
2. Next, solubility data²² for KNO_3 in water was regressed for the solubility product (K-SOL) coefficients: $A = 111.9424$, $B = -8683.153$, and $C = -15.95728$. The data fit is excellent.
3. Then, solubility data²² for KNO_3 in nitric acid solutions at 15, 20, 25, and 30°C was regressed for the activity coefficient parameters, listed in Table 5, for the ions of KNO_3 with HNO_3 and its ions. The data fit at 20 and 30°C, which is shown on Figure 12, is good at HNO_3 concentrations up to 25%. The data fit at 15 and 25°C is similar to that shown on Figure 12. Note that the GMELCC parameters (Table 5) for HNO_3 ($\text{K}^+ \text{NO}_3^-$) and ($\text{H}_3\text{O}^+ \text{NO}_3^-$) ($\text{K}^+ \text{NO}_3^-$) are relatively high in opposite directions which appears needed to obtain the desired curvature.
4. Finally, solubility data²² for solutions of KNO_3 and NaNO_3 was regressed to obtain the parameters for their ions listed in Table 5. The data fit is excellent at NaNO_3 concentrations to 20% and KNO_3 concentrations to 40%.

2.7 Solutions of Hydrochloric and Nitric Acids

Calculations of vapor compositions of hydrochloric acid solutions using the parameter set for $\text{HCl-H}_2\text{O}$ provided with the ASPEN PlusTM software were first evaluated by comparison with available data²⁵ and found to give calculated vapor-phase HCl concentrations that are over a factor of two low for dilute HCl solutions. It was then decided to develop a new parameter set for $\text{HCl-H}_2\text{O}$ and $\text{HCl-HNO}_3\text{-H}_2\text{O}$ solutions.

Figure 12. Comparison of calculated and measured²² solubilities of potassium nitrate in nitric acid solutions at 20 and 30°C (E96 0307).

Table 5. Activity coefficient parameters for aqueous mixtures of potassium nitrate with nitric acid and sodium nitrate.

Parameter	Species Pair	Value
GMELCC	H ₂ O (K+ NO ₃ -)	4.038739
GMELCC	(K+ NO ₃ -) H ₂ O	-3.106562
GMELCD	H ₂ O (K+ NO ₃ -)	845.6844
GMELCD	(K+ NO ₃ -) H ₂ O	-0.8084505
GMELCC	HNO ₃ (K+ NO ₃ -)	30
GMELCC	(H ₃ O+ NO ₃ -) (K+ NO ₃ -)	-25
GMELCC	(K+ NO ₃ -) (H ₃ O+ NO ₃ -)	-5.80576
GMELCC	(NA+ NO ₃ -) (K+ NO ₃ -)	1.124986
GMELCC	(K+ NO ₃ -) (NA+ NO ₃ -)	1.023171

The activity parameters listed in Table 6 were obtained by simultaneous regression of the following data sets:

- Equilibrium vapor composition and pressure data²⁵ (TPXY) for HCl-H₂O at 20, 55.2 and 75.9°C. (Only the sub-azeotropic part of the data set was used because all of our solutions are in this concentration range.)
- Equilibrium vapor composition and pressure data^{11,26} (TPXY) for HCl-HNO₃-H₂O at 200 and 760 torr.
- Osmotic coefficients²⁷ for dilute HCl solutions at 0, 25, 75 and 125°C which were calculated from heat of dilution measurements²⁷ over the temperature range from 25 to 350°C. (The direct heat of dilution data is not in a form that can be used by the ASPEN Plus DRS system.)
- Enthalpy of dilution¹⁴ for HCl solutions at 25°C. (This is the only data set including data for concentrated solutions.)

Numbers from handbook¹⁷ tables were not used in the data regression because they are extrapolations rather than measured data. The vapor pressure correlation (PLXANT), Henry's Law coefficients and thermodynamic properties of HCl were taken as provided by the ASPEN data bank.

Table 6. Activity coefficient parameters for aqueous solutions of HCl and HNO₃.

Parameter	Species Pair	Value
GMELCC	H2O (H3O+ Cl-)	7.195472
GMELCC	(H3O+ Cl-) H2O	-3.761581
GMELCD	H2O (H3O+ Cl-)	800.3416
GMELCD	(H3O+ Cl-) H2O	-394.9632
GMELCE	H2O (H3O+ Cl-)	-32.12354
GMELCE	(H3O+ Cl-) H2O	11.1879
GMELCC	HNO3 (H3O+ Cl-)	6.220643
GMELCC	(H3O+ Cl-) HNO3	-12.895
GMELCD	HNO3 (H3O+ Cl-)	962.7592
GMELCD	(H3O+ Cl-) HNO3	6372.017
GMELCC	(H3O+ NO3-) (H3O+ Cl-)	19
GMELCC	(H3O+ Cl-) (H3O+ NO3-)	2.220958
NRTL 1	HCl H2O	0.1461726
NRTL 1	H2O HCl	0.1822129
NRTL 1	HCl HNO3	3.523998
NRTL 1	HNO3 HCl	4.057333

The available data on vapor compositions over HCl solutions is deficient in lacking measured vapor composition data for HCl concentrations below five mole percent HCl (10 weight % HCl) and at temperatures above 75.9°C. The simultaneous regression of the data sets listed above uses (1) the enthalpy of dilution¹⁴ and osmotic coefficient²⁷ data to extrapolate to low HCl concentrations, and (2) the vapor composition data^{11,26} (TPXY) for HCl-HNO₃-H₂O and the osmotic coefficient²⁷ data to extrapolate to HCl solutions at boiling.

The results of the data regression is evaluated primarily by comparing vapor compositions calculated using the resulting activity parameters, which are listed in Table 6 with measured data points. As shown in Figure 13, the ASPEN Plus calculations with the derived parameters of partial pressures of HCl over aqueous HCl solutions agree well with the data points. As shown in Figures 14 and 15, the ASPEN calculations provide a plausible data correlation over the range of nitric acid concentrations in mole fraction of 0.03 to 0.15 (1.5 to 8 M). There is an apparent discrepancy for dilute solutions; however, the measured vapor HCl concentrations for these data points are in the range (about 1 ppm) where experimental errors are hard to avoid.

Figure 13. Comparison of calculated and measured²⁵ partial pressures of HCl over sub-azeotropic HCl solutions (E96 0308).

Figure 14. Comparison of calculated and measured¹¹ effect of HNO₃ concentration on vapor-to-liquid mole fraction ratio (Y/X) for HCl at 200 torr (E96 0309).

Figure 15. Comparison of calculated and measured²⁶ effect of HNO₃ concentration on vapor-to-liquid mole fraction ratio (Y/X) for HCl at 760 torr (G96-0189).

2.8 Solutions of Hydrofluoric and Nitric Acids

ASPEN Plus™ calculates HF chemical-reaction and vapor-liquid equilibria for aqueous solutions using NBS chemical thermodynamic values¹⁴ (for 25°C) plus activity coefficient and vapor pressure parameters provided in its data base. The validity of the vapor-liquid equilibria calculations was tested, as shown in Figures 16, 17 and 18, by comparing measured^{28,29,30,31} and calculated partial pressure or vapor compositions. The agreement of measured and calculated values in Figures 16, 17 and 18 shows that the parameters from the ASPEN Plus™ data base for HF-H₂O mixtures, listed in Table 7, are adequate without additional refinement.

The activity coefficients of HF and F⁻ ion were calculated, using the parameters of Table 7, at 25 and 100°C. The calculated activity coefficients at 25°C are shown on Figure 19. The activity coefficients for HF increase steadily with concentration while those for the F⁻ ion decrease steadily. The calculated activity coefficients at 100°C have curves of similar shape except that the values for HF are increased while the values for F⁻ ion are decreased. The low activity coefficients of HF (about 0.003 over much of the range at 25°C) indicates strong bonding with water.

The only available data for HF-HNO₃-H₂O solutions is VLE data³² at 25°C. The ASPEN data regression system could not achieve a satisfactory data fit using the previously-derived parameters for HF and HNO₃ solutions (primarily because the HNO₃-H₂O VLE data of this set conflicted with other HNO₃-H₂O VLE data at the same low concentration). The HF-HNO₃ interaction parameters obtained from regression of the 25°C data were not used because of their inaccuracies and uncertain applicability to higher temperatures. Test calculations indicate that these parameters have little effect on the calculated HF partial pressure when the fluoride is complexed with aluminum.

2.9 Solutions of Calcium Nitrate and Nitric Acid

The GMELCC parameters for aqueous solutions of calcium nitrate and nitric acid listed in Table 8 are: (1) the parameters for water and Ca(NO₃)₂ provided with the ASPEN Plus software and (2) parameters for HNO₃ and Ca(NO₃)₂ obtained by regression of VLE data³³ for boiling solutions of HNO₃ and Ca(NO₃)₂. Vapor-phase HNO₃ concentrations calculated using the parameters of Table 8 are compared with measured concentrations in Figure 20. The calculated vapor compositions are within 10% for the dilute Ca(NO₃)₂ concentrations usually typical of ICPP wastes but show an error on the low side that increases with Ca(NO₃)₂ concentration.

Regressions were also run including: (1) GMELCD terms, (2) GMELCC terms for the ion pair (H₃O⁺ NO₃⁻) (CA+2 NO₃⁻), and (3) the simultaneous regression of all the parameters of Table 7 (with some VLE data²⁴ for Ca(NO₃)₂ solutions included). None of them achieved a significant improvement in data fit.

G96-0190

Figure 16. Comparison of calculated and measured^{28,29,30} partial pressures of HF over aqueous solutions at 25, 40, 60 and 75°C (G96-0190).

Figure 17. Comparison of calculated and measured²⁹ partial pressures of HF over aqueous solutions at 30, 50 and 70°C (G96-0191).

G96-0192

Figure 18. Comparison of calculated and measured³¹ vapor compositions over aqueous HF solutions at 760 torr (G96-0192).

G96-0183

Figure 19. Calculated activity coefficients (mole fraction basis) of HF and fluoride ion at 25°C (G96-0183).

Table 7. Activity coefficient parameters for HF solutions.

Parameter	Species Pair	Value
NRTL 1	H2O HF	97.28083
NRTL 1	HF H2O	-2.297253
GMELCC	H2O (H3O+ F-)	15.12827
GMELCC	(H3O+ F-) H2O	-2.348784
GMELCC	HF (H3O+ F-)	9.667216
GMELCC	(H3O+ F-) HF	3.566598
GMELCD	H2O (H3O+ F-)	-2141.079
GMELCD	(H3O+ F-) H2O	-155.0825
GMELCD	HF (H3O+ F-)	-3161.984
GMELCD	(H3O+ F-) HF	-2071.534
GMELCE	H2O (H3O+ F-)	0.6771824
GMELCE	(H3O+ F-) H2O	-3.456933

Table 8. Activity coefficient parameters for aqueous mixtures of nitric acid and calcium nitrate.

Parameter	Species Pair	Value
GMELCC	H2O (CA+2 NO3-)	7.578
GMELCC	(CA+2 NO3-) H2O	-4.072
GMELCC	HNO3 (CA+2 NO3-)	9.554692
GMELCC	(CA+2 NO3-) HNO3	2.741511

Figure 20. Comparison of calculated and measured³³ effect on vapor-phase HNO_3 concentrations of adding $\text{Ca}(\text{NO}_3)_2$ to solutions initially containing 20% HNO_3 (G96-0184).

2.10 Solutions of Ferric Nitrate and Nitric Acid

Data found for $\text{Fe}(\text{NO}_3)_3\text{-H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3\text{-HNO}_3\text{-H}_2\text{O}$ solutions consists of a set¹² of $\text{Fe}(\text{NO}_3)_3\text{-HNO}_3\text{-H}_2\text{O}$ VLE data at atmospheric pressure and a partial set²¹ (no temperature) of $\text{Fe}(\text{NO}_3)_3\text{-HNO}_3\text{-H}_2\text{O}$ VLE data at reduced pressures. (Solubility data was not collected.) A regression of the atmospheric pressure VLE data¹² yielded the parameters of Table 9. Regressions were also run including GMELCD terms and GMELCC terms for the ion pair ($\text{H}_3\text{O}^+ \text{NO}_3^-$) ($\text{FE}+3 \text{NO}_3^-$), but none of them achieved a significant improvement in data fit. The data fit with the parameters of Table 9 is similar to the data fit for $\text{Al}(\text{NO}_3)_3\text{-HNO}_3\text{-H}_2\text{O}$ solutions shown in Figure 9. There is a negative error which increases with $\text{Fe}(\text{NO}_3)_3$ concentration from about 12% for 20% $\text{Fe}(\text{NO}_3)_3$ solutions to 45 to 60% for 50% $\text{Fe}(\text{NO}_3)_3$ solutions. A comparison of calculations with (non-regressable) data²¹ at 400 torr showed a large positive error (mostly because the nitric acid VLE calculations error high at 400 torr).

Table 9. Activity coefficient parameters for aqueous mixtures of nitric acid and ferric nitrate.

Parameter	Species Pair	Value
GMELCC	$\text{H}_2\text{O} (\text{FE}+3 \text{NO}_3^-)$	7.994493
GMELCC	$(\text{FE}+3 \text{NO}_3^-) \text{H}_2\text{O}$	-4.60052
GMELCC	$\text{HNO}_3 (\text{FE}+3 \text{NO}_3^-)$	9.093591
GMELCC	$(\text{FE}+3 \text{NO}_3^-) \text{HNO}_3$	2.850314

The data regression problem is that the electrolyte NRTL model cannot fit both the temperature and composition data (with the given chemistry) at for the higher $\text{Fe}(\text{NO}_3)_3$ concentrations. It fits the temperatures closely and calculates low vapor nitric acid concentrations. The regression can be constrained to fit the vapor compositions, but it then calculates erroneous temperatures [$+9^\circ\text{C}$ at 50% $\text{Fe}(\text{NO}_3)_3$].

2.11 Solutions of Minor Bivalent Nitrates and Nitric Acid

The waste solutions contain low concentrations of a number of bivalent cations (e.g., Cd^{+2} , Ni^{+2} , and Pb^{+2}) for which neither activity coefficient parameters nor the data from which to regress them are available. A useful approximation for use with these minor species is to borrow parameters from similar species for which adequate parameter sets are available. The use of the previously-developed activity coefficient parameters of calcium nitrate for cadmium nitrate appears appropriate because the ionic radii³⁴ of the cations are almost the same (0.99 vs. 0.97 Angstrom).

To provide activity coefficient parameters for another bivalent cation, VLE data¹² for $\text{Cu}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ were regressed to obtain the parameter set listed in Table 10. The cupric ion should be a suitable surrogate for the metal ions (e.g., nickel) which are near it in the periodic table and have similar ionic radii.

Table 10. Activity coefficient parameters for aqueous mixtures of nitric acid and cupric nitrate.

Parameter	Species Pair	Value
GMELCC	H ₂ O (CU+2 NO ₃ -)	6.942189
GMELCC	(CU+2 NO ₃ -) H ₂ O	-4.345659
GMELCC	HNO ₃ (CU+2 NO ₃ -)	9.058987
GMELCC	(CU+2 NO ₃ -) HNO ₃	2.902227

The lumping of minor cations expedites the ASPEN calculations without a significant effect on the vapor composition results. For example, the low-concentration, bivalent cations not needing definite tracking could be lumped as "Cd" or "Ni" using the activity coefficient parameters for calcium or cupric nitrate.

2.12 Mercury Chloride Solutions

The accurate modeling of mercury chemistry and behavior in ICPP waste solutions is important because mercury is a toxic and regulated substance which has an observable volatility when the wastes are evaporated. Most of the ICPP waste solutions are nitric acid solutions with sufficient chloride to react the mercury ions to HgCl₂ which is a slightly soluble solid with a measurable vapor pressure at boiling temperatures. Therefore, the modeling concentrated on the calculation of the partial pressure of HgCl₂ over aqueous solutions.

2.12.1 Thermochemical Parameters for HgCl₂

When ASPEN Plus™ retrieves its stored data on HgCl₂ it automatically selects for HgCl₂ a thermodynamic calculation route for high-temperature solids that does not provide reliable calculations for aqueous solutions. (The speciation calculations are incorrect.) Hence, a thermodynamic calculation route (or method) statement was inserted to switch the calculations to a standard thermodynamic calculation route (ASPEN or DIPPR) that can base the partial pressure calculation on the vapor pressure:

```
PROP-DATA THRSWT
IN-UNITS SI
PROP-LIST THRSWT
PVAL HGCL2 0 0 0 ;(or 0 0 101 for DIPPR)
```

It was then necessary to provide vapor-phase, thermochemical property data to allow the calculations by the method specified above which calculates the thermochemical properties of molecular species in solution at elevated temperatures by a vapor-phase route in which the specie is vaporized, heated as a vapor, and then redissolved in the solution. Critical properties must be supplied to allow the calculations to proceed. The actual value given does not make much difference for low-pressure calculations, but a number must be provided. So the following typical values were inserted:

PROP-DATA U-1
IN-UNITS SI
PROP-LIST PC / TC / ZC / VC
PVAL HGCL2 5E6 / 1000 / .2 / .1

The standard enthalpy of formation (DHFORM) of HgCl_2 vapor was obtained from a table³⁵ without a free energy (in the form¹⁴ used by ASPEN). The Gibbs free energy of formation (DGFORM) of HgCl_2 vapor was calculated by: (1) calculating the free energy of reaction for

from the one set³⁵ of enthalpy (H) and entropy (S) of formation values with the formula^{35,14}

$$\Delta G_R = \Delta H_R - T(\Delta S_R),$$

and then (2) adding the calculated ΔG_R to the available¹⁴ free energy of formations of Hg(g) and Cl_2 . (The calculation procedure was checked with HgI_2 for which a complete set¹⁴ of thermochemical parameters is available.) The calculated DGFORM and reference¹⁴ DHFORM were then inserted:

PROP-DATA DG-FORM
IN-UNITS SI
PROP-LIST DGFORM / DHFORM
PVAL HGCL2 -1.4202E+08 / -1.4326E+08

Values for the heat capacity (CPIG) of HgCl_2 vapor from the literature³⁵ were regressed to obtain a heat capacity correlation for HgCl_2 :

PROP-DATA CPIG
IN-UNITS SI
PROP-LIST CPIG
PVAL HGCL2 18651 94.7036 0 0 0 0 273 550

Heat of vaporization values, calculated from enthalpy values³⁵ for HgCl_2 vapor and solid, were regressed for the coefficients for the Watson heat of vaporization equation³⁶ with several values for the critical temperature which is a parameter in the Watson equation. The best data fit was obtained with a critical temperature of 1000 which was listed earlier. The Watson equation coefficients from the regression were then entered:

PROP-DATA DHVLWT
IN-UNITS SI
PROP-LIST DHVLWT
PVAL HGCL2 83.931E6 298 .1043099 .03841568 273

A literature³⁵ correlation for the vapor pressure of HgCl_2 was converted from $\log_{10}$ to $\ln$ form, checked against other data³⁷ and entered:

PROP-DATA PLXANT

IN-UNITS SI

PROP-LIST PLXANT

PVAL HGCL2 43.8965 -10741.5 0 0 -2.13 0 0 273 550

2.12.2 Activity Coefficients

The NRTL parameters for aqueous HgCl_2 solutions were calculated from solubility data²² converted to calculated vapor-liquid equilibrium based on: (1) the principle that the partial pressure of a solute in a saturated solution (i.e., in equilibrium with solid HgCl_2) is the same as the vapor pressure of the solid, and (2) the assumption that the partial pressure of water is proportional to its mole fraction. As a check, the same solubility data was converted to activity coefficients, based on unit activity of HgCl_2 in saturated solution, which were regressed for a second set of NRTL parameters. The HgCl_2 activity coefficients and partial pressures calculated with the second set of NRTL parameters agreed within 20 percent (and usually better) with those calculated using the first set of NRTL parameters. The first set of NRTL parameters was used:

PROP-DATA NRTL-1

IN-UNITS SI

PROP-LIST NRTL

BPVAL HGCL2 H2O 100 30000 .30 0.0 0.0 0.0 273 400

BPVAL H2O HGCL2 -1.86809 2244.667 .30 0.0 0.0 0.0 273 400

The activity coefficients of HgCl_2 , calculated with the above NRTL parameters, are shown in Figure 21 as a function of concentration and temperature. The lines at concentrations greater than the solubility are dashed because they are extrapolations for solutions that do not exist. The downward sloping shape of the curve is characteristic of the NRTL model. (Note that the activity curves, by definition, go to one at 100 percent HgCl_2 .) The calculated partial pressures of HgCl_2 at 80 and 100°C are shown in Figure 22. The convex shape comes because the activity coefficient is highest at low concentrations.

2.12.3 Chemical Speciation Calculations

As a test exercise, the chemical equilibria for the reactions of HgCl_2 with chloride ion:

Figure 21. Calculated activity coefficients of HgCl_2 in aqueous solution (G96-0193).

E96 0310

Figure 22. Calculated partial pressure of HgCl_2 over aqueous solutions (E96 0310).

was calculated, both with and without excess chloride, using the parameters from the earlier paragraphs for HgCl_2 and parameters from the ASPEN Plus data base for the ionic species. The calculated species distributions are given in Table 11, as percent of mercury in the feed, for a typical tank farm mercury concentration both with and without excess chloride. In both cases, the mercury is >99% as HgCl_2 . The percent as mercuric ion becomes extremely small with excess chloride. These calculations can be verified qualitatively at ambient temperature with reported³⁸ equilibrium constants.

When the equations given above for the chemical equilibria of the mercury complexes are included in calculations for a complex multi-specie mixture (e.g., most ICPP wastes), ASPEN Plus is sometimes unable to converge the chemical equilibrium calculations because there are too many interlinked equilibria relations. (The mercury chloride complexes are linked via HCl to all the acid species.) In these cases, the calculations are simplified by omitting the mercury chloride equilibria calculations and considering all of the mercury to be HgCl_2 . The calculations summarized in Table 11 indicate that this approximation results in an error of less than one percent at least when the $\text{Cl}:\text{Hg}$ ratio exceeds two.

Table 11. Calculated mercury species distributions as percentages at 100°C.

Specie	$\text{Cl}:\text{Hg} = 2$	$\text{Cl}:\text{Hg} = 4$
HgCl_2 , %	99.27	99.3
HgCl^+	0.716	3.3E-3
HgCl_3^-	1.75E-3	0.467
Hg^{+2}	0.014	3.1E-7
HgCl_4^{-2}	2.44E-6	0.223

2.13 Boric Acid Solutions

Boron is entered into the components list as boric acid (H_3BO_3) because boric acid will be the predominant boron form in the strongly acid solutions. The fluoride complexes of boric acid were not considered because Al and Zr ions form much stronger fluoride complexes. With excess Al ions in solution there is very little available fluoride ion in solution.

The ASPEN data base for boric acid was supplemented by inserting assumed critical properties (which are needed to run but have a negligible effect on the calculations). Heat capacity (CPIG^{36}) and heat of vaporization (DHVLWT^{36}) correlations were regressed from reference enthalphy data:³⁵

$$\text{CPIG} = 18651 \ 94.7036 \ (\text{SI units});$$

$$\text{DHVLWT} = 7.545\text{E}+7 \ 360 \ 0.38 \ (\text{SI units}).$$

The calculation of a boric acid volatilization is suppressed by inserting a negligible vapor pressure:

$$\text{PLXANT} = -1\text{E}+20 \text{ (SI units)}.$$

2.14 Undissolved Solids

Undissolved solids are represented by Al_2O_3 for which a full set of parameters is available in the ASPEN data base.

2.15 Zirconium Complexes

Zirconium ions are important because they complex fluoride ions. Low concentrations of Zr can be lumped with aluminum for HF equilibria calculations; however, Zr is often tracked separately on flowsheets. A full speciation calculation for the Zr complexes is usually not needed because of the low concentrations of Zr in most ICPP liquid wastes. (Also, ASPEN Plus™ has difficulty converging simultaneous equilibria calculations for both the Al and Zr fluoride complexes.)

The compromise treatment of the Zr fluoride complexes is based on calculations with the HFCALC³⁹ program which indicated that the Zr in the waste is predominantly in the form of ZrF_2^{+2} ion. When the Zr concentration is much less than the Al concentration, the Zr can be entered as ZrF_2^{+2} or ZrF^{+3} and the fluoride equilibria calculated only for the Al fluoride complexes. The activity coefficient parameters for Ca^{+2} and Fe^{+3} are used for ZrF_2^{+2} and ZrF^{+3} respectively.

2.16 Parameters for Solution Density

Accurate solution density calculations are important because the ICPP waste evaporators use density as a control parameter.

2.16.1 Clarke Model for Aqueous Solutions

ASPEN Plus™ calculates the densities of aqueous electrolytes using the two-parameter Clarke model³⁶ for the mole volume in solution (V_s) of a salt (ion pair):

$$V_s = C_{s1} + C_{s2} \cdot (x_s)^{1/2} / [1 + (x_s)^{1/2}]$$

where x_s is the apparent mole fraction of salt s ; and C_{s1} and C_{s2} are constants (called VLCLK) which are determined by regression of density data. For molecular solutes (including the non-ionized HNO_3 and HF), ASPEN Plus™ uses the Rackett correlation³⁶ for which characterizes each solute by a volume constant called RKTZRA.

2.16.2 Density Parameter Regression

The VLCLK parameters for NaNO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$ and $\text{Pb}(\text{NO}_3)_2$ listed in Table 12 were regressed from reference^{37,24} density data. For HNO_3 and HF , both the VLCLK (Table 12) and RKTZRA (Table 13) parameters were regressed from density data.^{37,24} Data at different temperatures was used when available; however, only ambient temperature data is available for most of the salts. The parameters for HCl and H_2SO_4 were taken from the ASPEN PlusTM data bank and verified. The RKTZRA parameter for boric acid was regressed from a vendor-supplied density.

The VLCLK parameters for the aluminum fluoride complexes could not be regressed due to lack of density data. They are based on a mixing rule¹ that postulates that the total volume of the ions is conserved in an ionic reaction. Thus, the VLCLK parameters for the aluminum fluoride complexes were calculated from the VLCLK parameters for $\text{Al}(\text{NO}_3)_3$, HNO_3 and HF . The calculated VLCLK parameters for AlF^{+2} and AlF_2^+ are also used for ZrF^{+3} and ZrF_2^{+2} , respectively.

2.16.3 Test Calculations for HLLW Tanks

The accuracy of the ASPEN density calculations for the ICPP wastes with the parameters of Tables 12 and 13 was tested by calculating densities for five HLLW storage tanks with measured compositions and densities. First, a total ion charge concentration based on the compositions was calculated as a check on the overall accuracy and completeness of the analyses. The speciation assumed for the end of the (buffered) acid titration was Al^{+3} , Na^+ , K^+ , Cd^{+2} , Ca^{+2} , Fe^{+3} , Pb^{+2} , Mn^{+2} , Ni^{+2} , Hg^{+2} , Zr^{+4} , H_3BO_3 , NO_3^- , Cl^- , F^- , MO_4^- , HSO_4^- and H_2PO_4^- . The total ion charge concentrations (i.e., sum of ion charge times concentration), which should be zero, has a root-mean-square misbalance of 0.4 M. This misbalance, which can result from analytical errors and omitted species, suggests an uncertainty of about 0.4 M in the overall analyses.

Solution densities were calculated using the density parameters of Table 12 and the following substitutions of species to cover minor species without density parameters:

$$\text{"Al"} = \text{Al} + \text{Zr},$$

$$\text{"Cd"} = \text{Cd} + \text{Mn} + \text{Ni},$$

$$\text{"Fe"} = \text{Fe} + \text{Cr}, \text{ and}$$

$$\text{"H}_2\text{SO}_4" = \text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4.$$

H_3BO_3 and HgCl_2 were omitted; and undissolved solids (UDS) were added in afterwards. Nitric acid concentrations were calculated based on both the acid analysis and the nitrate analysis to bracket the composition uncertainty. The solution densities calculated with both the higher and lower nitric acid concentrations were compared with the measured densities. The differences (calculated - measured)

Table 12. Clarke density parameters in liter/kmole.

Ion Pair	VLCLK 1	VLCLK 2
H3O+ CL-	34.551110	13.365810
NA+ NO3-	28.385720	22.252990
AL+3 NO3-	43.34014	89.50370
K+ NO3-	37.901020	24.333100
H3O+ NO3-	37.29077	38.85941
H3O+ F-	28.67853	15.01079
ALF+2 NO3-	34.72916	65.6551
ALF2+ NO3-	26.1100	41.8065
ZRF+3 NO3-	34.729	65.6551
ZRF2+2 NO3-	26.11	41.8065
FE+3 NO3-	52.58633	158.2994
CA+2 NO3-	29.73381	133.6407
CD+2 NO3-	39.70517	55.68283
PB+2 NO3-	36.43566	171.11562
H3O+ HS04-	54.80395	20.24347

Table 13. Rackett density parameters (SI).

Specie	RKTZRA
HF	0.1061636
HNO3	0.220779
H3BO3	0.2072285
UDS	0.3

are listed in Table 14 which shows a small but persistent underestimation of density. The average density difference of Table 14 exceeds the estimated density effects of the known omissions and substitutions (less than 0.001 g/ml each). The average error (on densities ranging from 1.12 to 1.26 g/ml) is 0.0083 g/ml low.

Table 14. Differences between calculated and measured densities.

Tank	Calculated - measured density, g/ml	
	High HNO ₃	Low HNO ₃
WM-180	-0.0125	-0.0335
WM-181	+0.0014	-0.0026
WM-183	+0.007	-0.004
WM-185	-0.0134	-0.0184
WM-189	-0.0034	-0.0044
Average	-0.0042	-0.0126

3. TESTING AND ADJUSTMENTS BASED ON LABORATORY TESTS OF WASTE EVAPORATION

The laboratory tests were two semi-batch evaporations and one batch evaporation done in bench-scale glassware with solutions representative of Na-bearing wastes in the ICPP waste storage tanks.

3.1 Test Operation

Two semi-batch evaporations were done in a 1-liter glass flask heated with an electric heating mantle. The vapor was condensed and drained into bottles for analysis. The top of the flask and the vapor line were heat-traced and insulated to prevent condensation on their surfaces. The flask had three large ports into which were inserted: (1) the vapor discharge line, (2) a corrosion probe, (3) two thermocouples, (4) a line for sampling the bottoms, and (5) a refill line.

The tests simulated the semi-batch operation planned for the HLLWE. In each test cycle, the initial feed (700 ml) was boiled until about 20 percent of the liquid had been evaporated and collected in the condensate-collection bottle. The evaporation was then suspended while: (1) the condensate-collection bottle was removed for analysis and replaced, (2) a 10-ml sample of the bottoms was taken for a density measurement, and (3) the flask was refilled to (approximately) its initial volume. The evaporation was then resumed. Two tests were run, one for 9 cycles and the other for 8 cycles.

The feeds for the tests were based on the feed anticipated, at the time of test planning, for the initial operation of the HLLWE. Differences from the expected initial HLLWE feed include: (1) the use of a worst-case chloride concentration to obtain worst-case corrosion rates in the bottoms, and (2) the use of substitutes for some low-concentration species. Substitutions are additional Al for Zr, additional Fe for Mn, and additional K for Cd, Ni, and Pb. The compositions of the test feeds are given in Table 15. The feed for the second run was prepared by adding HF (only) to the feed remaining after the first run to evaluate the effects of increased HF.

Table 15. Molar concentrations of solutes in feeds for semi-batch laboratory evaporations.

Specie	Target Feed Conc.	Run 1 Feed Analysis	Run 2 Feed Analysis
Acid	1.89	2.084	2.072
NO ₃	4.06	4.01	3.94
Cl	0.03	0.032	0.0307
F	0.112	0.109*, 0.166	0.168*, 0.20
SO ₄	0.035	0.033	0.042
Al	0.467	0.529	0.504
Na	0.405	0.456	0.439
K	0.079	0.090	0.079
Ca	0.079	0.0645	0.063
Cr(III)	0.010	0.011	0.0104
Fe	0.039	0.043	0.041

* concentration used in simulation.

The laboratory evaporations were continued about 40% beyond the expected HLLWE end point to a feed:bottoms ratio of 3.2 to check the operating margins for solids precipitation or any other adverse effect. Temperatures and corrosion rates were monitored throughout the two tests and recorded at the end of each cycle just before taking the samples of condensate and bottoms. The weights of each feed addition, condensate batch and sample were measured. The densities of all samples were measured. Feed and sample volumes were then calculated from weight and density. The feed and condensate samples (only three condensate samples from second run) were analyzed for composition.

The batch evaporation evaporated 800 ml of liquid, whose composition is given in Table 16, in an glass flask until 551 ml of condensate was collected. The condensate was collected in batches of about 58 ml with half the condensate batches being analyzed.

3.2 Simulation Models of Tests

ASPEN models were prepared for each of the laboratory evaporations. The models simulated the first seven stages (i.e., condensate samples) using a flash block for each stage. (The last one or two stages were omitted from the simulations because their concentrations are well in excess of those of interest to the HLLWE.) Vapor fractions and flow splits were adjusted until the calculated flows

Table 16. Molar concentrations of solutes in feed for batch laboratory evaporation and its simulation.

Specie	Conc. in test feed	Conc. used in simulation model
Acid	1.21	1.22
Al	0.58	0.579
B	0.0145	
Cd	0.0021	0.0187
Ca	0.034	0.034
Cl	0.0219	0.02
Cr(III)	0.0062	
F	0.0768	0.0768
Fe	0.0255	0.0322
Pb	0.001	
Mn	0.0137	
Hg	0.00194	0.00194 (as HgCl ₂)
Mo	0.0013	
Ni	0.0018	
K	0.146	0.146
Na	1.26	1.26
Zr	0.00067	
HSO ₄	0.049	0.049

matched the measured mass or volume of samples and products. The feed compositions for the simulations were as listed in Tables 14 and 15. The feed composition for the model of the batch evaporation was simplified by substituting increased Fe and Cd for minor cations.

3.3 Comparison of Calculations with Test Results

The test results are presented as a function of density because density is the parameter that is used to monitor the HLLWE operating cycle. The density cooled is used in place of density at boiling because the density could be measured only in cooled solution.

3.3.1 Temperature

The temperature of the boiling liquid in the semi-batch evaporations was measured with two (type K) thermocouples whose readings differed by about 1°C. (Both thermocouples were used with meters that had current calibration stickers.) Their accuracy was checked by measuring the boiling point of water (in the test flask) which should be 95.0°C at the barometric pressure (24.96 in. Hg) of the day. The measured boiling temperatures of water were 1.9 and 2.7°C high. It was decided that

the discrepancy was mostly due to the superheating needed to provide sufficient overpressure to form a vapor bubble on the smooth glass wall of the flask. This conclusion is based on observing that the measured temperature: (1) varied with boiling rate and (2) decreased with addition of a boiling chip. The superheating to form vapor bubbles will not occur in the HLLWE because metal surfaces have sufficient roughness to form vapor bubbles without significant superheating. The overpressure for the measured thermocouple discrepancies is estimated at about 50 torr (for the lower-reading thermocouple). The correction of 50 torr was then added to the barometric pressures to obtain the pressures used in the simulation models.

The boiling temperatures were also measured in the batch evaporation. However, their usability is questionable because of a major difference between readings from two different readout devices.

The boiling temperatures measured at the end of each semi-batch evaporation cycle (when bottoms density is measured) increased with evaporation as a nearly linear function of bottoms density from about 103°C at the start to about 114°C at the end of the test. The boiling temperatures calculated by the simulations averaged 0.3°C low (compared to the lower reading thermocouple) for the first evaporation and 0.9°C low for the second run. Both simulations can be considered within experimental error.

3.3.2 Liquid Density

The liquid densities calculated by the semi-batch evaporation simulations (at 25°C) were a little lower than the measured densities. The difference increased with evaporation from 0.005 and 0.0035 g/ml respectively in the feeds for the two runs to 0.03 and 0.05 g/ml at the end of the simulations. The comparison of the feed densities is the best comparison because analyzed compositions were obtained for the feeds but not the bottoms samples. (The calculated densities of the bottoms are based on calculated compositions rather than analyzed compositions.)

The discrepancies between calculated and measured feed densities are within the uncertainties of the feed composition. However, they do confirm a tendency to calculate slightly low. The density parameters most likely to be in error are those for the fluoride complexes.

3.3.3 Nitric Acid in Condensate

The measured and calculated condensate HNO_3 concentrations for the first semi-batch evaporation test are shown in Figure 23. Two data points are shown for each sample because the HNO_3 concentration was calculated based on both the total acid and nitrate concentrations in the condensate sample. Horizontal lines are drawn to the left of the data point to show the range over which the sample averaged the condensate composition. There is an uncertainty to the feed HNO_3 concentration because different HNO_3 concentrations are obtained using the acid and nitrate analyses. The set of three lines on Figure 23 shows the range of calculated condensate HNO_3 concentrations obtained using high, low and average values for feed HNO_3 concentration.

E96 0311

Figure 23. Condensate nitric acid concentration during semi-batch HLLWE simulation (E96 0311).

During the test evaporations, the concentrations of nitric acid in the condensate increased steadily with evaporation, as shown in Figure 23, to concentrations exceeding the concentration in the feed by the end of the test. The slope of the plots of calculated condensate HNO_3 concentration do not quite match the data. The calculated HNO_3 concentrations are high at the lower bottoms densities and low at the higher bottoms densities. A comparison of the averages of the measured and calculated HNO_3 concentrations shows the average calculated HNO_3 concentration being 13% high over the HLLWE operating range (to a bottoms Sp. G. of 1.37) and 4% low over the range of the simulation (to a bottoms Sp. G. of 1.42). The results of the second semi-batch evaporation test are essentially the same as shown on Figure 23 because the feed composition is nearly the same as for the first test. The condensate HNO_3 concentrations are not shown for the batch evaporation test because there are only two measured concentrations (whose agreement with the calculations is about the same as for Figure 23).

3.3.4 Chloride in Condensate

The measured chloride concentrations for the two semi-batch HLLWE simulation runs (whose Cl concentrations were similar) are shown on Figure 24. Again, a line is extended to the left of the data points to show the range represented by the sample.

The condensate Cl concentration for each test increased with evaporation, as is shown on Figure 24, to concentrations exceeding that in the feed. The initial calculated condensate Cl concentrations were about 100% high. The calculated condensate Cl concentrations were adjusted downward to the solid line with the empirically-determined (i.e., trial and error) parameters:

$$\text{GMELCC } (\text{M} + \text{NO}_3^-) (\text{M} + \text{Cl}^-) = 0$$

$$\text{GMELCC } (\text{M} + \text{Cl}^-) (\text{M} + \text{NO}_3^-) = -1$$

where M+ represents Na^+ , K^+ , Al^{+3} , Fe^{+3} , and Ca^{+2} . The line for the adjusted calculations still has a slope that is too low and an incorrect downward curl at the highest densities. No ASPEN parameter was found that would increase the slope of the plot of calculated Cl concentrations. A comparison of the averages of the measured and calculated Cl concentrations shows the average calculated Cl concentration being 24% high over the HLLWE operating range (to a bottoms Sp. G. of 1.37) and 2% high over the range of the simulation (to a bottoms Sp. G. of 1.42).

The ASPEN calculations, using the adjusting GMELCC parameters listed in the preceding paragraph, provided a similar fit to the condensate Cl concentration data from the batch evaporation as shown in Figure 25. The calculated condensate Cl concentrations are a little high at the start and a little low at the end of the evaporation.

3.3.5 Fluoride in Condensate

The primary difference between the two semi-batch test runs was a 50% increase in the fluoride concentration in the feed for the second run. The measured condensate F concentrations for the two semi-batch runs are shown in Figure 26. The condensate F concentration for the first run shows a

G96-0185

Figure 24. Condensate chloride concentration during semi-batch HLLWE simulation (G96-0185).

G96-0186

Figure 25. Condensate chloride concentration during batch waste simulant evaporation (G96-0186).

E96 0312

Figure 26. Condensate fluoride concentration during semi-batch evaporations (E96 0312).

steady increase over most of the evaporation followed by a leveling off at higher bottoms densities. The condensate F concentration for the second semi-batch run, which had increased F and a reduced Al:F ratio, increased throughout the run.

The initial calculated condensate F concentrations for the first run were high with a downward slope with increasing evaporation. The slope of the calculated vapor-phase HF curve was improved by: (1) deleting the GMELCC parameters from Table 4 for the sodium nitrate and aluminum nitrate ion pairs, and (2) using the GMELCC parameters for $\text{Al}(\text{NO}_3)_3$ from Table 3 and use them for solutions of AlF^{+2} as listed in Table 17. The calculated curves were then adjusted downward to those shown on Figure 26 by a trial-and-error adjustment of the DGAQFM (aqueous free energy of formation) for AlF^{+2} to $-8.156\text{E}+8$ j/kmole, which is slightly outside the range of reference^{14,40} DGAQFM values of $-8.03\text{E}+8$ to $-8.11\text{E}+8$ j/kmole. The resulting calculated condensate F concentration curve for the first run has about the same average value (over the range up to a liquid Sp. G. of 1.37) as the measured concentrations but the slope is still a little low. The calculated curve for the second run has the same low slope and averages about 50% high.

Table 17. Activity coefficient parameters for aqueous mixtures of nitric acid and AlF complexes.

Parameter	Species Pair	Value
GMELCC	H2O (AlF+2 NO3-)	29.95914
GMELCC	(AlF+2 NO3-) H2O	-10.1010
GMELCD	H2O (AlF+2 NO3-)	-5892.001
GMELCD	(AlF+2 NO3-) H2O	1470.918
GMELCE	H2O (AlF+2 NO3-)	-100
GMELCE	(AlF2+ NO3-) H2O	33.16584
GMELCC	HNO3 (AlF+2 NO3-)	2.192842
GMELCC	(AlF+2 NO3-) HNO3	-8.52746
GMELCD	HN03 (AlF+2 NO3-)	1562.688
GMELCD	(AlF+2 NO3-) HNO3	5736.824
GMELCE	HNO3 (AlF+2 NO3-)	93.7309
GMELCE	(AlF+2 NO3-) HNO3	-100
GMELCC	(H3O+ NO3-) (AlF+2 NO3-)	12.68662
GMELCC	(AlF+2 NO3-) (H3O+ NO3-)	6.911549
GMELCD	(H3O+ NO3-) (AlF+2 NO3-)	6092.308
GMELCD	(AlF+2 NO3-) (H3O+ NO3-)	-550.0901

The condensate fluoride concentrations calculated by the simulation of the batch evaporation followed the slope of the test data but were about 35 percent low. Thus, there is an apparent error which depends on the Al:F ratio. The calculated condensate fluoride concentrations are high for the second semi-batch evaporation, which had the lowest Al:F ratio (3:1), and low for the batch evaporation which had the highest Al:F ratio (7.5:1).

The calculation of the average F concentration in the condensate appears to have an error that varies with the Al:F ratio in the evaporator feed. The calculated average F concentration in the condensate is about right for the first semi-batch evaporation in which the Al:F ratio was 4.7, high for the second semi-batch evaporation in which the Al:F ratio was 3.0, and way low for the batch evaporation in which the Al:F ratio was 7.5. (However, difficulties in analyzing for low

concentrations of F in HNO_3 solutions may have contributed to the apparent error. The reported concentrations of 2 to 15 mg F/l are at the margin of the analytical method.) The error could result from errors in calculations of species activities or of the AlF^{+2} complexing equilibria. The calculated activity of the Al^{+3} ion is a likely source of error because the VLE calculations for $\text{Al}(\text{NO}_3)_3\text{-HNO}_3\text{-H}_2\text{O}$ also have an error (Figure 9) which increased with concentration. At the lower Al:F ratios (< 4.7) at which HF volatility is of concern, the calculated condensate F concentrations will be conservative.

3.3.6 Mercury Chloride

The calculated vaporization of HgCl_2 from boiling HLLW solutions was evaluated by comparison of calculated vapor compositions with compositions obtained by analysis of the condensate from the batch evaporation test. (The feed for the semi-batch evaporation did not contain mercury.) The calculated condensate concentrations of HgCl_2 were initially over a factor of ten lower than both the measured concentrations in the condensate. The calculated HgCl_2 concentrations for the condensate from the evaporation test were also lower than the concentrations of HgCl_2 in condensate from boiling $\text{HgCl}_2\text{-H}_2\text{O}$ solutions. This discrepancy was attributed to the absence of activity parameters (GMELCC) for interactions of the ions in solution with HgCl_2 . The missing activity parameters were obtained by a stepwise regression with postulated feed solutions of the same total normality (4.5 N) as used in the test assuming all solutions with the total normality of 4.5 N have the same vapor HgCl_2 concentrations (i.e., the measured concentrations). First, the parameters (GMELCC) for nitric acid and aluminum nitrate were regressed (together) with the measured condensate HgCl_2 concentrations and a feed containing 1.05 M HNO_3 and 1.15 M $\text{Al}(\text{NO}_3)_3$. Next, the parameters (GMELCC) for sodium nitrate were regressed, using the GMELCC parameters for nitric acid from the previous regression, with the measured condensate HgCl_2 concentrations and a feed containing 1.05 M HNO_3 and 3.45 M NaNO_3 . The set of GMELCC parameters for the interactions of the ion pairs with HgCl_2 listed in Table 18 are the GMELCC parameters obtained from the regressions applied as follows: (1) the GMELCC parameters for nitric acid are used for all the acids, (2) the GMELCC parameters for sodium nitrate are used for all the monovalent salts, (3) the GMELCC parameters for aluminum nitrate are used for all the trivalent salts and (4) averages of the GMELCC parameters for sodium nitrate and aluminum nitrate are used for the divalent salts.

The vapor-phase concentrations of HgCl_2 for the batch evaporation test were then calculated using the above list of GMELCC parameters and the measured feed composition and condensate:feed volume ratios. The calculated vapor-phase concentrations of HgCl_2 agreed reasonably well with the experimental measurements as is shown in Figure 27. It is uncertain whether the mercury chloride volatility would be effected by the relative distribution of ionic species in solution.

Table 18. Activity coefficient parameters for aqueous HgCl_2 solutions containing dissolved nitrates.

Parameter	Species Pair	Value
GMELCC	HBCL2 ($\text{H}_3\text{O}^+ \text{ NO}_3^-$)	3.81249
GMELCC	($\text{H}_3\text{O}^+ \text{ NO}_3^-$) HGCL2	2.12927
GMELCC	HBCL2 ($\text{H}_3\text{O}^+ \text{ HSO}_4^-$)	3.81249
GMELCC	($\text{H}_3\text{O}^+ \text{ HSO}_4^-$) HGCL2	2.12927
GMELCC	HGCL2 ($\text{Al}^{+3} \text{ NO}_3^-$)	8.67805
GMELCC	($\text{Al}^{+3} \text{ NO}_3^-$) HGCL2	12.0573
GMELCC	HGCL2 ($\text{Fe}^{+3} \text{ NO}_3^-$)	8.67805
GMELCC	($\text{Fe}^{+3} \text{ NO}_3^-$) HGCL2	12.0573
GMELCC	HGCL2 ($\text{Na}^+ \text{ NO}_3^-$)	8.057026
GMELCC	($\text{Na}^+ \text{ NO}_3^-$) HGCL2	11.4694
GMELCC	HGCL2 ($\text{K}^+ \text{ NO}_3^-$)	8.057026
GMELCC	($\text{K}^+ \text{ NO}_3^-$) HGCL2	11.4694
GMELCC	HGCL2 ($\text{Ca}^{+2} \text{ NO}_3^-$)	8.35
GMELCC	($\text{Ca}^{+2} \text{ NO}_3^-$) HGCL2	11.75
GMELCC	HGCL2 ($\text{Cd}^{+2} \text{ NO}_3^-$)	8.35
GMELCC	($\text{Cd}^{+2} \text{ NO}_3^-$) HGCL2	11.75
GMELCC	HGCL2 ($\text{AlF}^{+2} \text{ NO}_3^-$)	8.35
GMELCC	($\text{AlF}^{+2} \text{ NO}_3^-$) HGCL2	11.75

G96-0187

Figure 27. Comparison of calculated and measured concentrations of mercury as HgCl₂ in condensate from the batch evaporation test (G96-0187).

4. PROPERTIES FILE PROP-R9C

The property parameters developed in this study have been compiled in ASPEN insert file PROP-R9C which is in both the .BKP (backup) and .INP (input) forms. The PROP-R9C.INP file is listed in Appendix A.

4.1 Properties File Usage

The PROP-R9C.BKP file can be readily imported into a new ASPEN Plus™ program. Just start the ASPEN Plus™ Model Manager program in a directory containing PROP-R9C.BKP; then click "File", "Import", "PROP-R9C", and "Enter". After about five minutes, a program, containing the PROP-R9C parameters, will be set up waiting for a flowsheet.

Importing a properties file into an existing file as an upgrade is tricky because the ASPEN Plus™ import function does not delete all of the existing parameters (especially those from the ASPEN Plus™ data base) that are to be replaced. Two approaches to importing a properties file into an existing file are as follows:

1. A relatively safe approach begins with exporting a .INP file (ASCII text) of the existing program. Then use a text editor to copy the parameters paragraphs from PROP-R9C.INP (as a group) into the program (.INP) file placing them below the parameters to be replaced. The key consideration is that when ASPEN Plus™ runs a .INP file containing conflicting parameters, it uses the parameters listed last. (The file can be cleaned by removing obsolete parameters but this is not necessary.) An upgraded program .BKP file is formed by setting ASPMMB=ON and running the upgraded program .INP file. The upgraded program .BKP file is then imported to generate the upgraded Model Manager file.
2. Another import approach, using Model Manager, is to delete from the Model Manager program all parameter sets (e.g., the GMELCC parameters) containing parameters to be replaced. PROP-R9C.BKP can then be imported without conflict. The risk of this approach is that any parameters unique to the existing program will be lost.

After inserting PROP-R9C, or any other set of custom parameters, care must be taken not to click the Model Manager "Electrolytes" button which will replace the existing parameters with those in the ASPEN Plus™ data bank.

4.2 Parameter Set Verification

A series of PROP-TABLEs has been included in PROP-R9C to verify the parameter sets for the major chemical species. The PROP TABLEs are those used to generate some of the figures in this report. If the correct parameters are present, the PROP-TABLEs will reproduce the appropriate figure. (TRUE-COMPS=NO is needed for some of the tables.)

- PROP-TABLES Y-HNO3 and PPMX will verify parameters for $\text{HNO}_3\text{-H}_2\text{O}$ by reproducing Figures 2, 3, and 4.
- PROP-TABLE PP-HCL will verify parameters for $\text{HCl-H}_2\text{O}$ by reproducing Figure 13.
- PROP-TABLE HCL-HGH will verify parameters for $\text{HCl-HNO}_3\text{-H}_2\text{O}$ by reproducing Figure 14.
- PROP-TABLE Y-HF will verify parameters for $\text{HF-H}_2\text{O}$ by reproducing Figure 18.
- PROP-TABLE Y-EF760 will verify parameters for $\text{NaNO}_3\text{-HNO}_3\text{-H}_2\text{O}$ by reproducing Figure 7.
- PROP-TABLE EFI-AL20 will verify parameters for $\text{Al(NO}_3)_3\text{-HNO}_3\text{-H}_2\text{O}$ by reproducing Figure 9.

5. SUMMARY EVALUATION

This section provides a critical assessment of the set of parameters developed in this report and of the accuracy of VLE calculations using them with the ELECNRTL model.

5.1 Nitric Acid Solutions

The parameter set for nitric acid solutions provides good VLE calculations (i.e., vapor compositions within 25%) for nitric acid concentrations up to 60% (to 0.3 mole fraction) nitric acid at 25°C and from 15 to 60% nitric acid at 1 atm. However, the ELECNRTL model does not follow the changes with temperature of the shape of the VLE (Y vs. X) curves for dilute solutions. The calculated vapor HNO_3 concentrations error low at 1 atm for HNO_3 concentrations below about 15%, and error high for temperatures between 25°C and boiling.

5.2 Solutions of Nitric Acid and Nitrate Salts

The addition of nitrate salts to boiling nitric acid solutions increases the vapor-phase concentration of nitric acid as is shown on Figure 28 (which shows the experimental^{12,20,33} addition of nitrate salts to solution initially containing 20% HNO_3). The relative increase in vapor-phase HNO_3 concentration increases with valence and ionic charge:radius ratio from monovalent Na to tri-valent Al. The calculated vapor-phase HNO_3 concentrations, which are shown as dashed lines on Figure 28 for NaNO_3 , $\text{Ca(NO}_3)_2$, and $\text{Al(NO}_3)_3$, agree within 25% of the data for NaNO_3 concentrations to 20 mole % (about 10 M) but only to about 5 mole % (about 2.5 M) for the bivalent and trivalent ions. At the higher concentrations of bivalent and trivalent nitrate salts, the calculated vapor-phase HNO_3 concentrations are low.

Figure 28. Vapor compositions of boiling solutions made by adding various nitrate salts to a nitric acid solution initially containing 20 percent nitric acid (E96 0313).

One reason for the greater effect of the trivalent nitrate salts is that they contain more nitrate ions. In order to eliminate the effect of the number of nitrates per salt, the data from Figure 28 is replotted in Figure 29 against the mole fraction of nitrate ions from the salts (considering the HNO_3 as not hydrolyzed). The vapor-phase HNO_3 concentrations are now much closer to each other, but they still are ordered according to ionic charge:radius³⁴ ratio -- $\text{Al}^{+3} > \text{Fe}^{+3} > \text{Cu}^{+2} > \text{Ca}^{+2} > \text{Na}^+$. (Note that part of the difference in curve shapes may be because the NaNO_3 and $\text{Ca}(\text{NO}_3)_2$ data are from different data sets^{20,33} than the $\text{Cu}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and $\text{Al}(\text{NO}_3)_3$ data.¹²)

One approach that achieved a good fit of all the VLE data on Figure 28 over the full concentration range is the use of both a hydrated and unhydrated cation (e.g., Fe^{+3} and $\text{Fe}(\text{H}_2\text{O})_6^{+3}$) in equilibrium for each metal ion. The GMELCC parameters are then regressed for both the hydrated and unhydrated cations. The VLE calculations using the GMELCC parameters for both the hydrated and unhydrated cations fit the VLE data with a wide range of cation hydration equilibrium constants as long as there is a significant concentration of both hydrated and unhydrated cations in a ratio that changes with concentration. It is not certain whether the use of the hydrated cation equilibrium works because it is a more accurate description of the chemistry⁴¹ of concentrated electrolyte solutions, or because it provides additional parameters for regression. The hydration cation approach was not developed further because it aggravated the errors in the equilibrium calculations for complexing of the aluminum and fluoride ions.

5.3 Solutions of Hydrochloric and Nitric Acids

Some uncertainty about the parameters for the interactions of HNO_3 and HCl remains because of the wide scatter of the data (Figure 14) from which they were regressed. With an adjustment factor, the calculated vapor-phase HCl concentrations for the laboratory tests replicated the data reasonably well except for the most concentrated solutions. There is a small mis-match in Figure 24 of the slopes of the calculated and measured curves which probably originates in the inadequacies of the calculations for the $\text{Al}(\text{NO}_3)_3$ - HNO_3 - H_2O system. The calculated vapor-phase HCl concentration are within 25% for the feed for the laboratory tests; however, the discrepancy might increase if the evaporator feed composition changed.

5.4 Solutions of Hydrofluoric and Nitric Acids

The calculation of vapor-phase HF concentrations for solutions of HF complexed with aluminum ions has unresolved difficulties. The calculated curves of vapor-phase HF concentration vs. evaporation (Figure 26) has an inadequate slope and required an empirical adjustment of free energy of formation of AlF^{+2} to approximate the data. The problem probably arises from the errors in the activity coefficient calculation for the $\text{Al}(\text{NO}_3)_3$ - HNO_3 - H_2O system.

5.5 Other Molecular Solutes

The calculation of HgCl_2 volatility required the regression of activity coefficient parameters (e.g., GMELCC values) for the interaction of HgCl_2 with the other major molecules and ion pairs in the solution. The default calculations with the interaction parameters missing gave vapor-phase HgCl_2 concentrations that were orders of magnitude low. This is probably the case with other molecular

G96-0188

Figure 29. Vapor compositions of boiling solutions made by adding various nitrate salts to a nitric acid solution initially containing 20 percent nitric acid (G96-0188).

solutes in solution. Without the regression of interaction parameters for the molecule and the ion pairs in solution their calculated volatilities will error significantly low.

5.6 Calculated Local Excess Gibbs Free Energy Values

The local excess Gibbs free energy values (τ) at 100°C, calculated from the GMELCC, GMELCD, and GMELCE parameters listed in the earlier sections, for the interactions of water and nitric acid with the ion pairs of the salts and acids, are listed in Table 19 for comparison and discussion. The salt ion pairs are listed in order of decreasing cation charge:radius ratio³⁴. The values are calculated at 100°C because the primary application is evaporation. The values at 25°C for salts with GMELCD parameters are a little different than at 100°C.

The calculated local excess free energies of the molecule-ion pair interactions from Table 19 are plotted, for visualization, for some of the cations in Figure 30 as a function of ion charge:radius³⁴ ratio. (M^{+n} represents any cation of charge n .) The most obvious contrast shown by Figure 30 is the difference between the values for the $(M^{+n} NO_3^-) H_2O$ interactions and those for the $(M^{+n} NO_3^-) HNO_3$ interactions. The values for the $HNO_3 (M^{+n} NO_3^-)$ and the $H_2O (M^{+n} NO_3^-)$ interactions are mostly relatively close to each other; but the values for the $(M^{+n} NO_3^-) HNO_3$ interactions differ greatly from those for the $(M^{+n} NO_3^-) H_2O$ interactions (and also from the ASPEN PlusTM default value of -2 for an ion pair-molecule interaction). The $(M^{+n} NO_3^-) H_2O$ excess energies are negative (i.e., the ion pair reduces the activity of H_2O) while the $(M^{+n} NO_3^-) HNO_3$ excess energies are positive (i.e., the ion pair increases the activity of HNO_3).

The excess energy values for Ca, Cu, and Fe are fairly orderly and could be interpolated to obtain estimated GMELCC values (i.e., the excess energy without a temperature term) for metal nitrates for which there is no data on their nitric acid solutions. Estimates taken from Figure 30 should be better than default values.

The numbers shown on Figure 30 should be viewed with the following cautions: (1) those for Cu and Fe are based on a small data set;¹² and (2) the regressions for K, Na, and Al also regressed ion pair-ion pair parameters whose presence or absence can effect the values obtained for the ion pair-molecule energies. The ion pair-ion pair interaction energies appear to be most significant in the solubility calculations; however they have some effect on the VLE calculations. The interaction energies for the K^+ ion are significantly different from those of other ions probably because they were determined from solubility data and have large opposing values for ion pair-molecule and ion-pair-ion pair interaction energies.

5.7 Chemical Equilibria Calculation Convergence

The ASPEN Plus software contains convergence routines for calculating simultaneous chemical equilibria using any of its activity coefficient models. However, convergence becomes slow and sometimes fails when there are a large number of interlinked reactions. Note that the chloride and fluoride complexing reactions are interlinked via their acids. The chemical equilibria calculations often fail to converge when both the aluminum fluoride and mercury chloride equilibrium reactions are included. Hence, the solution is simplified when feasible by omitting minor reactions from the

Table 19. Local excess Gibbs free energies at 100°C calculated from GMELCC, GMELCD, and GMELCE parameters of this report.

Species Pair	Local Excess Gibbs Free Energy (Tau)
H2O (Al+3 NO3-)	11.829
H2O (Fe+3 NO3-)	7.9945
H2O (Cu+2 NO3-)	6.942
H2O (Ca+2 NO3-)	7.578
H2O (Na+ NO3-)	7.1556
H2O (K+ NO3-)	6.3051
H2O (H3O+ NO3-)	7.3645
H2O (H3O+ F-)	9.390
H2O (H3O+ Cl-)	8.5886
(Al+3 NO3-) H2O	-5.383
(Fe+3 NO3-) H2O	-4.60
(Cu+2 NO3-) H2O	-4.346
(Ca+2 NO3-) H2O	-4.072
(Na+ NO3-) H2O	-3.687
(K+ NO3-) H2O	-3.109
(H3O+ NO3-) H2O	-4.074
(H3O+ F-) H2O	-2.764
(H3O+ Cl-) H2O	-4.658
HNO3 (Al+3 NO3-)	6.381
HNO3 (Fe+3 NO3-)	9.094
HNO3 (Cu+2 NO3-)	9.059
HNO3 (Ca+2 NO3-)	9.555
HNO3 (Na+ NO3-)	17.477
HNO3 (K+ NO3-)	29.828
HNO3 (H3O+ NO3-)	9.457
HNO3 (H3O+ Cl-)	8.801
(Al+3 NO3-) HNO3	6.8465
(Fe+3 NO3-) HNO3	2.85
(Cu+2 NO3-) HNO3	2.902
(Ca+2 NO3-) HNO3	2.7415
(Na+ NO3-) HNO3	1.661
(K+ NO3-) HNO3	30
(H3O+ NO3-) HNO3	3.238
(H3O+ Cl-) HNO3	4.181

G96-0194

Figure 30. Local excess Gibbs free energies (Tau) for ion pair-molecule interactions calculated at 100°C (G96-0194).

chemistry. The full chemistry is calculated for a simplified composition; and then the minor reactions are omitted. For example, the mercury can be entered as HgCl_2 and the mercury chloride complexing reactions omitted with only minor errors because the concentrations of the other mercury chloride complexes are normally very small.

6. CONCLUSIONS ON WASTE EVAPORATION CALCULATIONS

The following summarizes the conclusions on calculations with the parameters of this report applicable to semi-batch operation of the ICPP High Level Liquid Waste Evaporator (HLLWE) at atmospheric pressure with liquid waste densities to 1.30 g/ml at boiling and 1.37 g/ml cooled:

- The calculated boiling temperatures appear accurate to within about 1°C . Barometric pressure fluctuations can cause boiling temperature variations of about 1°C .
- The calculated solution densities at ambient temperature are accurate to within 0.01 g/ml with a possible error on the low side. The calculated densities at boiling were not tested.
- The solubilities of sodium and aluminum nitrates can be calculated at ambient temperature for mixtures with nitric acid. Neither sodium or aluminum nitrate precipitates at the solution compositions of the HLLWE.
- The calculated concentrations of nitric acid in the condensate are within 25 percent.
- The calculated concentrations of hydrochloric acid in the condensate are within 50 percent.
- The calculated concentrations of hydrofluoric acid in the condensate average within a factor of two of actual concentrations. The calculated vapor HF concentrations are high at the start of an evaporation cycle and low at the end of the evaporation cycle.
- The mercury in the ICPP wastes is nearly all complexed with chloride as HgCl_2 . Its concentrations in the condensate can be calculated within 50 percent assuming it is all HgCl_2 .

7. REFERENCES

1. *ASPEN Plus™ Electrolytes Manual*, Aspen Technology, Inc., 1988, Ch. 10.
2. B. Mock, L. B. Evans, and C. C. Chen, "Thermodynamic Representation of Phase Equilibria of Mixed-Solvent Electrolyte Systems," *AIChE Journal*, 32, 1986, pp. 1655.
3. H. Renon, and J. M. Prausnitz, "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures," *AIChE Journal*, 14, 1968, pp. 135-144.
4. J. Potier, "Etude Ebulliometrique Du Systeme $\text{NO}_3\text{H}-\text{OH}_2$," *Alger, Sciences Physiques*, 4, (4), 1958, pp. 91-120.

5. W. Davis and H. J. De Bruin, "New Activity Coefficients of 0-100 Percent Aqueous Nitric Acid," *J. Inorg. Nucl. Chem.*, **26**, 1964, pp. 1069-1083.
6. M. A. Yakimov and V. Ya. Mishin, "Solution-Vapor Equilibrium of the Binary System $\text{HNO}_3\text{-H}_2\text{O}$ at 25, 35, and 50°C," *Soviet Radiochemistry*, **6**, (5), 1964, pp. 523-527.
7. C. L. Burdick and E. S. Freed, "The Equilibrium Between Nitric Oxide, Nitrogen Peroxide and Aqueous solution of Nitric Acid," *J. Am. Chem. Soc.*, **43**, 1921, pp. 526-530.
8. W. C. Sproesser and G. B. Taylor, "Vapor Pressures of Aqueous Solutions of Nitric Acid," *J. Am. Chem. Soc.*, **43**, 1921, pp. 1782-1787.
9. R. Flatt and F. Benguerrel, *Helvetica Chimica Acta*, **XLV**, 1962, pp. 1722-1726.
10. T. Boublik and K. Kuchynka, "Abhängigkeit der Zusammensetzung des Azeotropischen Gemisches des Systems Salpetersäure-Wasser von Druck," *Collection of Czechoslovak Chemical Communications*, **25**, 1960, pp. 579-582.
11. R. J. Braatz, *Fractional Distillation of Dilute Nitric Acid Solutions Containing Fluoride and Chloride Ions*, Y-B92-71, Oak Ridge National Laboratory, 1958.
12. A. N. Efimov, et. al., "On the Influence of Nitrates on the Composition of Vapor Phase Over Nitric Acid Solutions," *Treat. Storage High-Level Radioactive Wastes, Proc. Symp., Vienna 1962*, pp. 133-139.
13. A. A. Krawetz, *A Raman Spectral Study of Equilibrium in Aqueous Solutions of Nitric Acid*, thesis, University of Chicago, Chicago, IL, 1955.
14. D. D. Wagman, et. al., "The NBS Tables of Chemical Thermodynamic Properties," *Journal of Physical and Chemical Reference Data*, Vol 11, Supplement No. 2, 1982.
15. Kirk and Othmer, *Encyclopedia of Chemical Technology*, Vol. 15, pp. 855.
16. J. Prosek, *Uzucht-Csav*, thesis, Prague, Czechoslovakia, 1965.
17. R. H. Perry and C. H. Chilton (eds.), *Chemical Engineers' Handbook*, Fifth Ed., New York: New York: McGraw-Hill Book Company Inc., 1973, Table 3-68.
18. G. B. Taylor, "Vapor Pressure of Aqueous Solutions of Nitric Acid," *Ind. & Engr. Chem.*, **17**, (6), 1925, pp. 633-635.
19. S. I. Sandler, *Models for Thermodynamic and Phase Equilibria Calculations*, Marcel Dekker, Inc., 1995, pp. 630.

20. A. N. Efimov, et. al., "Liquid-Vapor Equilibrium in the System $\text{HNO}_3 - \text{H}_2\text{O} - \text{NaNO}_3$ and Variations of Boiling Point with Variation of the Liquid Composition Along Joins and Transversals of the Triangular Diagram," *J. of Appl. Chem. of USSR*, 47, (No. 9), 1974, pp. 2183-2184.
21. A. N. Efimov, et. al., "Physicochemical Bases and Calculation of Vaporization Processes for Highly Active Nitric Acid Solutions," *Atomnaya Energiya*, Vol. 39, No. 6, 1975, pp. 416-419.
22. W. F. Linke, *Solubilities, Inorganic and Metal-Organic Compounds*, Vol. 1, Van Nostrand, 1958, pp. 189-190, 250-252 and 1069-1072.
23. D. J. Chaiko, et. al., *Measurements of $\text{Al}(\text{NO}_3)_3$ Activities in Aqueous Nitrate Solutions*, ANL/CP-75257.
24. E. W. Washburn, et. al., *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol III, pp. 372.
25. M. C. Vrevskii, et. al., *Journal of the Russian Physico-Chemical Soc. (Chemical Part)*, 54, 1923, pp. 360-375.
26. P. F. Hagerty and A. N. Hixon, *Report on Vapor-Liquid Equilibrium of Nitric Acid Solutions Containing Chloride Ion*, University of Pennsylvania, TID-5146, 1953.
27. H. F. Holmes, et. al., "The Enthalpy of Dilution of $\text{HCl}(\text{aq})$ to 648K and 40 MPa, Thermodynamic Properties," *J. Chem. Thermodynamics*, 19, 1987, pp. 863-890.
28. J. C. Brosheer, et. al., "Vapor Pressure of Hydrofluoric Acid Solutions," *Ind. & Eng. Chem.*, 39, 1947, pp. 423-427.
29. P. A. Munter, et. al., "Partial Pressure Measurements on the System Hydrogen Fluoride-Water," *Ind. & Eng. Chem.*, 41, 1949, pp. 1504-1508.
30. N. Khaidukov, et. el., *J. Applied Chem. (USSR)*, 9, 1936, pp. 439-445.
31. P. A. Munter, et. al., "Hydrofluoric Acid-Water and Hydrofluoric Acid-Hydrofluorsilicic-Water," *Ind. & Eng. Chem.*, 39, 1947, pp. 427-431.
32. V. M. Vdovenko, et. al., "Study of the Thermodynamic Characteristics of the System $\text{HF}-\text{HNO}_3-\text{H}_2\text{O}$, I. Measurements of the Vapor Pressure of the Components of the Systems $\text{HF}-\text{H}_2\text{O}$ and $\text{HF}-\text{HNO}_3-\text{H}_2\text{O}$," *Soviet Radiochemistry*, 7, No. 1, 1964, pp. 45-47.
33. A. L. Shneerson, et. al., *Russian Journal of Physical Chemistry*, 39, (No. 6), 1965, pp. 744-746.
34. A. L. Horvath, *Handbook of Aqueous Electrolyte Solutions*, John Wiley & Sons, pp. 21.

35. O. Knacke, et. al., *Thermochemical Properties of Inorganic Substances*, Second Ed., 1991, Springer-Verlag, Berlin.
36. "Physical Property Methods and Models," *ASPEN Plus™ Reference Manual - Volume 2*, Aspen Technology, 1994.
37. *Handbook of Chemistry and Physics*, 35th Ed., pp. 2158.
38. R. M. Smith and A. E. Martell, *Critical Stability Constants*, Vol. 6, Second Supplement, pp. 457.
39. J. A. Murphy, *Determination of the Zirconium Fluoride Stability Constants by Direct Measurement of Equilibrium Hydrofluoric Acid Using the Amphoteric Response of Titanium and Hafnium Electrodes*, WINCO-1098, May 1992, Appendix F.
40. G. B. Naumov, et. al., *Handbook of Thermodynamic Data*, Atomizdat, Moscow, 1971, pp. 181.
41. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd. Ed., Butterworths, 1959.

Appendix A

Property Parameters File PROP-R9C

Appendix A

Property Parameters File PROP-R9C

;
;Input Summary created by ASPEN PLUS Rel. 9.2-1 at 09:48:51 Tue Jul 16, 1996
;Directory D:\ASPENRUN\PR-TEST Filename prop-r9c.inp
;

TITLE 'TEST OF MODIFICATION C OF REL 9 PARAMETERS'

IN-UNITS MET MASS-FLOW='KG/DAY' MOLE-FLOW='KMOL/DAY' &
VOLUME-FLOW='CUM/DAY' ENTHALPY-FLO='MMKCAL/HR' &
HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=PSI TEMPERATURE=C &
VOLUME=CUM DELTA-T=C HEAD=METER MOLEy-DENSITY='MOL/L' &
MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL' &
MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L' &
PDROP=BAR

DEF-STREAMS MIXCISLD ALL

SIM-OPTIONS

IN-UNITS SI

SIM-OPTIONS FLASH-MAXIT=100 MW-CALC=NO

DATABANKS ASPENPCD / AQUEOUS / SOLIDS / INORGANIC / &
PURECOMP

PROP-SOURCES ASPENPCD / AQUEOUS / SOLIDS / INORGANIC / &
PURECOMP

COMPONENTS

H2O H2O H2O /
HNO3 HNO3 HNO3 /
H3O+ H3O+ H3O+ /
NO3- NO3- NO3- /
HCL HCL HCL /
CL- CL- CL- /
HF HF HF /
F- F- F- /
HF2- HF2- HF2- /
NA+ NA+ NA+ /
NANO3 NANO3 NANO3 /
NANO3S NANO3 NANO3S /
K+ K+ K+ /

KNO3 KNO3 KNO3 /
 KNO3S KNO3 KNO3S /
 AL+3 AL+3 AL+3 /
 "AL(NO3)3" "AL(OH)3" "AL(NO3)3" /
 ANN * ANN /
 ANNS * ANNS /
 ALF+2 ALF+2 ALF+2 /
 ALF2+ ALF2+ ALF2+ /
 CA+2 CA+2 CA+2 /
 "CA(NO3)2" CAO "CA(NO3)2" /
 FE+3 FE+3 FE+3 /
 "FE(NO3)3" FECL3 "FE(NO3)3" /
 CD+2 CD+2 CD+2 /
 "CD(NO3)2" "CA(NO3)2" "CD(NO3)2" /
 PB+2 PB+2 PB+2 /
 "PB(NO3)2" PBSO4 "PB(NO3)2" /
 H2SO4 H2SO4 H2SO4 /
 HSO4- HSO4- HSO4- /
 SO4-- SO4-2 SO4-- /
 HGCL2 HGCL2 HGCL2 /
 H3BO3 H3BO3 H3BO3 /
 UDS AL2O3-1 UDS /
 NI+2 NI+2 NI+2 /
 "NI(NO3)2" NISO4 "NI(NO3)2" /
 ZR+4 ZR+4 ZR+4 /
 ZRF2+2 CA+2 ZRF2+2 /
 ZRF+3 FE+3 ZRF+3 /
 NAHSO4 NAHSO4 NAHSO4

HENRY-COMPS GLOBAL HCL

CHEMISTRY GLOBAL

IN-UNITS SI
 DISS NANO3 NA+ 1.0 / NO3- 1.0
 DISS "AL(NO3)3" AL+3 1.0 / NO3- 3.0
 DISS ANN AL+3 1.0 / NO3- 3.0 / H2O 9.0
 DISS KNO3 K+ 1.0 / NO3- 1.0
 DISS "FE(NO3)3" FE+3 1.0 / NO3- 3.0
 DISS "CA(NO3)2" CA+2 1.0 / NO3- 2.0
 DISS "CD(NO3)2" CD+2 1.0 / NO3- 2.0
 DISS "PB(NO3)2" PB+2 1.0 / NO3- 2.0
 DISS "NI(NO3)2" NI+2 1.0 / NO3- 2.0
 DISS NAHSO4 NA+ 1 / HSO4- 1
 STOIC 1 HCL -1.0 / H2O -1.0 / H3O+ 1.0 / CL- 1.0
 STOIC 2 HF -1.0 / H2O -1.0 / H3O+ 1.0 / F- 1.0

STOIC 3 HNO3 -1.0 / H2O -1.0 / H3O+ 1.0 / NO3- 1.0
 STOIC 4 AL+3 -1.0 / F- -1.0 / ALF+2 1.0
 STOIC 5 ALF+2 -1.0 / F- -1.0 / ALF2+ 1.0
 STOIC 6 H2SO4 -1.0 / H2O -1.0 / H3O+ 1.0 / HSO4- 1.0
 SALT NANO3S NA+ 1.0 / NO3- 1.0
 SALT ANNS AL+3 1.0 / NO3- 3.0 / H2O 9.0
 SALT KNO3S K+ 1.0 / NO3- 1.0
 K-SALT NANO3S A=-26.150630 B=-179.96680 C=3.774540
 K-SALT ANNS A=316.36850 B=-12511.940 C=-50.0
 K-SALT KNO3S A=111.94240 B=-8683.1530 C=-15.957280

FLOWSHEET

PROPERTIES ELECNRTL HENRY-COMPS=GLOBAL CHEMISTRY=GLOBAL &
 TRUE-COMPS=YES

PROP-DATA ANN-SC

IN-UNITS SI PRESSURE=BAR TEMPERATURE=C
 PROP-LIST MW / CHARGE / DHSFRM / DGSFRM / PC / TC / &
 ZC / VC
 PVAL "AL(NO3)3" 212.9960 / 0.0 / -1.0420E+09 / -7.270E+08 &
 / 5000.0 / 2000.0 / .20 / .10
 PVAL ANN 375.13480 / 0.0 / -3.757060E+09 / -2.94140E+09 &
 / 5000.0 / 2000.0 / .20 / .10
 PVAL ANNS 375.13480 / 0.0 / -3.757060E+09 / -2.94140E+09 &
 / 5000.0 / 2000.0 / .20 / .10
 PROP-LIST MW
 PVAL "CD(NO3)2" 236.40980
 PVAL "FE(NO3)3" 241.86170
 PVAL "PB(NO3)2" 331.19980
 PVAL "CA(NO3)2" 164.08980
 PROP-LIST MW / PC / TC / ZC / VC
 PVAL H3BO3 61.8330 / 300.0 / 1700.0 / .260 / .370

PROP-DATA HGCL2

IN-UNITS SI
 PROP-LIST MW / CHARGE / DHFORM / DGFORM / PC / TC / &
 ZC / VC / OMEGA / DGSFRM / DHSFRM / DGAQFM / &
 DHAQFM
 PVAL HGCL2 271.4960 / 0.0 / -1.43260E+08 / -1.42020E+08 &
 / 5000000.0 / 1000.0 / .20 / .10 / .750 / &
 -1.7860E+08 / -2.2430E+08 / -1.7320E+08 / -2.1630E+08

PROP-DATA MW

IN-UNITS SI PRESSURE=BAR TEMPERATURE=C

PROP-LIST MW / CHARGE

PVAL "FE(NO3)3" 241.86170 / 0.0

PVAL "PB(NO3)2" 331.19980 / 0.0

PROP-LIST MW

PVAL "NI(NO3)2" 182.71980

PVAL ZRF2+2 129.21680

PVAL ZRF+3 110.2168

PROP-DATA RKTZRA

IN-UNITS SI

PROP-LIST RKTZRA

PVAL HF .10616360

PVAL HNO3 .2207790

PVAL H3BO3 .20722850

PVAL UDS .30

PROP-DATA S025C-1

IN-UNITS SI

PROP-LIST DHAQFM / DGAQFM / S025C

PVAL ALF+2 -8.6077E+08 / -8.156E+08 / -165300

PROP-DATA ANN-TFN

IN-UNITS SI

PROP-LIST PLXANT

PVAL "AL(NO3)3" -1.0E+20 0.0 0.0 0.0 0.0 0.0 0.0 0.0 &
1000.0

PVAL ANN -1.0E+20 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0

PVAL ANNS -1.0E+20 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0

PVAL "CD(NO3)2" -1.0E+20 0.0 0.0 0.0 0.0 0.0 0.0 0.0 &
1000.0

PVAL H3BO3 -1.0E+20 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0

PROP-DATA CPAQ0

IN-UNITS SI

PROP-LIST CPAQ0

PVAL HF 39295 0.0

PVAL F- -105036 0.0

PVAL AL+3 38000 0.0

PROP-DATA CPIG

IN-UNITS SI

PROP-LIST CPIG

PVAL HGCL2 18651.0 94.70360 0.0 0.0 0.0 0.0 273.0 400.0 &
18651.0 94.7040 1.0

PVAL H3BO3 82080.0 -10.5260 .040940 -.000024970 6.4460E-09 &
-6.250E-13 200.0 1000.0 82080.0 -10.5260 1.0

PROP-DATA CPSP01

IN-UNITS SI

PROP-LIST CPSP01

PVAL "AL(NO3)3" 232000.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0

PVAL ANN 533500.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0

PVAL ANNS 533500.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.0

PROP-DATA DHVLWT

IN-UNITS SI

PROP-LIST DHVLWT

PVAL HGCL2 83931000.0 298.0 .104310 .03841570 273.0

PVAL H3BO3 75450000.0 360.0 .380

PROP-DATA PLXANT

IN-UNITS SI

PROP-LIST PLXANT

PVAL HGCL2 43.89650 -10741.50 0.0 0.0 -2.130 0.0 0.0 &
273.0 550.0

PVAL HNO3 -281.8730 0.0 0.0 -.1358020 58.15110 0.0 0.0 &
231.0 400.0

PROP-DATA HENRY-1

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR' &
HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C &
VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM' &
MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL' &
MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L' &
PDROP=BAR

PROP-LIST HENRY

BPVAL HCL H2O 46.940030 -7762.8320 0.0 0.0 -.14999390 &
126.850

PROP-DATA NRTL-1

IN-UNITS SI

PROP-LIST NRTL

BPVAL H2O HF 97.280830 0.0 .30 0.0 0.0 0.0 298.0 &
383.150

BPVAL HF H2O -2.2972530 0.0 .30 0.0 0.0 0.0 298.0 &
 383.150
 BPVAL HCL H2O .14617260 0.0 .30 0.0 0.0 0.0 273.0 &
 1000.0
 BPVAL H2O HCL .1822130 0.0 .30 0.0 0.0 0.0 273.0 1000.0
 BPVAL H2O HNO3 -3.6277170 65.864660 .050 0.0 0.0 0.0 &
 270.0 400.0
 BPVAL HNO3 H2O 90.0 0.0 .050 0.0 0.0 0.0 270.0 400.0
 BPVAL HCL HNO3 3.5240 0.0 .30 0.0 0.0 0.0 0.0 1000.0
 BPVAL HNO3 HCL 4.0573330 0.0 .30 0.0 0.0 0.0 0.0 1000.0
 BPVAL HGCL2 H2O 100.0 30000.0 .30 0.0 0.0 0.0 273.0 &
 400.0
 BPVAL H2O HGCL2 -1.868090 2244.6670 .30 0.0 0.0 0.0 &
 273.0 400.0

PROP-DATA VLCLK-1

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR' &
 HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C &
 VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM' &
 MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL' &
 MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L' &
 PDROP=BAR

PROP-LIST VLCLK

BPVAL AL+3 NO3- 43.340140 89.50370
 BPVAL H3O+ NO3- 32.544040 51.212350
 BPVAL H3O+ CL- 34.551110 13.365810
 BPVAL H3O+ HSO4- 54.803950 20.243470
 BPVAL NA+ SO4-- 8.6755260 123.26710
 BPVAL NA+ NO3- 26.065710 28.973860
 BPVAL K+ NO3- 37.901020 24.33310
 BPVAL H3O+ F- 28.678530 15.010790
 BPVAL ALF+2 NO3- 34.729160 65.65510
 BPVAL ALF2+ NO3- 26.110 41.80650
 BPVAL ZRF2+2 NO3- 26.11 41.8065
 BPVAL ZRF+3 NO3- 34.729 65.655
 BPVAL FE+3 NO3- 52.586330 158.29940
 BPVAL CA+2 NO3- 29.733810 133.64070
 BPVAL CD+2 NO3- 39.705170 55.682830
 BPVAL NI+2 NO3- 39.7050 55.6830
 BPVAL PB+2 NO3- 36.435660 171.115620

PROP-DATA GMELCC-1

IN-UNITS SI

PROP-LIST GMELCC

PPVAL H2O (H3O+ NO3-) -3.411562

PPVAL (H3O+ NO3-) H2O -1.379389
 PPVAL H2O (H3O+ CL-) 7.195472
 PPVAL (H3O+ CL-) H2O -3.761581
 PPVAL H2O (H3O+ F-) 15.128270
 PPVAL (H3O+ F-) H2O -2.3487840
 PPVAL H2O (H3O+ HSO4-) 6.3620
 PPVAL (H3O+ HSO4-) H2O -3.7490
 PPVAL H2O (H3O+ SO4--) 8.0
 PPVAL (H3O+ SO4--) H2O -4.0
 PPVAL H2O (NA+ NO3-) 8.509752
 PPVAL (NA+ NO3-) H2O -4.460697
 PPVAL H2O (NA+ CL-) 5.9801960
 PPVAL (NA+ CL-) H2O -3.7891680
 PPVAL H2O (NA+ HSO4-) 7.663000
 PPVAL (NA+ HSO4-) H2O -3.944000
 PPVAL H2O (NA+ SO4--) 7.689221
 PPVAL (NA+ SO4--) H2O -4.284786
 PPVAL H2O (K+ NO3-) 4.038739
 PPVAL (K+ NO3-) H2O -3.106562
 PPVAL H2O (K+ CL-) 8.288000
 PPVAL (K+ CL-) H2O -4.168000
 PPVAL H2O (K+ HSO4-) 8.101000
 PPVAL (K+ HSO4-) H2O -3.958000
 PPVAL H2O (CA+2 NO3-) 7.5780
 PPVAL (CA+2 NO3-) H2O -4.0720
 PPVAL H2O (CA+2 CL-) 10.47200
 PPVAL (CA+2 CL-) H2O -5.060000
 PPVAL H2O (CD+2 NO3-) 7.7960
 PPVAL (CD+2 NO3-) H2O -4.1090
 PPVAL H2O (CD+2 CL-) 7.836000
 PPVAL (CD+2 CL-) H2O -3.685000
 PPVAL H2O (PB+2 NO3-) 7.084000
 PPVAL (PB+2 NO3-) H2O -3.452000
 PPVAL HNO3 (H3O+ NO3-) 18.35049
 PPVAL (H3O+ NO3-) HNO3 28.03711
 PPVAL HCL (H3O+ CL-) 12.0
 PPVAL (H3O+ CL-) HCL -.0010
 PPVAL HCL (H3O+ HSO4-) 10.00000
 PPVAL (H3O+ HSO4-) HCL -2.000000
 PPVAL HCL (H3O+ SO4--) 15.00000
 PPVAL (H3O+ SO4--) HCL -8.000000
 PPVAL HCL (NA+ CL-) 15.0
 PPVAL (NA+ CL-) HCL -8.0
 PPVAL HF (H3O+ F-) 9.6672160
 PPVAL (H3O+ F-) HF 3.5665980

PPVAL H2SO4 (H3O+ CL-) 10.00000
 PPVAL (H3O+ CL-) H2SO4 -2.000000
 PPVAL H2SO4 (H3O+ HSO4-) 12.9920
 PPVAL (H3O+ HSO4-) H2SO4 -2.9810
 PPVAL H2SO4 (H3O+ SO4--) 8.000000
 PPVAL (H3O+ SO4--) H2SO4 -4.000000
 PPVAL (H3O+ CL-) (H3O+ HSO4-) .9536271
 PPVAL (H3O+ HSO4-) (H3O+ CL-) 0.0
 PPVAL (NA+ CL-) (NA+ SO4--) -11.44869
 PPVAL (NA+ SO4--) (NA+ CL-) -.2697454
 PPVAL (NA+ CL-) (K+ CL-) 1.360000
 PPVAL (K+ CL-) (NA+ CL-) -1.023000
 PPVAL HNO3 (NA+ NO3-) -29.90617
 PPVAL (NA+ NO3-) HNO3 -33.52829
 PPVAL (H3O+ NO3-) (NA+ NO3-) 5.284384
 PPVAL (NA+ NO3-) (H3O+ NO3-) -0.6550303
 PPVAL HNO3 (K+ NO3-) 29.82778
 PPVAL (K+ NO3-) HNO3 30.0
 PPVAL (H3O+ NO3-) (K+ NO3-) -25
 PPVAL (K+ NO3-) (H3O+ NO3-) -5.80576
 PPVAL HNO3 (H3O+ CL-) 6.220643
 PPVAL (H3O+ CL-) HNO3 -12.8950
 PPVAL (H3O+ NO3-) (H3O+ CL-) 19.0
 PPVAL (H3O+ CL-) (H3O+ NO3-) 2.220958
 PPVAL H2O (AL+3 NO3-) 29.95914
 PPVAL (AL+3 NO3-) H2O -10.10100
 PPVAL HNO3 (AL+3 NO3-) 2.192842
 PPVAL (AL+3 NO3-) HNO3 -8.52746
 PPVAL (H3O+ NO3-) (AL+3 NO3-) 12.68662
 PPVAL (AL+3 NO3-) (H3O+ NO3-) 6.911549
 ; PPVAL (NA+ NO3-) (AL+3 NO3-) -0.7859297
 ; PPVAL (AL+3 NO3-) (NA+ NO3-) 7.959875
 PPVAL H2O (ALF+2 NO3-) 29.95914
 PPVAL (ALF+2 NO3-) H2O -10.10100
 PPVAL HNO3 (ALF+2 NO3-) 2.192842
 PPVAL (ALF+2 NO3-) HNO3 -8.52746
 PPVAL (H3O+ NO3-) (ALF+2 NO3-) 12.68662
 PPVAL (ALF+2 NO3-) (H3O+ NO3-) 6.911549
 ; PPVAL (NA+ NO3-) (ALF+2 NO3-) -0.7859297
 ; PPVAL (ALF+2 NO3-) (NA+ NO3-) 7.959875
 ; PPVAL (ALF+2 NO3-) (AL+3 NO3-) 0.5
 ; PPVAL (AL+3 NO3-) (ALF+2 NO3-) -1.5
 PPVAL HNO3 (CA+2 NO3-) 9.554692
 PPVAL (CA+2 NO3-) HNO3 2.741511
 PPVAL HNO3 (CD+2 NO3-) 10.0

PPVAL (CD+2 NO3-) HNO3 -2.0
 PPVAL H2O (FE+3 NO3-) 7.994493
 PPVAL (FE+3 NO3-) H2O -4.60052
 PPVAL HNO3 (FE+3 NO3-) 9.093591
 PPVAL (FE+3 NO3-) HNO3 2.850314
 PPVAL (NA+ NO3-) (NA+ CL-) 0
 PPVAL (NA+ CL-) (NA+ NO3-) -1
 PPVAL (AL+3 NO3-) (AL+3 CL-) 0
 PPVAL (AL+3 CL-) (AL+3 NO3-) -1
 PPVAL (K+ NO3-) (K+ CL-) 0
 PPVAL (K+ CL-) (K+ NO3-) -1
 PPVAL (FE+3 NO3-) (FE+3 CL-) 0
 PPVAL (FE+3 CL-) (FE+3 NO3-) -1
 PPVAL (CA+2 NO3-) (CA+2 CL-) 0
 PPVAL (CA+2 CL-) (CA+2 NO3-) -1
 PPVAL H2O (ALF2+ NO3-) 7.578
 PPVAL (ALF2+ NO3-) H2O -4.072
 PPVAL HNO3 (ALF2+ NO3-) 9.5547
 PPVAL (ALF2+ NO3-) HNO3 2.7415
 PPVAL (K+ NO3-) (NA+ NO3-) -1.02317
 PPVAL (NA+ NO3-) (K+ NO3-) 1.124986
 PPVAL HGCL2 (H3O+ NO3-) 3.81249
 PPVAL (H3O+ NO3-) HGCL2 2.12927
 PPVAL HGCL2 (H3O+ HSO4-) 3.81249
 PPVAL (H3O+ HSO4-) HGCL2 2.12927
 PPVAL HGCL2 (AL+3 NO3-) 8.67805
 PPVAL (AL+3 NO3-) HGCL2 12.0573
 PPVAL HGCL2 (FE+3 NO3-) 8.67805
 PPVAL (FE+3 NO3-) HGCL2 12.0573
 PPVAL HGCL2 (NA+ NO3-) 8.057026
 PPVAL (NA+ NO3-) HGCL2 11.4694
 PPVAL HGCL2 (K+ NO3-) 8.057026
 PPVAL (K+ NO3-) HGCL2 11.4694
 PPVAL HGCL2 (CA+2 NO3-) 8.057026
 PPVAL (CD+2 NO3-) HGCL2 11.4694
 PPVAL HGCL2 (CD+2 NO3-) 8.057026
 PPVAL (CA+2 NO3-) HGCL2 11.4694
 PPVAL HGCL2 (ALF+2 NO3-) 8.057026
 PPVAL (ALF+2 NO3-) HGCL2 11.4694

PROP-DATA GMELCD-1

IN-UNITS SI

PROP-LIST GMELCD

PPVAL H2O (H3O+ NO3-) 4021.066
 PPVAL (H3O+ NO3-) H2O -1005.608

PPVAL H2O (H3O+ CL-) 800.3416
 PPVAL (H3O+ CL-) H2O -394.9632
 PPVAL H2O (H3O+ F-) -2141.0790
 PPVAL (H3O+ F-) H2O -155.08250
 PPVAL H2O (H3O+ HSO4-) 1958.20
 PPVAL (H3O+ HSO4-) H2O -583.20
 PPVAL H2O (H3O+ SO4--) 0.0
 PPVAL (H3O+ SO4--) H2O 0.0
 PPVAL H2O (NA+ CL-) 841.51810
 PPVAL (NA+ CL-) H2O -216.36460
 PPVAL H2O (NA+ SO4--) 565.5983
 PPVAL (NA+ SO4--) H2O -56.83768
 PPVAL H2O (K+ CL-) 0.0
 PPVAL (K+ CL-) H2O -4.700000
 PPVAL HNO3 (H3O+ NO3-) -2595.605
 PPVAL (H3O+ NO3-) HNO3 -9671.993
 PPVAL HCL (H3O+ CL-) .0
 PPVAL (H3O+ CL-) HCL .0
 PPVAL HCL (H3O+ HSO4-) 0.0
 PPVAL (H3O+ HSO4-) HCL 0.0
 PPVAL HCL (H3O+ SO4--) 0.0
 PPVAL (H3O+ SO4--) HCL 0.0
 PPVAL HCL (NA+ CL-) .0
 PPVAL (NA+ CL-) HCL .0
 PPVAL HF (H3O+ F-) -3161.9840
 PPVAL (H3O+ F-) HF -2071.5340
 PPVAL H2SO4 (H3O+ HSO4-) -1732.90
 PPVAL (H3O+ HSO4-) H2SO4 -162.30
 PPVAL H2SO4 (H3O+ SO4--) 0.0
 PPVAL (H3O+ SO4--) H2SO4 0.0
 PPVAL (H3O+ CL-) (H3O+ HSO4-) -201.7466
 PPVAL (H3O+ HSO4-) (H3O+ CL-) 0.0
 PPVAL (NA+ CL-) (NA+ SO4--) 3757.483
 PPVAL (NA+ SO4--) (NA+ CL-) -133.6117
 PPVAL (NA+ CL-) (K+ CL-) -440.5000
 PPVAL (K+ CL-) (NA+ CL-) 331.4000
 PPVAL H2O (NA+ NO3-) -505.2884
 PPVAL (NA+ NO3-) H2O 288.6656
 PPVAL HNO3 (NA+ NO3-) 17681.22
 PPVAL (NA+ NO3-) HNO3 13131.2
 PPVAL (H3O+ NO3-) (NA+ NO3-) 0
 PPVAL (NA+ NO3-) (H3O+ NO3-) 0
 PPVAL HNO3 (H3O+ CL-) 962.7592
 PPVAL (H3O+ CL-) HNO3 6372.017
 PPVAL H2O (AL+3 NO3-) -5892.001

PPVAL (AL+3 NO3-) H2O 1470.918
 PPVAL HNO3 (AL+3 NO3-) 1562.688
 PPVAL (AL+3 NO3-) HNO3 5736.824
 PPVAL (NA+ NO3-) (AL+3 NO3-) 0.0
 PPVAL (AL+3 NO3-) (NA+ NO3-) 0.0
 PPVAL (H3O+ NO3-) (AL+3 NO3-) 6092.308
 PPVAL (AL+3 NO3-) (H3O+ NO3-) -550.0901
 PPVAL H2O (ALF+2 NO3-) -5892.001
 PPVAL (ALF+2 NO3-) H2O 1470.918
 PPVAL HNO3 (ALF+2 NO3-) 1562.688
 PPVAL (ALF+2 NO3-) HNO3 5736.824
 PPVAL (H3O+ NO3-) (ALF+2 NO3-) 6092.308
 PPVAL (ALF+2 NO3-) (H3O+ NO3-) -550.0901
 PPVAL H2O (K+ NO3-) 845.6844
 PPVAL (K+ NO3-) H2O -0.8

PROP-DATA GMELCE-1

IN-UNITS SI

PROP-LIST GMELCE

PPVAL H2O (H3O+ NO3-) .0
 PPVAL (H3O+ NO3-) H2O .0
 PPVAL H2O (H3O+ CL-) -32.12354
 PPVAL (H3O+ CL-) H2O 11.1879
 PPVAL H2O (H3O+ F-) .67718240
 PPVAL (H3O+ F-) H2O -3.4569330
 PPVAL H2O (H3O+ HSO4-) -4.5990
 PPVAL (H3O+ HSO4-) H2O 4.4720
 PPVAL H2O (NA+ CL-) 7.43350
 PPVAL (NA+ CL-) H2O -1.1004180
 PPVAL H2O (NA+ SO4--) -14.08276
 PPVAL (NA+ SO4--) H2O 8.547499
 PPVAL HNO3 (H3O+ NO3-) -82.78977
 PPVAL (H3O+ NO3-) HNO3 47.90918
 PPVAL HCL (H3O+ CL-) .0
 PPVAL (H3O+ CL-) HCL .0
 PPVAL HCL (H3O+ SO4--) 0.0
 PPVAL (H3O+ SO4--) HCL 0.0
 PPVAL H2SO4 (H3O+ HSO4-) -30.1260
 PPVAL (H3O+ HSO4-) H2SO4 .8060
 PPVAL (NA+ CL-) (NA+ SO4--) 60.25378
 PPVAL (NA+ SO4--) (NA+ CL-) -4.303000
 PPVAL H2O (AL+3 NO3-) -100
 PPVAL (AL+3 NO3-) H2O 33.16584
 PPVAL HNO3 (AL+3 NO3-) 93.7309
 PPVAL (AL+3 NO3-) HNO3 -100

PPVAL H2O (ALF+2 NO3-) -100
PPVAL (ALF+2 NO3-) H2O 33.16584
PPVAL HNO3 (ALF+2 NO3-) 93.7309
PPVAL (ALF+2 NO3-) HNO3 -100

PROP-DATA GMELCN-1

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR' &
HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C &
VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM' &
MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL' &
MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L' &
PDROP=BAR

PROP-LIST GMELCN

PPVAL H2O (H3O+ F-) .20
PPVAL H2O (H3O+ HSO4-) .20
PPVAL H2O (NA+ CL-) .20
PPVAL H2O (NA+ SO4--) .20
PPVAL HCL (H3O+ SO4--) .10
PPVAL HCL (NA+ CL-) .10
PPVAL H2SO4 (H3O+ HSO4-) .20
PPVAL (H3O+ HSO4-) H2SO4 .20
PPVAL HCL (NA+ NO3-) .10
PPVAL HCL (AL+3 NO3-) .10

PROP-SET MF-HNO3 MASSFRAC SUBSTREAM=MIXED COMPS=HNO3 PHASE=V

PROP-SET MOLECONC

IN-UNITS MET VOLUME-FLOW='CUM/HR' ENTHALPY-FLO='MMKCAL/HR' &
HEAT-TRANS-C='KCAL/HR-SQM-K' PRESSURE=BAR TEMPERATURE=C &
VOLUME=CUM DELTA-T=C HEAD=METER MOLE-DENSITY='KMOL/CUM' &
MASS-DENSITY='KG/CUM' MOLE-ENTHALP='KCAL/MOL' &
MASS-ENTHALP='KCAL/KG' HEAT=MMKCAL MOLE-CONC='MOL/L' &
PDROP=BAR

PROPNAME-LIS MOLECONC SUBSTREAM=MIXED PHASE=L

PROP-SET PP-HCL

IN-UNITS SI

PROPNAME-LIS PPMX UNITS='TORR' SUBSTREAM=MIXED COMPS=HCL

PROP-SET PPMX

IN-UNITS SI

PROPNAME-LIS PPMX UNITS='TORR' SUBSTREAM=MIXED COMPS=HNO3 &
H2O

PROP-SET TEMP

IN-UNITS SI

PROPNAME-LIS TEMP UNITS='C' SUBSTREAM=MIXED PHASE=T

PROP-SET Y-HCL

IN-UNITS SI

PROPNAME-LIS MOLEFRAC SUBSTREAM=MIXED COMPS=HCL PHASE=V

PROP-SET Y-HF

IN-UNITS SI

PROPNAME-LIS MASSFRAC SUBSTREAM=MIXED COMPS=HF PHASE=V

PROP-SET Y-HNO3

IN-UNITS SI

PROPNAME-LIS MOLEFRAC SUBSTREAM=MIXED COMPS=HNO3 PHASE=V

CONV-OPTIONS

PARAM CHECKSEQ=NO

STREAM-REPOR NOZEROFLOW MOLEFLOW NOMASSFLOW MOLEFRAC MASSFRAC &
PROPERTIES=MOLECONC

PROPERTY-REP NOPARAMS

PROP-TABLE EFI-AL20 FLASHCURVE

IN-UNITS SI PRESSURE=TORR TEMPERATURE=C

MASS-FLOW H2O 70.0 / HNO3 10.0 / "AL(NO3)3" 20.0

STATE VFRAC=0.0

VARY PRES

RANGE LIST=760.0 400.0

VARY MASS-FLOW COMP=HNO3

RANGE LIST=20.0

VARY MASS-FLOW COMP=H2O

RANGE LIST=80.0

VARY MASS-FLOW COMP="AL(NO3)3"

RANGE LIST=0.0 11.10 25.0 42.90 66.70 100.0

TABULATE PROPERTIES=TEMP MF-HNO3

PROP-TABLE HCL-HGH FLASHCURVE

IN-UNITS SI PRESSURE=TORR TEMPERATURE=C

MOLE-FLOW H2O 80.0 / HNO3 20.0 / HCL 20.0

STATE PRES=760.0 VFRAC=0.0

VARY MOLE-FRAC COMP=HCL

RANGE LIST=.00030 .00060 .0020 .060

VARY MOLE-FRAC COMP=HNO3
RANGE LIST=.0030 .030 .10 .150 .220
TABULATE PROPERTIES=Y-HCL TEMP

PROP-TABLE PP-HCL FLASHCURVE

IN-UNITS SI PRESSURE=TORR TEMPERATURE=C
MOLE-FLOW H2O 80.0 / HCL 20.0
STATE VFRAC=0.0
VARY TEMP
RANGE LIST=20.0 55.20 75.90
VARY MOLE-FRAC COMP=HCL
RANGE LIST=.0250 .050 .060 .070 .080 .090 .10 .110 .120 &
.130
TABULATE PROPERTIES=Y-HCL PP-HCL

PROP-TABLE PPMX FLASHCURVE

IN-UNITS SI PRESSURE=TORR TEMPERATURE=C
MOLE-FLOW H2O 80.0 / HNO3 20.0
STATE VFRAC=0.0
VARY TEMP
RANGE LIST=25.0 50.0
VARY MOLE-FRAC COMP=HNO3
RANGE LIST=.0250 .050 .10 .150 .20 .250 .30
TABULATE PROPERTIES=PPMX

PROP-TABLE Y-EF760 FLASHCURVE

IN-UNITS SI PRESSURE=TORR TEMPERATURE=C
MOLE-FLOW H2O .000810185 / HNO3 .000231481 / NANO3 &
.000115740
STATE PRES=760.0 VFRAC=0.0
VARY MOLE-FRAC COMP=HNO3
RANGE LIST=.030 .060 .090 .120 .150
VARY MOLE-FRAC COMP=NANO3
RANGE LIST=0.0 .030 .060 .090 .120 .150 .180 .210
TABULATE PROPERTIES=Y-HNO3 TEMP

PROP-TABLE Y-HF FLASHCURVE

IN-UNITS SI PRESSURE=TORR TEMPERATURE=C
MOLE-FLOW H2O .001041666 / HF .000115740
STATE PRES=760.0 VFRAC=0.0
VARY MASS-FRAC COMP=HF
RANGE LIST=.050 .10 .150 .20 .250
TABULATE PROPERTIES=Y-HF TEMP

PROP-TABLE Y-HNO3 FLASHCURVE
IN-UNITS SI PRESSURE=TORR TEMPERATURE=C
MASS-FLOW H2O 80.0 / HNO3 20.0
VARY PRES
RANGE LIST=200.0 600.0 760.0
VARY VFRAC
RANGE LIST=0.0
VARY MOLE-FRAC COMP=HNO3
RANGE LIST=.020 .040 .060 .10 .150 .20 .250 .30
TABULATE PROPERTIES=Y-HNO3 TEMP

;
;
;
;
;
;
;
;