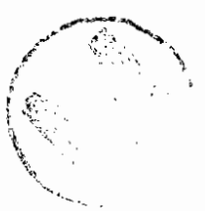
Title 40 CFR Part 191
Compliance Certification
Application
for the
Waste Isolation Pilot Plant

SOTERM Attachment 2

THIS PAGE INTENTIONALLY LEFT BLANK



WIPP PA

User's Manual

for

NONLIN, Version 2.0

Document Version 1.0

WPO #30740

January 31, 1996

Table of Contents

List of Figures

List of Tables

1.0 INTRODUCTION

The program NONLIN fits parameters for a designated aqueous electrolyte model to experimental data on osmotic coefficients, mineral solubility, emf, or solvent extraction. Although NONLIN has two aqueous electrolyte models for excess free energy available, the Davies equations (Davies, 1962) and Pitzer's aqueous electrolyte model (Pitzer [1973] and coworkers), this document will discuss only the Pitzer model, which is used to support the 1996 WIPP Performance Assessment (PA) calculations.

For the 1996 WIPP PA calculation, NONLIN is used to calculate Pitzer parameters and standard chemical potentials of actinide chemical species. The calculated values will be added to the CHEMDAT data base used by a program called FMT. CHEMDAT contains the Harvie-Møller-Weare (HMW) database (Harvie et al., 1984; Felmy and Weare, 1986) for nonradioactive electrolyte systems and the actinide series of radioactive elements, such as americium(III) and neptunium(V). FMT is a chemical equilibrium modeling code, also used to support the 1996 WIPP PA calculations. The FMT User's Manual, WPO 28119, documents both the CHEMDAT data base and the FMT code.

1.1 Software Identifier

Code Name: NONLIN
WIPP Prefix: NL_
Version Number: 2.0 08/23/96
Platforms: FORTRAN 77 for Open VMS AXP, version 6.1, on DEC Alpha machines and Power Macintosh 7100

1.2 Points of Contact

1.2.1 Code Sponsor

Sandra C. Babb
Sandia National Laboratories
Albuquerque, NM 87185-0661
Voice: (505) 844-7396 or (505) 848-0126
Fax: (505) 844-2018 or (505) 848-0881

1.2.2 Code Consultants

Robert C. Moore
Sandia National Laboratories
Albuquerque, NM 87185-1342
Voice: (505) 848-0146
Fax: (505) 848-0881

Craig F. Novak
Sandia National Laboratories
Albuquerque, NM 87185-1320
Voice: (505) 848-0619
Fax: (505) 848-0622

1.2.3 Code Author

Andrew R. Felmy
Batelle Pacific Northwest Laboratory
Richland, WA 99352
Voice: (509) 372-6296
Fax: (509) 372-6328

2.0 FUNCTIONAL REQUIREMENTS

R.1 NONLIN fits parameters for Pitzer's aqueous electrolyte model to experimental data on mineral solubility.

R.2 NONLIN fits parameters for Pitzer's aqueous electrolyte model to experimental data on solvent extraction.

R.3 NONLIN fits parameters for Pitzer's aqueous electrolyte model to experimental data for apparent stability.

3.0 REQUIRED USER TRAINING AND/OR BACKGROUND

In order to run the NONLIN code successfully, the user will need a basic knowledge of one of the following platforms:

- Open VMS and Digital Equipment Co.'s (DEC's) Digital Command Language (DCL), if running the code on the DEC platform
- Power Macintosh 7100 operation, if running the code on a Macintosh platform.

To interpret the results of NONLIN, a chemistry background is required. A user should have a:

- BS in Chemistry, or the equivalent
- familiarity with the Pitzer model for activity coefficient of electrolytes
- sound understanding of chemical reaction equilibrium analysis.

To understand how the NONLIN code works and the theory and algorithms upon which NONLIN is based, the user should also have a basic understanding of:

- equilibrium thermodynamics and solution chemistry
- linear algebra (through senior undergraduate level)
- numerical methods (graduate or senior level undergraduate level).

4.0 DESCRIPTION OF THE MODELS AND METHODS

NONLIN solves chemical equilibrium problems, as defined by the linear material balance equations and the nonlinear reaction equilibrium equations as given in standard chemical thermodynamics texts such as Denbigh (1981) and Smith and Van Ness (1975).

More specifically, NONLIN couples the GMIN free-energy chemical equilibrium program with the MINPACK least squares minimization routines. NONLIN can be used to interpret (i.e., fit) experimental concentration data such as

- solubility (i.e., the total dissolved concentration of element X in aqueous electrolyte of composition Y)

- electromotive force (emf)
- isopiestic data
- solvent extraction data (i.e., the distribution of element X between an aqueous and an organic phase)
- ion exchange data
- apparent stability constant data (i.e., the molal ion quotients for intra-aqueous reactions).

4.1 GMIN Chemical Equilibrium Model

The GMIN chemical equilibrium program is explained in detail by Felmy (1990) and Felmy (1995). Sections 4.1.1 and 4.1.3 of the following discussion are largely excerpted from that source. Section 4.1.2, which explains the Pitzer activity coefficient formalism, is excerpted from Felmy and Weare (1986).

4.1.1 Thermodynamic Model

The mathematical basis of GMIN is based on the development of an algorithm for solving the chemical equilibrium problem that is based on a constrained minimization of the Gibbs free energy.

NONLIN, as used in support of the 1996 WIPP PA calculation, makes use of the following general equations that GMIN can solve:

- chemical potential for water solvent in aqueous phase:

$$\frac{\mu_{H_2O}}{RT} = \frac{\mu^0_{H_2O}}{RT} - \frac{W}{1000}\left(\sum_{i=1}^{ns} m_i\right)\phi \qquad (4\text{-}1)$$

- chemical potential for solute species in aqueous phase:

$$\frac{\mu_i}{RT} = \frac{\mu_i^0}{RT} + \ln m_i + \ln \gamma_i \qquad (4\text{-}2)$$

where

μ_i = chemical potential of species *i*

μ_i^0 = standard chemical potential of species *i*

R = the gas constant

T = absolute temperature

W = molecular weight of water

ns = the total number of chemical species

m_i = molality of species i

ϕ = osmotic coefficient

γ_i = activity coefficient of species i.

While GMIN contains two formulations for activity coefficients for aqueous species, only one formulation is used in support of the WIPP PA calculation. This model is based on the work by Pitzer (1979) and coworkers. In this model, the activity coefficients are expressed in a virial-type expansion.

4.1.2 The Pitzer Activity Coefficient Formalism

The Pitzer activity coefficient formalism is a set of mathematical equations for calculating activity coefficients for aqueous species, and is valid from dilute systems through the concentrated brine concentrations observed at the WIPP Site. The theoretical and historical development of this formalism can be traced though Pitzer (1991), particularly Chapter 3, and references therein.

The implementation of the Pitzer activity coefficient formalism within NONLIN is based on the forms of the equations as presented in Harvie and Weare (1980), Harvie et al. (1984), and Felmy and Weare (1986). Because there is no difference in the mathematical formulation provided by these references, only the equations in Felmy and Weare (1986) are presented below. The interested reader will find a comprehensive presentation of these equations in the three cited publications.

The activities of the species a_i can be defined by the following equation:

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n} = \mu_i = \mu_i^0 + RT\ln a_i . \tag{4-3}$$

where G = Gibbs free-energy function, P = pressure, n_i = number of moles of species i, and activity is defined for each solute species i by

$$a_i = \gamma_i m_i \tag{4-4}$$

and, for the solvent, by

$$\ln a_{H_2O} = \frac{-W}{1000}\left(\sum_i m_i\right)\phi , \tag{4-5}$$

where

m_i = the molality of the solute species,

W = the molecular weight of water,

$\sum_i m_i$ = the sum over all solutes (cations (c), anions (a), and neutrals(n)), and

ϕ = the osmotic coefficient.

While the chemical potentials for pure phases (e.g., minerals) are constant at fixed temperature and pressure, the fugacity of gas-phase species, f_i, is defined as follows:

$$\frac{\mu_i}{RT} = \frac{\mu_i^0}{RT} + \ln(f_i). \tag{4-6}$$

The remaining variables that lack explicit definition are the excess functions γ_i and $(\phi - 1)$. These functions, rewritten below, are modeled using the semiempirical equations of Pitzer (1973) and co-workers. (Note that, in the Pitzer equations presented below, I = ionic strength, and that subscripts *M*, *X*, and *N* refer to cations, anions, and neutrals, respectively. The remaining terms are explained following the presentation of the Pitzer equations.)

$$(\phi-1) = \frac{2}{\left(\sum_i m_i\right)}\left\{-\frac{A^\phi I^{3/2}}{1+bI^{1/2}} + \sum_c\sum_a m_c m_a\left(B^\phi_{ca} + ZC_{ca}\right) + \sum_{c<c'}\sum m_c m_{c'}\left(\Phi^\phi_{cc'} + \sum_a m_a \psi_{cc'a}\right)\right.$$
$$+\sum_{a<a'}\sum m_a m_{a'}\left(\Phi^\phi_{aa'} + \sum_c m_c \psi_{aa'c}\right) + \sum_n\sum_c m_n m_c \lambda_{nc} \tag{4-7}$$
$$\left.+\sum_n\sum_a m_n m_a \lambda_{na} + \sum_n\sum_c\sum_a m_n m_c m_a \zeta_{nca}\right\}$$

$$\ln\gamma_M = z_M^2 F + \sum_a m_a\left(2B_{Ma} + ZC_{Ma}\right) + \sum_c m_c\left(2\Phi_{Mc} + \sum_a m_a \psi_{Mca}\right)$$
$$+\sum_{a<a'}\sum m_a m_{a'}\psi_{aa'M} + |z_M|\sum_c\sum_a m_c m_a C_{ca} + \sum_n m_n\left(2\lambda_{nM}\right) + \sum_n\sum_a m_n m_a \zeta_{naM} \tag{4-8}$$

$$\ln\gamma_X = z_M^2 F + \sum_c m_c\left(2B_{Xc} + ZC_{Xc}\right) + \sum_a m_a\left(2\Phi_{Xa} + \sum_c m_c \psi_{Xca}\right) + \sum_{c<c'}\sum m_c m_{c'} \psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca} + \sum_n m_n\left(2\lambda_{nX}\right) + \sum_n \sum_c m_n m_c \zeta_{ncX} \quad (4\text{-}9)$$

$$\ln\gamma_N = \sum_c m_c\left(2\lambda_{Nc}\right) + \sum_a m_a\left(2\lambda_{Na}\right) + \sum_c \sum_a m_c m_a \zeta_{Nca} \quad (4\text{-}10)$$

$$F = -A^{\phi}\left(\frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b}\ln\left(1+bI^{1/2}\right)\right) + \sum_c \sum_a m_c m_a B'_{ca} + \sum_{c<c'}\sum m_c m_{c'} \Phi'_{cc'} + \sum_{a<a'}\sum m_a m_{a'} \Phi'_{aa'} \quad (4\text{-}11)$$

where $b = 1.2$ for all electrolyes.

$$C_{MX} = \frac{C^{\phi}_{MX}}{2|Z_M Z_X|^{1/2}} \quad (4\text{-}12)$$

$$Z = \sum_i |z_i| m_i \quad (4\text{-}13)$$

A^{ϕ} is one third of the Debye-Hückel limiting slope (A in the following empirical equation):

$$\ln\gamma_i^{DH} = -\frac{A\sqrt{I}}{1+Ba_i\sqrt{I}} + \dot{B}_i I, \quad (4\text{-}14)$$

as presented on page 981 of Harvie and Weare [1980].) Here A^{ϕ} is a function of temperature and equals 0.39 at 25°C. The second virial coefficients, B, are empirical expansions and are given the following ionic strength dependence:

$$B^{\phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} e^{-\alpha_1\sqrt{I}} + \beta^{(2)}_{MX} e^{-\alpha_2\sqrt{I}} \quad (4\text{-}15)$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} g\left(\alpha_1\sqrt{I}\right) + \beta^{(2)}_{MX} g\left(\alpha_2\sqrt{I}\right) \quad (4\text{-}16)$$

$$B'_{MX}=\beta^{(1)}_{MX}\frac{g'(\alpha_1\sqrt{I})}{I}+\beta^{(2)}_{MX}\frac{g'(\alpha_2\sqrt{I})}{I} \tag{4-17}$$

The functions g and g' are defined by

$$g(x)=2\frac{(1-(1+x)e^{-x})}{x^2} \tag{4-18}$$

$$g'(x)=-2\frac{\left(1-\left(1+x+\frac{x^2}{2}\right)e^{-x}\right)}{x^2} \tag{4-19}$$

with $x = \alpha_1\sqrt{I}$ or $= \alpha_2\sqrt{I}$. When either cation M or anion X is univalent, $\alpha_1 = 2.0$ and $\alpha_2 = 12$. For 2 - 2 pairs, $\alpha_1 = 1.4$ and $\alpha_2 = 12$. For 2 - 3 and higher pairs, $\alpha_1 = 1.4$ and $\alpha_2 = 50$. The dimensions of α_1 and α_2 are $kg^{1/2}mole^{-1/2}$. The virial coefficients, Φ, which depend upon ionic strength, are given the following form:

$$\Phi^{\phi}_{ij}=\theta_{ij}+{}^{E}\theta_{ij}(I)+I{}^{E}\theta'_{ij}(I) \tag{4-20}$$

$$\Phi_{ij}=\theta_{ij}+{}^{E}\theta_{ij}(I) \tag{4-21}$$

$$\Phi'_{ij}={}^{E}\theta'_{ij}(I) \tag{4-22}$$

The functions, ${}^{E}\theta_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$, are functions only of ionic strength and the electrolyte pair type.

The activity coefficient parameters, λ_{ni} and ζ_{nij}, represent the interactions between ions and neutral species. The third virial coefficients, C^{ϕ}_{MX} and ψ_{ijk}, are also assumed to be independent of ionic strength.

The following is the complete set of parameters that define the model for nonideal behavior of electrolyte solutions:

- $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, and C^{ϕ}_{MX} for each cation-anion pair
- θ_{ij} for each cation-cation and anion-anion pair
- ψ_{ijk} for each cation-cation-anion and anion-anion-cation triplet
- λ_{ni} and ζ_{nij} for ion-neutral and ion-ion-neutral interactions.

NONLIN minimizes the sum of the errors squared for the standard chemical potential of user-specified species by adjusting the values of the thermodynamic parameters specified by the user.

These are the Pitzer parameters NONLIN solves for using thermodynamic data.

4.1.3 Free-Energy Minimization Approach

The free-energy minimization problem in GMIN is formulated as

$$\text{minimize } G = \sum_{j=1}^{ns} \mu_j n_j \tag{4-23}$$

subject to the following mass-balance constraint

$$\sum_{j=1}^{ns} a_{ji} n_j = b_i, \qquad i = 1,\ldots,m_c \tag{4-24}$$

and the following charge-balance constraint

$$\sum_{j=1}^{nas} z_j n_j = 0 \tag{4-25}$$

and

$$n_j \geq 0 \qquad \text{for all species } j \tag{4-26}$$

where

ns = the total number of chemical species

n_j = mole number of species j

a_{ji} = number of moles of component i in species j

b_i = total number of moles of element i

m_c = number of linearly independent mass-balance constraints

nas = total number of aqueous species j

z_j = charge on species j

The free-energy minimization approach is fully documented in Harvie, Greenberg, and Weare (1987).

4.2 NONLIN Parameter Calculation

NONLIN calculates the Pitzer ion interaction parameters by using a non-linear least squares fitting algorithm. The code calculates values for user-specified aqueous solution and solid thermodynamic parameters, including the standard chemical potentials for ion pairs. NONLIN calculates the function to be minimized; i.e., the difference between solid and solution chemical potentials, and the Jacobian (the derivative of the chemical potential difference with respect to the adjustable parameters). The adjustable parameters, discussed in detail in Section 7.1, are the Pitzer parameters and the standard chemical potential of the chemical species to be fitted. Andrew R. Felmy is the code author of both NONLIN and GMIN, a chemical equilibrium code called by NONLIN. Pacific Northwest Laboratory maintains MINPACK, a set of matrix routines called by GMIN.

5.0 CAPABILITIES AND LIMITATIONS OF THE SOFTWARE

The chemical data base files and the problem definition files must be compatible; i.e., the species must be characterized in the data base before it is referenced in the problem. NONLIN capabilities are discussed at the beginning of Section 1.

6.0 USER INTERACTIONS WITH THE SOFTWARE

6.1 Overview

NONLIN requires six input data files— GMIN, INPUT, COMP, BINARYP, TERNARYP, and LAMBDA. The problem is defined by the GMIN and INPUT files. The GMIN file defines the chemical species to be considered. The INPUT file contains the experimental data and initial estimates for the Pitzer parameters or standard chemical potentials to be fitted. The last four files COMP, BINARYP, TERNARYP, and LAMBDA are the chemical data base files. These files contain species names and unique ID numbers, chemical characteristics, and Pitzer parameters. All the input files are discussed in detail in Section 7.0.

NONLIN generates one file OUTPUT. This file lists the problem definition as read from the GMIN and INPUT files, chemical species considered, and the best fit to the experimental data set(s).

Figure 6-1 illustrates all the input and output files used by NONLIN.

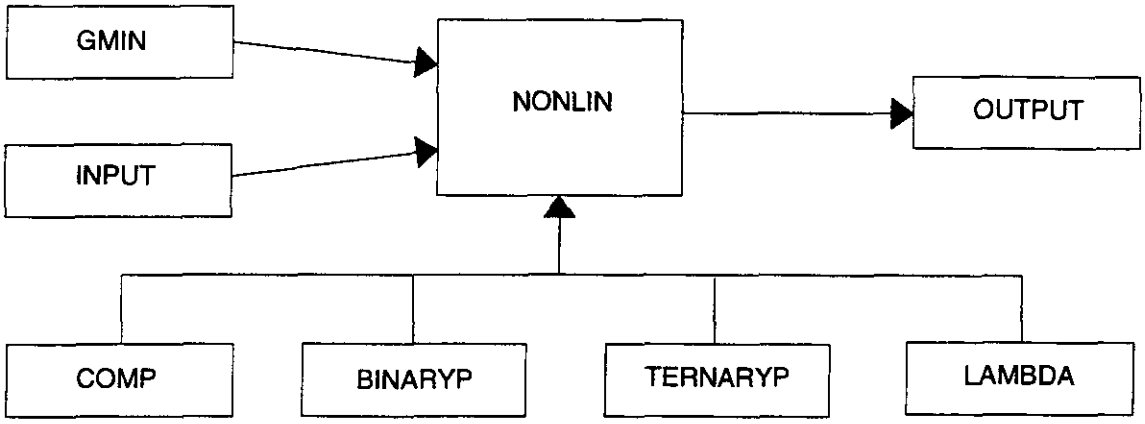


Figure 6-1. Input and Output Files for NONLIN.

6.2 User-Supplied Input Files

Using a convenient editor, the user creates the GMIN file and the INPUT file for a problem. The user should check the COMP, BINARYP, TERNARYP, and LAMBDA files to be sure that the required species and Pitzer parameters are included there.

6.3 Executing NONLIN

6.3.1 DEC Environment

The user can access the command file NL_NONLINC.COM to run NONLIN on the Sandia NWER network, using Digital's Alpha machine BEATLE. This file is located in the NL library. All files in the library are under control of Digital's Configuration Management System (CMS). This library contains NONLIN data base files, source code, and command files. The user can retrieve the command file NL_NONLINC.COM from the NL library using the CMS "fetch" command. For ease in executing NONLIN, the command file should be in the same directory where the input files reside.

6.3.1.1 Fetching the Command File NL_NONLINC.COM from CMS

To retrieve the command file NL_NONLINC.COM, the user logs into BEATLE and types the symbol "nonpa_cms_syms" to define other CMS symbols, followed by the command "libnl" to specify the NL library. Then the user locates the directory/subdirectory where his/her input files reside by typing in a "set default (sd)" command. The command "cfe nl_nonlinc.com" copies the command file into the user's current directory. The lines are:

```
$nonpa_cms_syms
$libnl
$sd [username.user_inputfile_directory]
$cfe nl_nonlinc.com
```

The command file can be copied from directory to directory. The user does not need to fetch the file each time. NL_NONLINC.COM also issues the lines "nonpa_cms_syms" and "libnl" automatically, making typing them unnecessary.

6.3.1.2 Running NL_NONLINC.COM

To execute "@NL_NONLINC" the user must always be logged into BEATLE. The user should be in the directory that contains the .IN and .GMIN files before starting NL_NONLINC. To execute the command, the user types:

```
$@ NL_NONLINC
```

The user will be prompted to supply a **substring** for the COMP, BINARYP, TERNARYP, and LAMBDA files and the GMIN and INPUT file names. To retrieve a list of all data base files, the user can simply type in ".DAT" since all of the NONLIN data base files have the string ".DAT" as the extension. Or, the user can type in any substring of the data base file name (e.g., COMP_960130). The GMIN and INPUT filestem names can be independent (e.g., SOLUB_01.IN and SOLUB_00.GMIN) or the same (e.g., AM_ACET.IN and AM_ACET.GMIN).

After listing the data base files that match the substring specified, the user is prompted to select each data base file. The user may select a file by copying and pasting the file name to the waiting request, by double clicking on one of the file names listed, or by typing the entire name.

WARNING: The NL_NONLINC command deletes all data base files with the "NL_" prefix and ".DAT" extension from the user's current directory before fetching any of the four data base files.

6.3.2 Macintosh Environment

The Macintosh executable icon for NONLIN is called PMacNonlin. To start the code, the user double clicks, either with a mouse or track ball, on the PMacNonlin icon. The chemical data base files must be located in the same folder that contains the executable icon. After starting the icon, the program will use the files explicitly labeled BINARYP, COMP, TERNARYP, and LAMBDA in the icon's folder.

A suggested method for organizing folders or directories while running NONLIN on the Macintosh is shown in Figure 6-2 and Figure 6-3. Using this approach, files are grouped as follows:

- all chemical data base files (BINARYP, COMP, TERNARYP and LAMBDA) and the PMacNonlin icon in one folder labeled "HMW_ACTINIDE_DB," as shown in Figure 6-2. New species can be added to these existing chemical database files without affecting the results of calculations performed using previous versions of these database files, as long as a consistent ID numbering scheme is maintained (Sections 7.3 through 7.6).

- the GMIN and INPUT files in another folder. Beneath a major folder labeled "TEST CASES," Figure 6-3 shows two problem-labeled folders, "Am_Acet" and "SOLUB," each containing the GMIN and INPUT files for the solvent extraction and mineral solubility problems, respectively. By default, the OUTPUT file will be placed in the same folder that contains the GMIN and INPUT files.

A screen titled "Output from PMacNonlin" displays the file prompts and writes the file names on the screen after the user has responded to all prompts. The user makes a selection through a window display by navigating the folders or directory tree and double clicking on a file name.

The user can set a folder or directory before selecting or naming any file. The prompts direct the user to:

1. Select INPUT File

2. Select GMIN File

3. Enter OUTPUT File Name

6.4 Setting up and Running Solubility Problem

The user supplies the GMIN and INPUT files. The HMW_ACTINIDE_DB chemical data base files are defined in COMP, BINARYP, TERNARYP, and LAMBDA. The INPUT file has a variable named "ndtyp," which defines the type of experimental data. Solubility data is denoted by setting the "ndtyp" variable to -1.

6.5 Setting up and Running Apparent Stability Constant Problem

NONLIN may be used to fit apparent stability constant data by setting up the problem as a solubility calculation. A detailed discussion and an example problem are provided in Appendix A.

6.6 Setting up and Running Extraction Problem

For a solvent extraction problem, the input files are the same as those for an solubility problem (as listed in Section 6.4). Solvent extraction data is denoted by setting the "ndtyp" variable to -4 in the INPUT file.

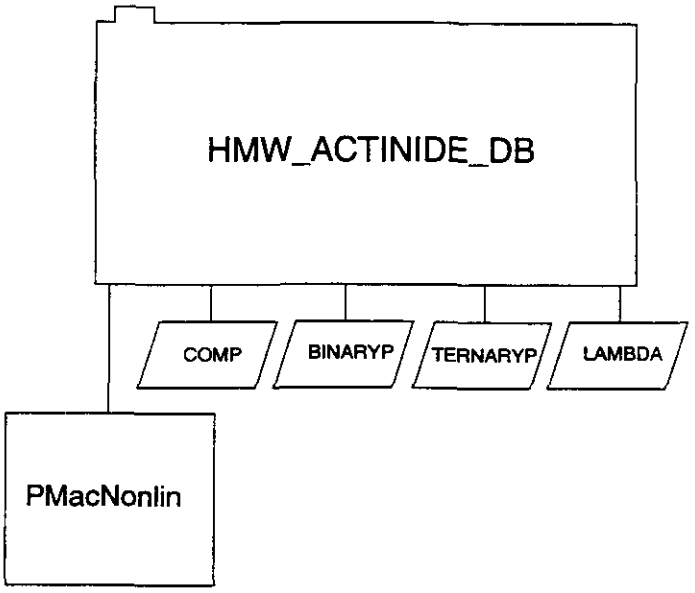


Figure 6-2. Suggested data base folder organization for Macintosh environment.

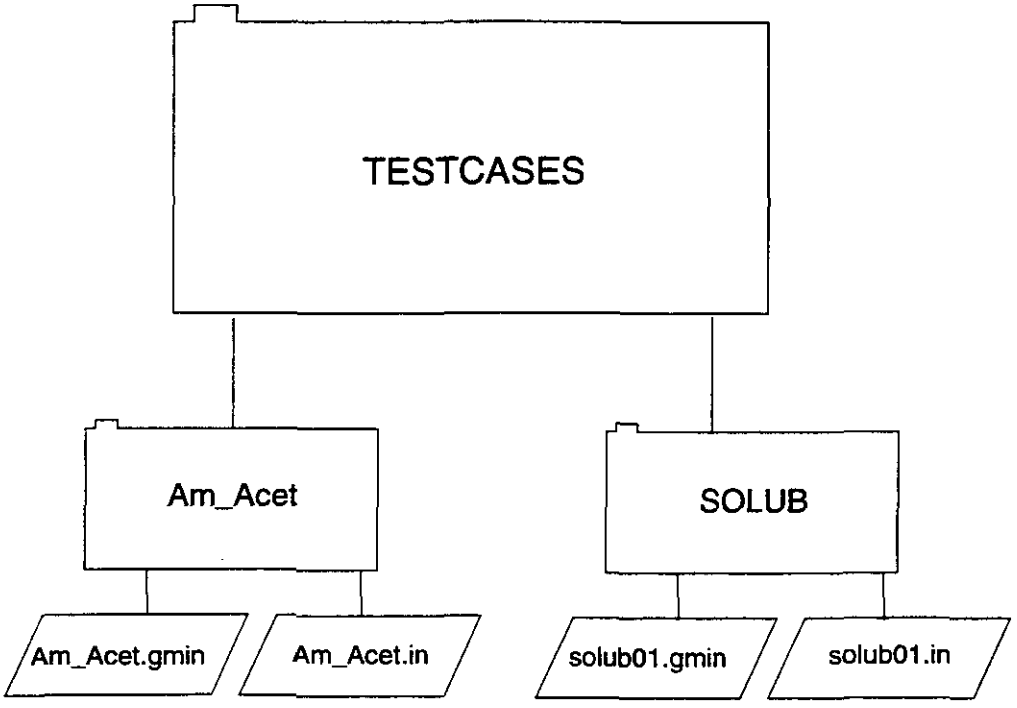


Figure 6-3. Suggested problem folder organization for Macintosh environment.

7.0 DESCRIPTION OF INPUT FILES

Of the six input files for NONLIN (see Figure 6-1), the user sets up the problem in the two files GMIN and INPUT. The other four files COMP, BINARYP, TERNARYP, and LAMBDA are the input chemical data base files. All files are text-based files and can be edited by the user using a convenient text editor.

Although NONLIN reads the INPUT file with both fixed-field and free field-formats[1], it reads all other data files using fixed-field formats only. There are two distinct independent numbers - the parameter key number and the species ID number. Although both numbers have six digits, they are not related in any way. The parameter key number is used only in the INPUT file while the species ID number is used in the other five files. To allow a species to be added or deleted easily, files are terminated by either a zero or a minus one in the ID number field. Blank lines and comments can be inserted with caution. Comments may be placed at the bottom of the file, or, in some cases, at the end of a line where NONLIN does not read them. Comments are used throughout the chemical data base files and the sample files to help the human reader identify the species on a line and document the source of the data or the fields in the file.

A description of all six input files follows.

7.1 GMIN

The GMIN file species are the chemical species to be considered in a particular computer run. The species ID numbers used in GMIN must correspond to species definitions in the COMP file. In addition, aqueous species may have ion interaction parameters specified in BINARYP, TERNARYP, or LAMBDA, but these are not required.

The six-digit ID number is assigned by the user. The first digit is the phase indicator, and can be 0, 1, 2, 3, or 4 for aqueous, solid, solid solution, and two types of adsorbed species, respectively. Only aqueous and solid species are relevant to WIPP use of this code, so only phase types 0 and 1 will be considered henceforth.

The assignment of the remaining five digits is arbitrary, with the only constraint being that each six-digit combination must be unique. The following conventions are suggested to help provide a method to assign ID numbers. Let the second and third digits correspond to the atomic number of the metallic portion of the species (if any) and the fourth and fifth digits correspond to the nonmetallic portion (if any). Use the final digit is used to break redundancies. These scheme is illustrated in Figure 7-1.

For example, the species IDs could be 012000 for aqueous Mg^{++}, 000170 for aqueous Cl^{-}, and 012170 for the $MgCl^{+}$ pair.

---

[1] "Fixed-field format" means that input data is read precisely in the columns specified by the code; "free-field format" means that the input numbers are independent of column formatting (i.e., the numbers in the input file are simply separated by spaces, tabs, or carriage returns). For example, in the sample INPUT file provided in Appendix C, lines 1 through 3, only the first 16 columns are read using a fixed-field format; lines 6 - 37 are read using the free-field format. However, the sample GMIN file provided in Appendix B must be read in its entirety using a fixed-field format input specification.

The order of the species in the file is important. The first species must be water, followed by cations, anions, and neutral species. The solid species are listed last.

The mole numbers for the species are read from the INPUT file. The mole numbers in GMIN file should be set to zero for aqueous species, and nonzero for solid species.

Table 7-1 lists the GMIN file parameters. The "LINE" column refers to the line numbers listed in the EXTR_00.GMIN file. The "Variable Name" column corresponds to the NONLIN program variables. "Permissible Value" column is the only set of values permitted for use with this program. Any other values have unknown consequences.

The EXTR_07.GMIN listing shows a "-1" on line 11 denoting the end of all species. NONLIN will ignore any lines that follow line 11. On lines 3-8 and line 10, NONLIN ignores the comment at the end of the lines following the species ID and mole number.

In Appendix D the sample input file SOLUB_00.GMIN lists six aqueous species and one solid species. NONLIN ignores any lines after line 11.

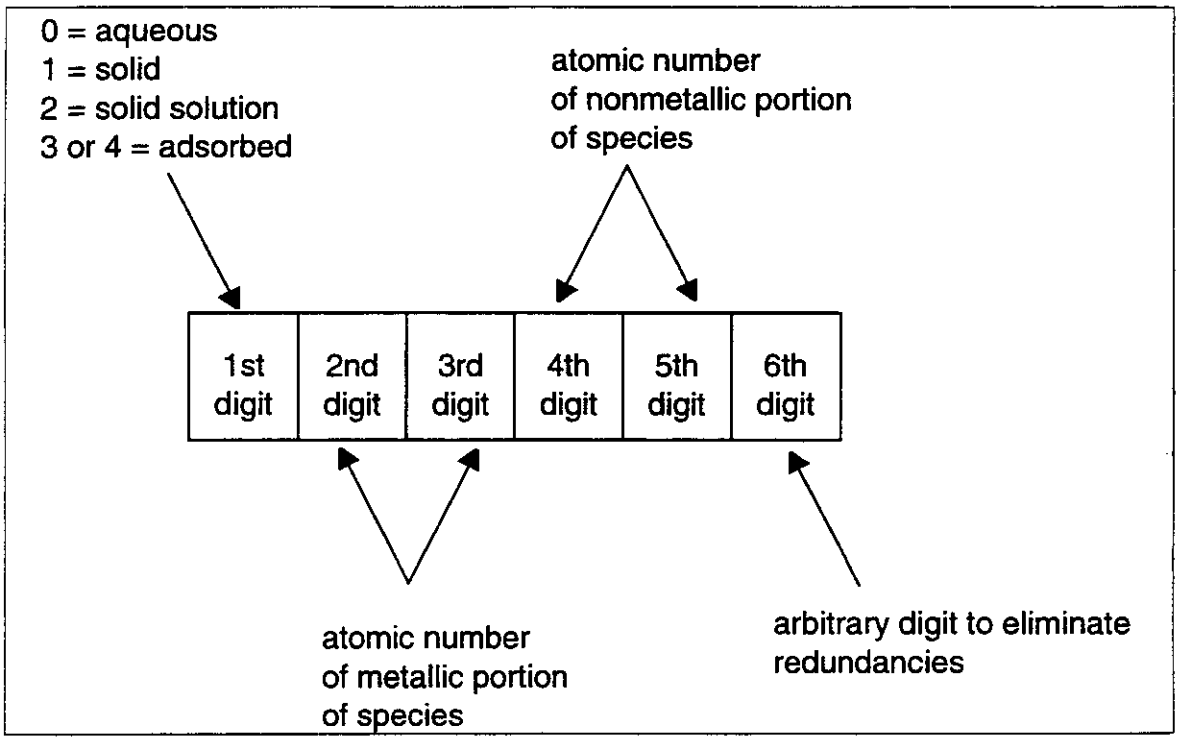


Figure 7-1. Format for six-digit species ID number.

Table 7-1. GMIN File Parameters (Line Numbers Correspond to Sample Listing in Appendix B)

Line	Frmt	Col	Variable Name	Permissible Value	Description
1	1x,I5	1-6	idebg1	0 or 1	normal mode or debug mode, prints intermediate calculations while iterating
	I5	7-11	isopt	0	flag setting the Pitzer ion interaction model
	I5	12-16	idopt	0	flag setting the non-ideal free energy model
	I5	17-21	iphopt	0 or 1	flag for printing species concentrations at end of iterative cycle print after each iteration
2	I3	1-3	iads	0	no adsorption option
3	I6	1-6	id(1)	001080	species ID number for water (water must be listed first)
	F15.3	7-21	x(1)	0.0	unused mole number (read from INPUT file)
4-8	I6	1-6	id(i)		list of aqueous species
	F15.3	7-21	x(i)	0.0	unused mole number (read from INPUT file)
9	I6	1-6	id(i)	000000	end of aqueous species
10	I6	1-6	id(i)	200000-299999	list of solid species
	F15.3	7-21	x(i)	0.0	unused mole number (read from INPUT file)
11	I6	1-6	id(i)	-1	end of all species
12					comment line

7.2 INPUT

The INPUT file is used to specify the experimental data and the thermodynamic parameter(s) to be fitted to the data. The first section lists the parameters to be fitted. In the first two columns, a "-1" is used to signal the end of the parameter list. The next section contains one or two data sets that are used to fit the parameters. Figure 7-2 illustrates the sectioning of an INPUT file using the lines in EXTR_07_EXACT.IN, Appendix C as an example. If there were another experimental data set, it would start on line 22.

In the first section the parameter key is a six-digit number whose structure is divided into three fields where

first and second digits	=	type of parameter
third and fourth digits	=	first ion number
fifth and sixth digits	=	second ion number

The parameter key index table relevant to WIPP use of NONLIN is shown in Table 7-2.

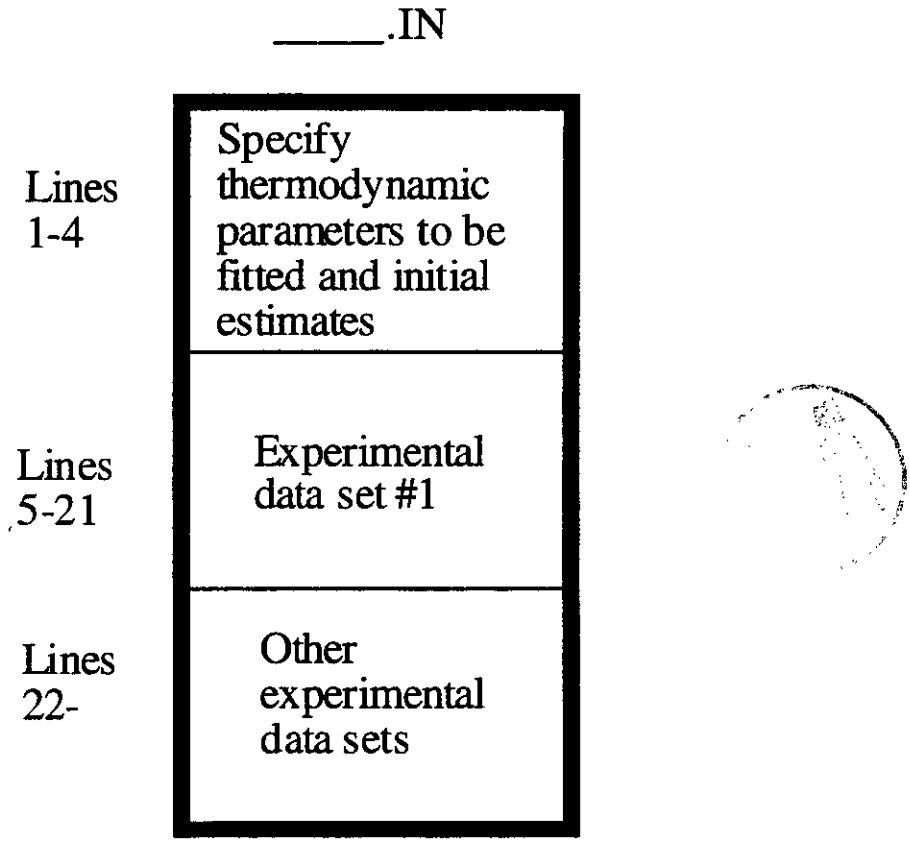
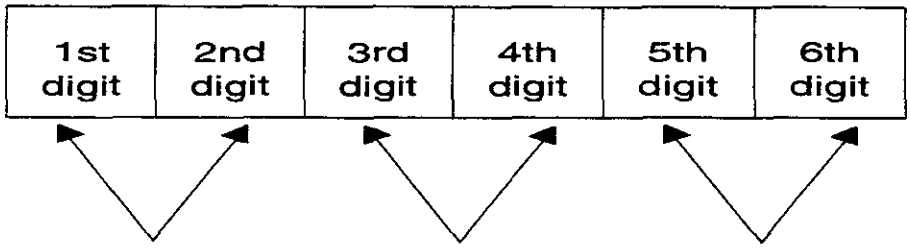


Figure 7-2. Sections of the INPUT file.

Table 7-2. Parameter Key Index Table



Adjustable parameter	Type	First Ion	Second Ion
$\mu°/RT$ (standard chemical potential)	00	00	species position number
$\beta^{(0)}$ (cation-anion pair)	01	cation number	anion number
$\beta^{(1)}$ (cation-anion pair)	02	cation number	anion number
$\beta^{(2)}$ (cation-anion pair)	03	cation number	anion number
C_{MX} (cation-anion pair)*	04	cation number	anion number
θ_{ij} (cation-cation pair)	05	00	cation-cation number
θ_{ij} (anion-anion pair)	06	00	anion-anion number
Ψ_{ijk} (cation-cation-anion triplet)	07	cation-cation number	anion number
Ψ_{ijk} (anion-anion-cation triplet)	08	anion-anion number	cation number
λ (cation-neutral)	09	neutral number	cation number
λ (anion-neutral)	10	neutral number	anion number
λ (neutral-neutral)	11	neutral number	neutral number
ζ_{ijk} (ion-ion-neutral)	12	neutral-cation number	anion number

*C^{ϕ}_{MX} may be computed from C_{MX} by using equation 12 (Section 4.1.2).

To illustrate, consider the species list in Appendix C, i.e.,

	Cation Number	Anion Number	Species Position Number
H_20			01
Na^+	01		02
Th^{++++}	02		03
H^+	03		04
OH^-		01	05
ClO_4^-		02	06

Na^+, Th^{++++}, and H^+ have cation numbers 01, 02, and 03, respectively; OH^- and ClO_4^- have anion numbers 01 and 02, respectively. (The number must be 2 digits.) Neutral species follow the same pattern.

Cation-cation, anion-anion, and neutral-cation numbers are more complicated to specify. These are assigned as follows, illustrated for the cations above. The first cation (Na+) is taken pairwise with the other cations (Th++++, H+) in the order in the list; i.e., Na+ - Th++++ is pairwise interaction 01, Na+ - H+ is pairwise interaction 02. With these, all Na+- cation interactions are specified. The next cation (Th++++) is then taken pairwise with the remaining cations, which in this case is only H+; i.e., Th++++ - H+ is pairwise interaction 03. (Th++++ - Na+ is the same as Na+ - Th++++). Anion-anion and neutral-cation numbers are handled similarly. If the above illustration contained a neutral aqueous species, here called NeuSpec#1, the numbering would be as given in the table below:

	Cation-Cation Number	Anion-Anion Number	Neutral-Cation Number
Na^+ - Th^{++++}	01		
Na^+ - H^+	02		
Th^{++++} - H^+	03		
OH^- - ClO_4^-		01	
NeuSpec#1 - Na^+			01
NeuSpec#1 - Th^{++++}			02
NeuSpec#1 - H^+			03

Therefore, for this illustration, $\theta_{Na^+-Th^{++++}}$ is represented by 050001, and $\psi_{H^+-Th^{++++}-ClO_4^-}$ is represented by 070302.

The OUTPUT file in the section titled "ADJUSTED PARAMETERS" echo prints the parameters that are being fitted by listing the parameters and the species names. This section should be examined to verify that the parameter numbers were selected correctly. This section is listed in Appendix J, lines 102-105; Appendix K, lines 94-95; and Figure A-5, lines 99-103.

When a species parameter is to be fitted, NONLIN ignores the value assigned to that species in the appropriate data base file(s).

The second section of the INPUT file lists an experimental data set, the number of data points, and the data type on one line followed by the data points. A "-1", "0", or a blank line may be used to signal the end of all experimental data sets. A line-by-line description of the INPUT file is provided below in Table 7-3, using the sample listing of EXTR_07_EXACT.IN in Appendix C.

Table 7-3 lists the INPUT file parameters. The "LINE" column refers to the line numbers listed in the EXTR_07_EXACT.IN file. The "Variable Name" column corresponds to the NONLIN program variables. The "Permissible Value" column is the only set of values permitted for use with this program. Any other values have unknown consequences.

Table 7-3. INPUT File Parameters (Line Numbers Correspond to Sample Listing in Appendix C)

Line	Frmt	Col	Variable Name	Permissible Value	Description
1-3	3I2	1-6	ipar1(i), ipar2(i), ipar3(i)	000000-999999	ID of the i^{th} parameter to adjust
	F10.4	7-16	parv(i)	real number	estimate of the i^{th} parameter value (best guess)
4	I2	1-2	ipar1(i)	-1	end of parameters to fit
5	I5	1-5	ndata(k)	1-99999	number of data points in the k^{th} data set
	I5	6-10	ndtyp(k)	1,0,-1,-2,-3, or -4	type of experimental data (1=emf data, 0=osmotic data, -1=solubility data or solid solution data, -2=solid solution data in stoichiometric saturation, -3=adsorption data, -4=solvent extraction data)
6-21	free field		y(i)	positive real number	molar concentration in organic phase for extraction data otherwise set to 0.0 for all other data types
	free field		pph(i)	positive real number	target ph value if a fixed ph value is desired otherwise set to 0.0
	free field		mole(i, j), j=2,nas	positive real number>0	mole numbers for all species except water where water as mole(i,1) is set to 55.508373 within the code
22	I5	1-5	ndata(k)	0 or -1	end of all data sets
23					comment line (not read by NONLIN)

The next data set, if any, would begin on line 22 and would include the number of data points, the type of data, and all of its data points, following the format provided in lines 5 through 21. However, the EXTR_07_EXACT.IN listing shows a "-1" on line 22, which denotes the end of all data sets. NONLIN will ignore any lines that follow line 22. On lines 1-3 NONLIN also ignores the comment following each estimate. The EXTR_07_EXACT.IN shows that the user has

specified three parameters to be fitted (the standard chemical potential $\mu°/RT$, $\beta^{(0)}$, and C_{MX}) with an experimental extraction data set of 16 points.

Line 25 in the IN file of Appendix C, included only for the benefit of the user, shows the value type in each column for data specification. The first column, for extraction problems, is the concentration of the extracted species in the organic phase, here represented by mORG. The second column represents the pH ($=-\log_{10} a_{H^+}$) in all problem types, but is used only when the pH is to remain fixed, which is not the case in either Appendix C or E. The remaining columns give initial estimate molalities for all the aqueous species (except H_2O) from the GMIN file, and in the same order. (By definition, water is always 55.5 moles H_2O/kg H_2O.) These initial estimates should be charge balanced to best represent the chemical system.

In Appendix E the sample input file SOLUB_01.IN shows one parameter, $\mu°/RT$, to be fitted with an experimental solubility data set of 7 data points. On line 3 the data type is set to "-1" for solubility data. NONLIN ignores lines 12-15.

The file SOLUB_01.IN in Appendix E is similar to EXTR_07_EXACT.IN in Appendix C. The first two entries on line 1 indicate that the standard chemical potential of species number 6 (199001 in the GMIN file, corresponding to $H_2Ox•2\ H_2O(s)$) is to be fitted. The -1 (line 2) terminates the list of parameters to be fitted. Line 3 indicates that there are seven data points of type -1 (solubility data). Lines 4 - 10 provide the following data:

- The first column is zero by definition in solubility problems.
- The second column is pH, which is only used when pH is fixed (not in this run).
- The remaining columns correspont to (charge-balanced) species molalities.

These are illustrated in comment line 15 in Appendix E.

The apparent constant stability sample input file AM_ACET.IN in Appendix A, Figure A-2 shows four parameters to be fitted ($\mu°/RT$, $\beta^{(0)}$, $\beta^{(1)}$ and C_{MX}) using the solubility data set of 6 data points. On line 6 the data type is set to "-1" for solubility data.

7.3 COMP Data Base File

Table 7-4 lists the COMP file parameters. The COMP file contains a list of chemical species, the species stoichiometry and charge, and the dimensionless standard chemical potential. The temperature of the thermodynamic data is specified at 25 ° C. The COMP file contains all the species that could be considered by NONLIN in its calculations. The species list must begin with water, followed by other aqueous species, and then the solid species. The list of all chemical species must end with a "-1".

*****NOTE*****

The COMP file listed in Appendix F is not necessarily the file that will be used to support the WIPP 1996 PA calculations. Additional species and elements may be added to the file that will be used to support the 1996 WIPP PA calculations.

Table 7-4. COMP File Parameters (Line Numbers Correspond to Sample Lising in Appendix F)

Line	Frmt	Col	Variable Name	Permissible Value	Description
1-40	I6	1-6	idtmp	000000-999999	six digit species ID number where H_2O must always be the first species declared
	A12	7-16	intmp		name of species
	1x	18			
	I2	19-20	iztmp		charge of species
	F15.3	21-35	u0tmp		standard chemical potential of the species (μ_i°/RT)
	1x	36			
	10(I2, F4.1)	37-96	nt(j),v(j), j=1,10	0-99, 0.0-9999.	atomic number and stoichiometric coefficients for elements comprising the species (i.e. H =1, O = 8, Np = 93, etc.)
41	I6	1-6	idtmp	000000	blank line (species ID = 0)
42	I6	1-6	idtmp	-1	denotes the end of species list

A blank line may be inserted anywhere in the COMP file and the species ID will be assigned the value 0. In this file, the blank line can be used to separate groups of species to improve file readability, e.g., lines 6, 11, and 13. A "-1" on line 42 denotes the end of all species. NONLIN will ignore any comments that follow after the end of species list.

7.4 BINARYP Data Base File

The BINARYP file contains the species ID number in each binary interaction considered (e.g., Na^+-Cl^-, K^+-Cl^-) and the Pitzer ion-interaction parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C_{MX}) for binary systems. The binary interaction list must end with a "000000". A cation anion pair and their Pitzer parameters may be inserted anywhere in this file. Blank lines are not allowed in this file until the end of the list.

In Table 7-5, which describes the input parameters for BINARYP, the "Variable Name" column lists the NONLIN program variables.

*****NOTE*****

The BINARYP file listed in Appendix G is not necessarily the file that will be used to support the WIPP 1996 PA calculations. Additional species and elements may be added to the file that will be used to support the 1996 WIPP PA calculations.

Table 7-5. BINARYP File Parameters (Line Numbers Correspond to Sample Listing in Appendix G)

Line	Frmt	Col	Variable Name	Permissible Value	Description
1-20	I6	1-6	id1	000000-999999	ID of the cation species
	1x	7			
	I6	8-13	id2	000000-999999	ID of the anion species
	F7.3	14-20	tb0		$\beta^{(0)}$ parameter for the cation-anion interaction
	F7.3	21-27	tb1		$\beta^{(1)}$ parameter for the cation-anion interaction
	F7.3	28-34	tb2		$\beta^{(2)}$ parameter for the cation-anion interaction
	F7.3	35-41	tcmx		C_{MX} parameter
21	I6	1-6	id1	000000	end of binary interactions
22-23					comments

NONLIN will ignore any lines following a blank line or a species ID number of "000000".

7.5 TERNARYP Data Base File

The TERNARYP file contains Pitzer ion-interaction parameters θ_{ij} for anion-anion and cation-cation systems and ψ_{ijk} for anion-anion-cation and cation-cation-anion systems. Species can be inserted in any order. For the file listed in Appendix I, the same species ID numbers in the first column were grouped together. Blank lines are not allowed in this file until the end of the list.

In Table 7-6, which describes the parameters in the TERNARYP file, the "Variable Name" column lists the NONLIN program variables.

NONLIN will ignore any comments that follow after species ID number 000000, the end of all ternary species parameters.

*****NOTE*****

The TERNARYP file listed in Appendix H is not necessarily the file that will be used to support the WIPP 1996 PA calculations. Additional species and elements may be added to the file that will be used to support the 1996 WIPP PA calculations.

Table 7-6. TERNARYP File Parameters (Line Numbers Correspond to Sample Listing in Appendix H)

Line	Frmt	Col	Variable Name	Permissible Value	Description
1-5, 10-11	I6	1-6	id1	000000-999999	ID of cation species
	1x	7			
	I6	8-13	id2	000000-999999	ID of cation species
	F7.3	14-20	ttc		θ_{ij} for cation-cation species
	1x	21			
	20(I6,1x,F7.3,1x)	22-320	id3(j1), tpsic(j1), j1=1,20		ID of anion species and ψ_{ijk} for cation-cation-anion species
6-9	I6 1x	1-6 7	id1	000000-999999	ID of anion species
	I6	8-13	id2	000000-999999	ID of anion species
	F7.3	14-20	ttc		θ_{ij} for anion-anion species
	1x	21			
	20(I6,1x,F7.3,1x)	22-320	id3(j1), tpsic(j1), j1=1,20		ID of cation species and ψ_{ijk} for anion-anion-cation species
12	I6	1-6		000000	end of all neutral parameters

7.6 LAMBDA Data Base File

The LAMBDA file (described in Table 7-7) contains Pitzer ion-interaction lambda parameters for neutral species. The species interactions include: neutral-cation, neutral-cation-anion, neutral-anion, and neutral-neutral.

NOTE

The LAMBDA file listed in Appendix I is not necessarily the file that will be used to support the WIPP 1996 PA calculations. Additional species and elements may be added to the file that will be used to support the 1996 WIPP PA calculations.

Table 7-7. LAMBDA File Parameters (Line Numbers Correspond to Sample Listing in Appendix I)

Line	Frmt	Col	Variable Name	Permissible Value	Description
1-2	I6	1-6	id1	000000-999999	ID of the neutral species
	1x	7			
	I6	8-13	id2	000000-999999	ID of cation species
	F7.3	14-20	tlambda		λ parameter for neutral-cation species
	1x	21			
	20(I6,1x,F7.3,1x)	22-27	id3(j1), thol(j1), j1=1,20		for neutral-cation species, ID of anion species and λ parameter for neutral-cation-anion species; a neutral-cation pair may have from zero to twenty anion species and lambda values
None[2]	I6	1-6	id1	000000-999999	ID of the neutral species
	1x,I6	7-13	id2	000000-999999	ID of anion species
	F7.3	14-20	tlambda		λ parameter for neutral-anion species
None[3]	I6	1-6	id1	000000-999999	ID of the neutral species
	1x,I6	7-13	id2	000000-999999	ID of neutral species
	F7.3	14-20	tlambda		λ parameter for neutral-neutral pair
3	I6	1-6		000000	end of neutral species list

[2] No corresponding line numbers in Appendix I since there are no neutral-anion species in the file.

[3] No corresponding line numbers in Appendix I since there are no neutral-neutral species in the file.

In Table 7-7, the "Variable Name" column lists the NONLIN program variables. The neutral species can be inserted in any order. A value for a neutral-cation pair, even if it is zero, must be assigned in order to specify a triplet neutral-cation-anion interaction. For the file in Appendix H, the same neutral species were grouped together with the cations first, and then the anions. There are no neutral-neutral parameters considered in NONLIN. Blank lines are not allowed in this file until the end of the list.

NONLIN will ignore any lines that follow after species ID number 000000, the end of all lambda parameters.

8.0 ERROR MESSAGES

NONLIN is not a particularly user-friendly code. NONLIN will detect errors in species ID numbers and in counting the total number of allowed species. The code will not automatically detect all errors in preparing the GMIN or INPUT files, or the interaction of these input files with the chemical model data files. Therefore, care should be taken to avoid errors. It is important that output from NONLIN be examined to see if it makes sense.

At the end of the OUTPUT file, a successful NONLIN run will display a set of lines with the header "FINAL APPROXIMATE SOLUTION" and the species ID with the converged parameter value. However, the presence of these lines may not necessarily indicate a set of valid values. There may still be errors in any of the files and the entire OUTPUT listing should be scanned carefully.

Error messages are usually listed at the end of the OUTPUT file before NONLIN terminates. A pair of single quotes within a message enclosing a phrase starting with 'value of ...' indicates that the run time value in NONLIN will be listed. A listing of the error messages follows.

- The following messages are printed when the nonlinear routine does not converge:

```
********** ITERATION DID NOT CONVERGE *******
**** MATRIX WITH ZERO ROW IN DECOMP
NO CONVERGENCE IN IMPROV MATRIX NEARLY SINGULAR
**** SINGULAR MATRIX IN DECOMP, ZERO DIVIDE IN SOLVE
********** ITERATION DID NOT CONVERGE *******
```

  If any of the above messages are displayed, the user should start with another set of initial estimates in the INPUT file. If the second message "MATRIX WITH ZERO ROW IN DECOMP" is displayed, the charge balance may be incorrect.

- The following messages are printed when there are more than two solid solution data sets in the INPUT file:

```
**  MORE THAN TWO SOLID SOLUTION DATA SETS  ***
***** ONLY TWO DATA SETS WITH EQUAL POINTS ALLOWED **
```

  If any of the above messages are displayed, the user should limit the number of solubility data sets to two in the INPUT file. In addition, for a data type of -2, the number of data points must be the same in both sets. However, this mode of running NONLIN is not used for the WIPP.

- The following message is printed when a species is listed in the GMIN file and is not in the chemical model data files:

```
SPECIES 'value for ID' NOT FOUND IN DATA FILE
```

If the above message is displayed, the user may have an incorrect species ID in the GMIN file or may need to add the species and its Pitzer parameters to the chemical model data files, i.e., the COMP, BINARYP, LAMBDA, and TERNARYP files.

- The following message is printed when the species listed in the GMIN file exceeds 16:

```
TOO MANY AQUEOUS AND ADSORBED SPECIES
```

If the above message is displayed in the GMIN file, the user should verify that the "000000" species or a blank line separates the aqueous from the solid species or the user should reduce the number of aqueous and adsorbed species.

9.0 DESCRIPTION OF OUTPUT FILE

NONLIN generates an OUTPUT (.OUT) file. The OUTPUT file lists the problem identity, echo prints the input data, computes the goodness of fit using the initial estimates (before any adjustments are made to the key parameters), continues to iterate until the absolute value of the error tolerance test converges to a value $\leq 10^{-5}$, and then prints the final solution.

Table 9-1 explains the OUTPUT (.OUT) file generated from the problem called EXTR_07_EXACT. The "Line" column refers to the line numbers listed in EXTR_07_EXACT.OUT. "Variable Name" column shows applicable NONLIN program variables and some formulas.

Table 9-1. OUTPUT File Description (Line Numbers Correspond to Sample Listing in Appendix J)

Line	Variable Name	Description
1	versn	notation; program name 'NONLIN' and version number
3		notation; code author
5-7	infnm, gmfnm, oufnm	user-supplied input file name, GMIN file name and output file name
9-21		table of aqueous and solid species and characteristics
	id(i), name(i), a(i,j), j=1,ncomp	species from GMIN, name from COMP, mole number from GMIN, charge and standard chemical potential from COMP
23		title for table of constraint equations

24	ncol(j), j=1,ncomp	column labels where 0 is charge and all others are elemental atomic numbers
25-31	name(i), a(i,j) j=1,ncomp	for each species--name, charge, and number of atoms in one molecule or ion
33		notation; closed two files
35-38	cofnm, bifnm, tefnm, lafnm	chemical data base file names
40		notation; Pitzer activity coefficient model used
42-48	name(jpc(i)), name(jpa(j)), b0(i,j), b1(i,j), b2(i,j),cmx(i,j)	table of single electrolyte parameters; listing cation-anion binary interactions, $\beta^{(0)}$, $\beta^{(1)}$,$\beta^{(2)}$, and C_{MX} parameters for i^{th} cation, j^{th} anion interactions
50-58		table of ternary electrolyte parameters; listing cation-cation-anion, if any; anion-anion-cation, if any
52	name(jpa(k)), k=1,na	column labels of anion species
53-55	name(jpc(i), name(jpc(j), tc(nt), (psic(nt,k), k=1,na)	cation-cation ternary interaction parameter, θ_{ij} and any cation-cation-anion ternary interaction parameters, Ψ_{ijk}
57	name(jpc(k)), k=1,nc	column labels of cation species
58	name(jpa(i), name(jpa(j), ta(nt), (psia(nt,k), k=1,nc)	anion-anion ternary interaction parameters, θ_{ij} and any anion-anion-cation ternary interaction parameters, Ψ_{ijk}
None[4]		table of neutral ion parameters, if any
	name(jpn(k), k=1,nn	column labels of neutral species
	name(jpc(i)), (clamb(j,i), j=1,nn)	neutral-cation species and binary interaction values, λ_{ij}
	name(jpa(i)), (alamb(j,i), j=1,nn)	neutral-anion species and binary interaction values, λ_{ij}

[4] No corresponding line numbers in Appendix J since there are no neutral ion parameters in the file.

	name(jpn(i)), (nlamb(j,i), j=1,nn)	neutral-neutral species and binary interaction values, λ_{ij}
None[5]		table of higher order lambdas, if any
	name(jpa(k)), k=1,na	column labels of anion species
	name(jpn(i), name(jpc(j), (holamb(nt,k), k=1,na)	neutral-cation-anion species and ternary interaction values, ζ_{ijk}
60-62	ns, ncomp, irank	count of species, components and independent constraints
64	ndtyp(k)	type of experimental data for data set #1
66-85		table listing the experimental data points
69	name(i),i=2,nas	column labels of species
70-85	mole(i,j),j=2,nas	input molality of each species
		type of experimental data for data set #k with table #k, where k=2...ndataset
87-99	parv(j),j=1,npar, fnorm	solution vector and norm from evaluating function at the initial estimates and each subsequent adjustment to the estimates
102-106	ipar1(i), name1, name2, name3, parv(i)	table of adjusted parameters: the parameter, species either (name1) or (name1 and name2) or (name1, name2 and name3) of first and second ions, and final fit value
107-125	y(m),sigma	calculated difference for data set #1, using the initial estimates
127-129	adev,sdev	adev = $\sum$abs(sigma)/ndatat; sdev = $(\sum(\text{sigma}*\text{sigma})/\text{ndatat})^{0.5}$
		calculated difference for data set #k, where k=2...ndataset; adev,sdev
131-149		table of final molalities
133	names(i),i=2,nas	column labels of species names

[5] No corresponding line numbers in Appendix J since there are no higher order lambdas in the file.

134-149	mole(i,j),j=2,nas	calculated molality for each species
151-169		table of final log activities
153	names(i),i=2,nas	column labels of species names
154-169	tloga(i,j),j=2,nas	calculated log activity for each species
171-189		table of calculated log activity coefficients
173	names(i),i=2,nas	column labels of species names
174-189	(tloga(i,j)-log10(mole(i,j)), j=2,nas	calculated log activity coefficients for each species
191		notation; system at equilibrium
192-278		standard chemical potential, $\beta^{(0)}$, and C_{MX}
280	fnorm	norm of the solution vector
283	info	exit parameter
286 - 291	ipar1(i), ipar2(i), ipar3(i), parv(i)	table of approximate solutions

10.0 REFERENCES

References from this manual (NONLIN)

Davies, C.W. 1962. *Ion Association.* Butterworths, London.

Denbigh, K. 1981. *The Principles of Chemical Equilibrium.* Cambridge: Cambridge University Press.

Dongarra, J.J., C.B. Moler, J.R. Bunch, and G.W. Stewart. 1979. *LINPACK User's Guide.* The Society for Industrial and Applied Mathematics, Philadelphia.

Felmy, A.R. 1990. *GMIN: A Computerized Chemical Equilibrium Model Using A Constrained Minimization of the Gibbs Free Energy.* PNL-7281. Richland, Washington: Pacific Northwest Laboratory.

Felmy, A.R. 1995. "GMIN, A Computerized Chemical Equilibrium Program Using a Constrained Minimization of the Gibbs Free Energy: Summary Report," *Chemical Equilibrium and Reaction Models*, SSSA Special Publication 42, Soil Science Society of America, American Society of Agronomy, 677 S. Segoe Rd., Madison WI 53611, USA., pp. 377-407

Felmy, A.R., and J.H. Weare. 1986. "The Prediction of Borate Mineral Equilibria in Natural Waters: Application to Searles Lake, California." *Geochimica et Cosmochimica Acta*, Vol. 50: pp. 2771-2783.

Gill, P.E., and W. Murray. 1974. "Newton-Type Methods for Unconstrained and Linearly Constrained Optimization." *Mathematical Programming*, Vol. 7: pp. 311-350.

Greenberg, J.P., J.H. Weare, and C.E. Harvie. 1985. "An Equilibrium Computation Algorithm for Complex Highly Nonideal Systems: Application to Silicate Phase Equilibria." *High Temperature Science*, Vol. 20: pp. 141-162.

Harvie, C.E., J.P. Greenberg, and J.H. Weare. 1987. "A Chemical Equilibrium Algorithm for Highly Non-ideal Multiphase Systems: Free Energy Minimization." *Geochimica et Cosmochimica Acta*, Vol. 51 #5: pp. 1045-1057.

Harvie, C.E., N. Møller, and J.H. Weare. 1984. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strength at 25°C." *Geochimica et Cosmochimica Acta*, Vol. 48: pp. 723-751.

Harvie, C.E., and J.H. Weare. 1980. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-Cl-SO_4-H_2O System from Zero to High Concentration at 25°C." *Geochimica et Cosmochimica Acta*, Vol. 44: pp. 981-997.

Novak, C.F., and S.C. Babb. 1996. "WIPP PA User's Manual for FMT, Version 2.0". WPO # 28119, Albuquerque, New Mexico: Sandia National Laboratories.

Novak, C.F., and K.E. Roberts. 1994. *Thermodynamic Modeling of Neptunium(V) Solubility in Na-CO_3-HCO_3-Cl-ClO_4-H-OH-H_2O Electrolytes*. SAND94-0805C. Albuquerque, New Mexico: Sandia National Laboratories.

Pitzer, K.S. 1991. *Activity Coefficients in Electrolyte Solutions*. Boca Raton, Florida: CRC Press. Second Edition.

Pitzer, K.S. 1973. "Thermodynamics of Electrolytes I: Theoretical Basis and General Equations." *Journal of Physical Chemistry*, Vol. 77: pp. 268-277.

Pytkowicz, R. M. 1979. *Activity Coefficients in Electrolyte Solutions*. Boca Raton, Florida: CRC Press. First Edition.

Smith, J.M., and H.C. Van Ness. 1975. *Introduction to Chemical Engineering Thermodynamics*. New York: McGraw-Hill.

References from GMIN user's manual and technical reference (i.e., Felmy, 1990):

Davies, C.W. 1962. *Ion Association* . Butterworths, London.

Davis, J.A., R.O. James, and J.O. Leckie. 1978. "Surface Ionization and Complexation at the Oxide/Water Interface: I. Computation of Electrical Double Layer Properties in Simple Electrolytes." *Journal of Colloid and Interface Science*, Vol. 63: pp. 480-499.

Dongarra, J.J., C.B. Moler, J.R. Bunch, and G.W. Stewart. 1979. *LINPACK User's Guide*. The Society for Industrial and Applied Mathematics, Philadelphia.

Felmy, A.R. 1988. *Equilibrium and Nonequilibrium Transformations in Evaporites: Development and Application of Thermodynamic Models*.. PhD Dissertation, The University of California, San Diego, La Jolla, California.

Felmy, A.R., and J.H. Weare. 1986. "The Prediction of Borate Mineral Equilibria in Natural Waters: Application to Searles Lake, California." *Geochimica et Cosmochimica Acta*, Vol. 50: pp. 2771-2783.

Felmy, A.R., D.C. Girvin, and E.A. Jenne. 1984. *MINTEQ - A Computer Program for Calculating Aqueous Geochemical Equilibria*. EPA 600/3-84-032, U.S. Environmental Protection Agency, Office of Research and Development, Athens, Georgia.

Gill, P.E., and W. Murray. 1974. "Newton-Type Methods for Unconstrained and Linearly Constrained Optimization." *Mathematical Programming*, Vol. 7: pp. 311-350.

Greenberg, J.P., J.H. Weare, and C.E. Harvie. 1985. "An Equilibrium Computation Algorithm for Complex Highly Nonideal Systems: Application to Silicate Phase Equilibria." *High Temperature Science*, Vol. 20: pp. 141-162.

Guggenheim, E.A. 1967. *Thermodynamics*. North Holland, New York.

Harvie, C.E., J.P. Greenberg, and J.H. Weare. 1987. "A Chemical Equilibrium Algorithm for Highly Non-ideal Multiphase Systems: Free Energy Minimization." *Geochimica et Cosmochimica Acta*, Vol. 51 #5: pp. 1045-1057.

Parkhurst, D.L., D.C. Thorstenson, and L.N. Plummer. 1980. *PHREEQE - A Computer Program for Geochemical Calculations.* Water Resources Investigations 80-96, U.S. Geological Survey, Washington, D.C.

Pitzer, K.S. 1973. "Thermodynamics of Electrolytes I: Theoretical Basis and General Equations." *Journal of Physical Chemistry*, Vol. 77: pp. 268-277.

Pitzer, K.S. 1991. *Activity Coefficients in Electrolyte Solutions.* Boca Raton, Florida: CRC Press.

Plummer, L.N., and E. Busenberg. 1987. "Thermodynamics of Aragonite-Strontianite Solid Solutions: Results from Stoichiometric Solubility at 25 and 76°C." *Geochimica et Cosmochimica Acta*, Vol. 51: pp. 1393-1411.

Strang, G. 1980. *Linear Algebra and Its Applications.* Academic Press, New York.

Van Zeggeren, F., and S.H. Storey. 1970. *The Computation of Chemical Equilibria.* Cambridge University Press, London.

Westall, J. 1979. *MICROQLII. Computation of Adsorption Equilibria in BASIC.* EAWAG, CH-8600, Swiss Federal Institute, Duebendorf, Switzerland.

Wolery, T.J. 1979. Calculation of Chemical Equilibrium between Aqueous Solutions and Minerals. The EQ3/6 Software Package. UCRL-52658, Lawrence Livermore Laboratory, Livermore, California.

Zachara, J.M., D.L. Girvin, R.L. Schmidt, and C.T, Resch. 1987. "Chromate Adsorption on Amorphous Iron Oxyhydroxide in the Presence of Major Groundwater Ions." *Environmental Science and Technology*, Vol. 21(6): pp. 589-594.

Journal articles that provide data for use in NONLIN:

Felmy, A.R., and D. Rai. 1992. "An Aqueous Thermodynamic Model for a High Valence 4:2 Electrolyte Th^{4+}-SO_4^{2-} in the System Na^+-K^+-Li^+-NH_4^+ -SO_4^{2-} -HSO_4^- -H_2O to High Concentration." *Journal of Solution Chemistry*, Vol. 21 #5: pp. 407-423.

Felmy, A.R., D. Rai, and R.W. Fulton. 1990. "The Solubility of $AmOHCO_3(c)$ and the Aqueous Thermodynamics of the System Na^+-Am^{3+}-HCO_3^- -OH^--H_2O." *Radiochimica Acta*, Vol. 50: pp. 193-240.

Felmy, A.R., D. Rai, and M.J. Mason. 1991. "The Solubility of Hydrous Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model." *Radiochimica Acta*, Vol. 55: pp. 177-185.

Felmy, A.R., D. Rai, J.A. Schramke, and J.L. Ryan. 1989. "The Solubility of Plutonium Hydroxide in Dilute Solution and in High-Ionic-Strength Chloride Brines." *Radiochimica Acta*, Vol. 48: pp. 29-35.

Harvie, C.E., and J.H. Weare. 1980. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-Cl-SO_4-H_2O System from Zero to High Concentration at 25°C." *Geochimica et Cosmochimica Acta*, Vol. 44: pp. 981-997.

Harvie, C.E., N. Møller, and J.H. Weare. 1984. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strength at 25°C." *Geochimica et Cosmochimica Acta*, Vol. 48: pp. 723-751.

Novak, C.F., and K.E. Roberts. 1994. *Thermodynamic Modeling of Neptunium(V) Solubility in Na-CO_3-HCO_3-Cl-ClO_4-H-OH-H_2O Electrolytes*, SAND94-0805C. Albuquerque, New Mexico: Sandia National Laboratories.

Rai, D., A.R. Felmy, and R.W. Fulton. 1994. "The Nd^{3+} and Am^{3+} Ion Interactions with SO_4^{2-} and their Influence on $NdPO_4$(c) Solubility." *Journal of Solution Chemistry*, submitted June 1994.

Rao, L., D. Rai, A.R. Felmy, and RW. Fulton. 1994. "Solubility of $NaNd(CO_3)_2 \cdot 6H_2O$ in Concentrated Sodium Carbonate and Sodium Bicarbonate Solutions." *Radiochimica Acta*, Vol. ___: ___-___. SAND94-1948J.

Roy, R.N., K.M. Vogel, C.E. Good, W.B. Davis, L.N. Roy, D.A. Johnson, A.R. Felmy, and K.B. Pitzer. 1992. "Activity Coefficients in Electrolyte Mixtures: HCl + $ThCl_4$ + H_2O for 5°–55°C." *Journal of Physical Chemistry*, Vol. 96: pp. 11065-11072.

11.0 APPENDICES

Note

The numbers to the left of each line in Appendices A through K are not actually present in the files and screen displays; they are used solely to reference the lines in this guide

Note

The sample files and displays provided in Appendices A through K are examples *only*. They *are not* necessarily representative of files used to support the 1996 WIPP PA regulatory calculation.

Appendix A - Example for Calculating Thermodynamic Parameters from Apparent Stability Constants

NONLIN was not originally designed to fit apparent stability constant data. However, because of the flexibility of thermodynamics, apparent stability constant data can be rewritten to look like a system of solubility data, and these data can then be fitted in the usual way with NONLIN. This section describes and illustrates this process for the 1:1 americium acetate complex.

The complexation of Am(III) with acetate ion proceeds according to the reaction

$$Am^{3+} + Ac^{-} \leftrightarrow AmAc^{2+} \tag{A-1}$$

with the corresponding equilibrium expression

$$\beta^{\circ} = \frac{\gamma_{AmAc^{2+}}}{\gamma_{Am^{3+}}\gamma_{Ac^{-}}} \frac{m_{AmAc^{2+}}}{m_{Am^{3+}} m_{Ac^{-}}} \tag{A-2}$$

or

$$\beta^{app} = \beta^{\circ}\frac{\gamma_{Am^{3+}}\gamma_{Ac^{-}}}{\gamma_{AmAc^{2+}}} = \frac{m_{AmAc^{2+}}}{m_{Am^{3+}} m_{Ac^{-}}} \tag{A-3}$$

where β° is the thermodynamic stability constant and β^{app} is the apparent stability constant. We can define a fictitious solid AmAc/Am/Ac(s) based on reaction A-1, giving

$$AmAc/Am/Ac(s) \leftrightarrow AmAc^{2+} - Am^{3+} - Ac^{-} \tag{A-4}$$

which has the corresponding solubility product expression

$$K_{sp} = \frac{\gamma_{AmAc^{2+}}}{\gamma_{Am^{3+}}\gamma_{Ac^{-}}} \frac{m_{AmAc^{2+}}}{m_{Am^{3+}} m_{Ac^{-}}} \tag{A-5}$$

Note that the solubility expression in Equation A-5 is identical to that for the stability constant in Equation A-2. For this reason, by declaring the fictitious solid in Equation A-4, we can fit apparent stability constant data as if it were solubility data.

At equilibrium, the change in Gibbs free energy of reaction A-4 is zero by definition. Using this fact, we can rearrange the condition for equilibrium of Equation A-4 to the expression

$$\left[\left(\frac{\mu^\circ}{RT}\right)_{AmAc^{2+}} - \left(\frac{\mu^\circ}{RT}\right)_{AmAc/Am/Ac(s)}\right] + \ln\left(\gamma_{AmAc^{2+}}\, m_{AmAc^{2+}}\right) = \left(\frac{\mu}{RT}\right)_{Am^{3+}} + \left(\frac{\mu}{RT}\right)_{Ac^-} \qquad \text{(A-6)}$$

In Equation A-6 we will generally know the quantities on the right hand side of the equation, i.e., the dimensionless standard chemical potentials and the appropriate activity coefficient parameters for the uncomplexed species; all unknown quantities are on the left hand side. Thus, this method can be used to fit both the standard chemical potential of the aqueous complex, in this case $AmAc^{2+}$, and the activity coefficient parameters that contribute to $\gamma_{AmAc^{2+}}$. This method fits the standard chemical potential for the linear combination shown in square brackets in Equation A-6. Because we are not interested in the value for $\left(\frac{\mu^\circ}{RT}\right)_{AmAc/Am/Ac(s)}$ we can specify that $\left(\frac{\mu^\circ}{RT}\right)_{AmAc/Am/Ac(s)} = 0$ for the calculation and fit a value for $\left(\frac{\mu^\circ}{RT}\right)_{AmAc^{2+}}$ directly. Alternatively, we can arbitrarily assign a value $\left(\frac{\mu^\circ}{RT}\right)_{AmAc^{2+}} = 0$ and fit the linear combination in the brackets above, which will yield a fitted value equal to $-\left(\frac{\mu^\circ}{RT}\right)_{AmAc^{2+}}$.

An additional subtlety must be addressed in fitting apparent stability constant data. These data provide information on the molality quotients of the various species in solution, which in the illustration are Am^{3+}, Ac^-, and $AmAc^{2+}$. In order to fit these apparent stability constant values, the individual concentrations of the species Am^{3+}, Ac^-, and $AmAc^{2+}$ must be constrained to be constant throughout the computer run. This can be accomplished by adding "constraint" elements, called "CE" for short, to the species in question. Consider the following table of stoichiometries.

	0 (charge)	95 (Am(III))	89 (Acetate)	71 (CE#1)	72 (CE#2)	73 (CE#3)
Am3+	3	1	0	0	1	0
Ac–	–1	0	1	1	0	0
AmAc2+	2	1	1	0	0	1
AmAc/Am/Ac(s)	0	0	0	–1	–1	1

One can see by inspection that the linear combination of the stoichiometries as specified in Equation A-1 holds. By declaring the stoichiometries of the species in this way, the molality values, as specified in the INPUT file, are constrained to remain constant throughout the fitting run. This means that the input values of $m_{Am^{3+}}$, m_{Ac^-}, and $m_{AmAc^{2+}}$ will remain the same throughout the run.

The final step is specifying input concentrations $m_{Am^{3+}}$, m_{Ac^-}, and $m_{AmAc^{2+}}$ that correspond to the apparent stability constant data. A simple way to accomplish this would be to arbitrarily assign values to $m_{Am^{3+}}$ and m_{Ac^-} and then calculate the values for $m_{AmAc^{2+}}$ from the apparent stability constant data and Equation A-3.

The required NONLIN files for this example are given below. This problem calculates the dimensionless standard chemical potential of the fictitious solid AmAc/Am/Ac(s) (which is equal to the dimensionless standard chemical potential of $AmAc^{2+}$) and the ion interaction parameters $\beta^{(0)}_{AmAc^{2+}\text{ - }Cl^-}$, $\beta^{(1)}_{AmAc^{2+}\text{ - }Cl^-}$, and $C^{\phi}_{AmAc^{2+}\text{ - }Cl^-}$. Figure A-1 is the GMIN file. Figure A-2 is the INPUT file, giving the parameters to be fitted and the initial estimates for those parameter values on lines 1 to 4, terminated with the –1 on line 5. Line 6 indicates that there are six data

points of solubility type data, and lines 7 through 12 give the species concentrations. Data input is terminated with the –1 on line 13.

The COMP file is given in Figure A-3. Note that the fictitious solid phase AmAc/Am/Ac(s) is included (line 34) and that the stoichiometries of Am^{3+}, Ac^{-}, and $AmAc^{2+}$ (lines 16, 22, and 19, respectively) have been modified by the addition of constraint elements as discussed above.

The BINARYP file is given in Figure A-4. The default value of ion interaction parameters is zero if they are not explicitly included in the BINARYP, TERNARYP, or LAMBDA files.

The results of the NONLIN run are given in the OUTPUT file of Figure A-5. The following are some points to note here: lines 9 to 33 echo print the input species names and IDs and the specified stoichiometries, as read from COMP; lines 44 to 65 echo print the ion interaction parameters read from BINARYP, TERNARYP, and LAMBDA; lines 71-82 echo print the input molalities read from INPUT; lines 84-95 print the estimates of parameter values in each fitting iteration (and the initial set, line 84, are the values given in lines 1 to 4 of the INPUT file); and lines 99 to 103 present the best-fit parameter values along with specification of what those parameters are (in human, not computer, symbology). Finally, note that the "equilibrated" molalities, i.e., lines 165 to 173, are identical to the input molalities because of the constraint elements that were added.

To compare the input values to the model-calculated values, perform the following steps:

1. Remove the fictitious elements from the COMP file.

2. Add the newly regressed parameters to the data base and run NONLIN without fitting any parameters. (Note that in this sample problem the fictitious elements 71, 72, and 73 have been removed from the COMP file. See lines 17, 20, 23, and 34 in Figure A-3 and compare with corresponding line numbers in Appendix F.)

3. Add the newly regressed standard chemical potential, as shown on line 20 in Appendix F.

4. Add the Pitzer parameters to the BINARYP file (see line 21 in Figure A-4). Note that C^{ϕ} is calculated using Equation 4-12 (on page 10); i.e.,

$$C^{\phi}_{AmAc^{2+}\,Cl^-} = C_{AmAc^{2+}\,Cl^-} \cdot 2 \cdot \left|Z_{AmAc^{2+}} Z_{Cl^-}\right|^{1/2} \qquad \text{(A-7)}$$

substituting in the values provided at the end of Figure A-5, one gets

$$\begin{aligned} C^{\phi}_{AmAc^{2+}\,Cl^-} &= -3.5943059 \times 10^{-2} \cdot 2 \cdot |2 \cdot 1|^{1/2} \\ &= -1.02 \times 10^{-1} \end{aligned} \qquad \text{(A-8)}$$

5. Run NONLIN without fitting any parameters, using the GMIN file in Figure A-6, the input file shown in Figure A-7, and the COMP database file shown in Figure A-8 (the same binary database file is used as before; see Figure A-4). The final output is shown in Figure A-9.

Figure A-10 contrasts the β_{app} calculated using Equation A-3 from the input molalitities (lines 75 to 80 in Figure A-9) with the β_{app} line using the curve-fitted final molalities (lines 101 to 106 in Figure A-9).

Note that in this sample problem NONLIN reports an abnormal termination condition because there is no solid phase to equilibrate with. This outcome is logical because NONLIN equilibrated the aqueous phase and then realized there was no solid phase (i/e., no AmAc/Am/Ac(s)) present.

The problem could be run by treating the solid phase as if it existed by adding the following species to the COMP file: AmAc/Am/Ac(s). The resulting GMIN file is shown in Figure A-11. The COMP database and output files are shown in Figures A-12 and A-13, respectively. WHEN the above species is added, NONLIN terminates normally. However, this calculation really has no

meaning. The new solid species AmAc/Am/Ac(s) is a solid with no chemical element in it, which can be thought of as an "empty" or "virtual" solid that solely satisfies NONLIN's need for a solid phase to equilibrate with.

See Table 7-1 for explanation of this listing.

```
0     0     0     0
0
001080       0.00000000        1   0 H2O
011000       0.00000000        2   1 Na+
001000       0.00000000        3   2 H+
095001       0.00000000        4   3 Am+++F
095891       0.00000000        5   4 AmAc++F
000170       0.00000000        6   1 Cl-
000891       0.00000000        7   2 Ac-F
000000
195890       0.00000000        8 AmAc/Am/Ac(s)
-1
-1
```

Figure A-1. Sample Input File: AM_ACET.GMIN

See Table 7-3 for explanation of this listing.

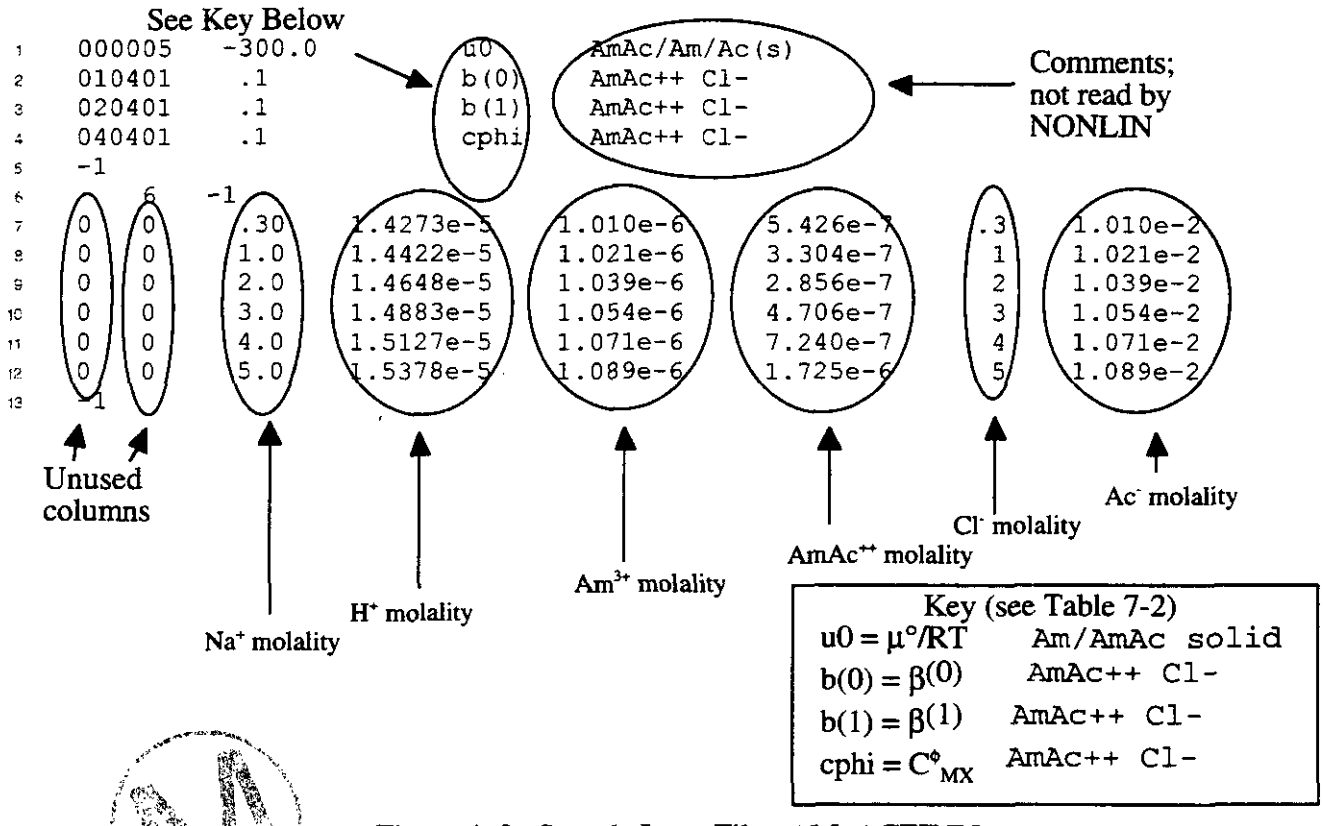


Figure A-2. Sample Input File: AM_ACET.IN

See Table 7-4 for explanation of this listing.

```
001080H2O              0        -95.6635  1 2.0 8 1.0

001000H+               1         000.000  1 1.0
011000Na+              1        -105.651 11 1.0
019000K+               1        -113.957 19 1.0

000080OH-             -1         -63.435  1 1.0 8 1.0
000161HSO4-           -1        -304.942 16 1.0 8 4.0 1 1.0
000170Cl-             -1        -52.9550 17 1.0
017080ClO4-           -1          -73.81 17 1.0 8 4.0

000050B(OH)3(aq)       0        -390.810  5 1.0 8 3.0 1 3.0

090000Th++++           4        -284.227 90 1.0
093080Np(V)O2+         1        -369.109 93 1.0 8 2.0
095000Am+++            3        -241.694 95 1.0
095001Am+++F           3        -241.694 95 1.072 1.0

095890AmAc++           2        -395.358 95 1.089 1.0
095891AmAc++F          2         999.999 95 1.089 1.073 1.0

000890Ac-             -1        -147.347 89 1.0
000891Ac-F            -1        -147.347 89 1.071 1.0

000990Ox=             -2          -272.2 99 1.0
001990HOx-            -1         -281.94 99 1.0 1 1.0
001991H2Ox(aq)         0         -284.99 99 1.0 1 2.0

093890NpO2Ac(aq)       0        -519.800 93 1.0 8 2.089 1.0

101990H2Ox.2H2O(s)     0         999.999 99 1.0 1 6.0 8 2.0
111990Na2Ox(s)         0         999.999 99 1.011 2.0

195890AmAc/Am/Ac(s)    0           0.000 73 1.071-1.072-1.0

199002Na+/NpO2+EX                 999.999 93-1.011 1.0 8-2.0
199003Na+/Th++++EX                999.999 90-1.011 4.0

111170       Halite              -154.990 17 1. 11 1.
119172      Sylvite              -164.840 19 1. 17 1.

    -1
```

Figure A-3. Listing of AM_ACET_COMP.DAT

See Table 7-5 for explanation of this listing.

```
011000 000170  .0765  .2664   .000 .00127   Na+ - Cl-
011000 000161  .0454   .398   .000  .0000   Na+ - HSO4-
011000 000080  .0864   .253   .000  .0044   Na+ - OH-
011000 017080  .0554 0.2755   .000-.00118   Na+ - ClO4-
011000 001990 -.0307  .000    .000   .000   Na+ - HOx-
011000 000990  .0028  1.661   .000   .027   Na+ - Ox=
011000 000890  .1426  .22     .000-.00629   Na+ - Ac-
011000 000891  .1426  .22     .000-.00629   Na+ - Ac-F
019000 000170 .04835  .2122   .000-.00084   K+ - Cl-
019000 000161 -.0003  .1735   .000   .000   K+ - HSO4-
019000 000080  .1298   .320   .000  .0041   K+ - OH-
001000 000170  .1775  .2945   .000  .0008   H+ - Cl-
001000 000161  .2065  .5556   .000   .000   H+ - HSO4-
001000 017080  .1747 0.2931   .000 .00819   H+ - ClO4-
090000 000170 1.092   13.7   -160.  -.112   Th++++ - Cl-  Roy et al. 1992
090000 017080 1.186   27.3    .000 -.0566  Th++++ - ClO4-  GRC Extr Data
093080 000170  .1415  .281    .000   .000   NpO2+ - Cl-   NFRK95
093080 017080  .257   .180    .000  .0081   NpO2+ - ClO4- NFRK95
095000 000170  .6117 5.403    .000 -.0284   Am+++ - Cl-
095001 000170  .6117 5.403    .000 -.0284   Am+++F - Cl-
095890 000170  .2270 2.154    .000 -.102    AmAc++ - Cl-
000000

cation anion   beta0 beta1   beta2  cphi
```

Figure A-4. Sample listing of AM_ACET_BINARYP.DAT

See Table 9-1 for explanation of this listing.

```
 NONLIN   V2.0

 NONLIN was developed by A.R. Felmy

 INPUT      file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET.IN;1
 GMIN       file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET.GMIN;1
 OUTPUT     file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET.OUT;1

            AQUEOUS SPECIES

   ID       NAME            MOLES        Z    u0rt
  1080H2O                0.000000000000   0.    -95.663
 11000Na+                0.000000000000   1.   -105.651
  1000H+                 0.000000000000   1.      0.000
 95001Am+++F             0.000000000000   3.   -241.694
 95891AmAc++F            0.000000000000   2.    999.999
   170Cl-                0.000000000000  -1.    -52.955
   891Ac-F               0.000000000000  -1.   -147.347
          SOLID PHASES

   ID       NAME            MOLES        Z    u0rt
195890AmAc/Am/Ac(s     0.000000000000    0.       0.000

            CONSTRAINT EQUATIONS
                   0      1      8      11     95     72     89     73     17     71
H2O              0.0    2.0    1.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
Na+              1.0    0.0    0.0    1.0    0.0    0.0    0.0    0.0    0.0    0.0
H+               1.0    1.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0
Am+++F           3.0    0.0    0.0    0.0    1.0    1.0    0.0    0.0    0.0    0.0
AmAc++F          2.0    0.0    0.0    0.0    1.0    0.0    1.0    1.0    0.0    0.0
Cl-             -1.0    0.0    0.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0
Ac-F            -1.0    0.0    0.0    0.0    0.0    0.0    1.0    0.0    0.0    1.0
AmAc/Am/Ac(s     0.0    0.0    0.0    0.0    0.0   -1.0    0.0    1.0    0.0   -1.0

 Closed input files GMIN and COMP

 COMP       file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_COMP.DAT;1
 BINARYP    file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_BINARYP.DAT;1
 TERNARYP   file name is U1:[SCBABB.NONLIN.INPUTFILES]TERNARYP.DAT;1
 LAMBDA     file name is U1:[SCBABB.NONLIN.INPUTFILES]LAMBDA.DAT;1

          non-ideal electrolyte parameters

          single electrolyte parameters
Na+          Cl-              0.07650     0.26640     0.00000     0.00127
Na+          Ac-F             0.14260     0.22000     0.00000    -0.00629
H+           Cl-              0.17750     0.29450     0.00000     0.00080
H+           Ac-F             0.00000     0.00000     0.00000     0.00000
Am+++F       Cl-              0.61170     5.40300     0.00000    -0.02840
Am+++F       Ac-F             0.00000     0.00000     0.00000     0.00000
AmAc++F      Cl-              0.00000     0.00000     0.00000     0.00000
AmAc++F      Ac-F             0.00000     0.00000     0.00000     0.00000

          ternary electrolyte parameters

                                          Cl-         Ac-F
Na+          H+                0.03600    -0.00400    0.00000
Na+          Am+++F            0.00000     0.00000    0.00000
Na+          AmAc++F           0.00000     0.00000    0.00000
H+           Am+++F            0.00000     0.00000    0.00000
H+           AmAc++F           0.00000     0.00000    0.00000
Am+++F       AmAc++F           0.00000     0.00000    0.00000

                                         Na+         H+          Am+++F      AmAc++F
Cl-          Ac-F             -0.09000    0.01029     0.00000     0.00000     0.00000

 TOTAL NUMBER OF SPECIES =  8
 NUMBER OF COMPONENTS    =  10
 INDEPENDENT CONSTRAINTS =  7

            SOLUBILITY DATA

            input molalities

     Na+          H+          Am+++F      AmAc++F     Cl-         Ac-F
  3.000E-01   1.427E-05   1.010E-06   5.426E-07   3.000E-01   1.010E-02
  1.000E+00   1.442E-05   1.021E-06   3.304E-07   1.000E+00   1.021E-02
  2.000E+00   1.465E-05   1.039E-06   2.856E-07   2.000E+00   1.039E-02
  3.000E+00   1.488E-05   1.054E-06   4.706E-07   3.000E+00   1.054E-02
  4.000E+00   1.513E-05   1.071E-06   7.240E-07   4.000E+00   1.071E-02
  5.000E+00   1.538E-05   1.089E-06   1.725E-06   5.000E+00   1.089E-02
```

Figure A-5. Sample Output File: AM_ACET.OUT (1 of 3)

```
 -3.0000E+02   1.0000E-01   1.0000E-01   1.0000E-01
              L2 NORM OF THE RESIDUALS  2.3449283E+02



 -3.9536E+02   2.2701E-01   2.1540E+00 -3.5943E-02
              L2 NORM OF THE RESIDUALS  1.4263862E-01



 -3.9536E+02   2.2701E-01   2.1540E+00 -3.5943E-02
              L2 NORM OF THE RESIDUALS  1.4263862E-01



          ADJUSTED PARAMETERS
  u0rt(                        AmAc++F      )  -3.9535830E+02
    b0(            AmAc++F     Cl-          )   2.2700551E-01
    b1(            AmAc++F     Cl-          )   2.1540417E+00
   cmx(            AmAc++F     Cl-          )  -3.5943059E-02

 DATA SET( 1)

  input     calc       diff
 0.000000000000000E+000   6.896275256025319E-003
 0.000000000000000E+000  -3.441260316461126E-002
 0.000000000000000E+000   8.104134361121851E-002
 0.000000000000000E+000  -9.661210626001093E-002
 0.000000000000000E+000   5.533810069229617E-002
 0.000000000000000E+000  -1.225101013483254E-002

 AVERAGE DEVIATION   =   4.7759E-02

 STANDARD DEVIATION =   5.8232E-02

FINAL MOLALITIES

Na+          H+           Am+++F       AmAc++F      Cl-          Ac-F
   3.000E-01   1.427E-05   1.010E-06   5.426E-07   3.000E-01   1.010E-02
   1.000E+00   1.442E-05   1.021E-06   3.304E-07   1.000E+00   1.021E-02
   2.000E+00   1.465E-05   1.039E-06   2.856E-07   2.000E+00   1.039E-02
   3.000E+00   1.488E-05   1.054E-06   4.706E-07   3.000E+00   1.054E-02
   4.000E+00   1.513E-05   1.071E-06   7.240E-07   4.000E+00   1.071E-02
   5.000E+00   1.538E-05   1.089E-06   1.725E-06   5.000E+00   1.089E-02

FINAL LOG ACTIVITIES

Na+          H+           Am+++F       AmAc++F      Cl-          Ac-F
  -6.728E-01  -4.958E+00  -7.403E+00  -6.823E+00  -6.758E-01  -2.160E+00
  -1.827E-01  -4.901E+00  -7.718E+00  -7.167E+00  -1.853E-01  -2.207E+00
   1.261E-01  -4.771E+00  -7.834E+00  -7.338E+00   1.237E-01  -2.212E+00
   3.310E-01  -4.625E+00  -7.836E+00  -7.244E+00   3.287E-01  -2.194E+00
   4.960E-01  -4.472E+00  -7.775E+00  -7.215E+00   4.938E-01  -2.160E+00
   6.408E-01  -4.315E+00  -7.671E+00  -7.038E+00   6.385E-01  -2.116E+00

Calculated Log Activity Coefficients

Na+          H+           Am+++F       AmAc++F      Cl-          Ac-F
      -0.1500      -0.1130      -1.4077      -0.5573      -0.1529      -0.1643
      -0.1827      -0.0602      -1.7272      -0.6858      -0.1853      -0.2161
      -0.1749       0.0630      -1.8505      -0.7936      -0.1773      -0.2290
      -0.1461       0.2022      -1.8589      -0.9171      -0.1485      -0.2168
      -0.1060       0.3484      -1.8043      -1.0750      -0.1083      -0.1901
      -0.0582       0.4981      -1.7082      -1.2750      -0.0604      -0.1529

SOLID PHASE NOW IN EQUILIBRIUM

 DATA SET( 1)

  input     calc       diff
 0.000000000000000E+000   0.000000000000000E+000
 0.000000000000000E+000   0.000000000000000E+000
 0.000000000000000E+000   0.000000000000000E+000
 0.000000000000000E+000   0.000000000000000E+000
 0.000000000000000E+000   0.000000000000000E+000
 0.000000000000000E+000   0.000000000000000E+000

 AVERAGE DEVIATION   =   0.0000E+00

 STANDARD DEVIATION =   0.0000E+00
```

Figure A-5. Sample Output File: AM_ACET.OUT (2 of 3)

```
 FINAL  MOLALITIES

 Na+           H+           Am+++F       AmAc++F      Cl-          Ac-F
    3.000E-01   1.427E-05   1.010E-06   5.426E-07   3.000E-01   1.010E-02
    1.000E+00   1.442E-05   1.021E-06   3.304E-07   1.000E+00   1.021E-02
    2.000E+00   1.465E-05   1.039E-06   2.856E-07   2.000E+00   1.039E-02
    3.000E+00   1.488E-05   1.054E-06   4.706E-07   3.000E+00   1.054E-02
    4.000E+00   1.513E-05   1.071E-06   7.240E-07   4.000E+00   1.071E-02
    5.000E+00   1.538E-05   1.089E-06   1.725E-06   5.000E+00   1.089E-02

 FINAL LOG ACTIVITIES

 Na+           H+           Am+++F       AmAc++F      Cl-          Ac-F
  -6.728E-01  -4.958E+00  -7.403E+00  -6.823E+00  -6.758E-01  -2.160E+00
  -1.827E-01  -4.901E+00  -7.718E+00  -7.167E+00  -1.853E-01  -2.207E+00
   1.261E-01  -4.771E+00  -7.834E+00  -7.338E+00   1.237E-01  -2.212E+00
   3.310E-01  -4.625E+00  -7.836E+00  -7.244E+00   3.287E-01  -2.194E+00
   4.960E-01  -4.472E+00  -7.775E+00  -7.215E+00   4.938E-01  -2.160E+00
   6.408E-01  -4.315E+00  -7.671E+00  -7.038E+00   6.385E-01  -2.116E+00

 Calculated Log Activity Coefficients

 Na+           H+           Am+++F       AmAc++F      Cl-          Ac-F
      -0.1500      -0.1130      -1.4077      -0.5573      -0.1529      -0.1643
      -0.1827      -0.0602      -1.7272      -0.6858      -0.1853      -0.2161
      -0.1749       0.0630      -1.8505      -0.7936      -0.1773      -0.2290
      -0.1461       0.2022      -1.8589      -0.9171      -0.1485      -0.2168
      -0.1060       0.3484      -1.8043      -1.0750      -0.1083      -0.1901
      -0.0582       0.4981      -1.7082      -1.2750      -0.0604      -0.1529

       FINAL L2 NORM OF THE RESIDUALS   1.4263862E-01


      EXIT PARAMETER                        3


       FINAL APPROXIMATE SOLUTION


      0  0  5   -3.9535830E+02
      1  4  1    2.2700551E-01
      2  4  1    2.1540417E+00
      4  4  1   -3.5943059E-02
```

Figure A-5. Sample Output File: AM_ACET.OUT (3 of 3)

```
1   0     0     0     0
2   0
3   001080      0.00000000        1   0 H2O
4   011000      0.00000000        2   1 Na+
5   001000      0.00000000        3   2 H+
6   095000      0.00000000        4   3 Am+++
7   095890      0.00000000        5   4 AmAc++
8   000170      0.00000000        6   1 Cl-
9   000890      0.00000000        7   2 Ac-
10  000000
11  -1
12  -1
13
```

Figure A-6. Sample Input File: AM_ACET_POST_ABN.GMIN

```
1   -1
2        6    -1
3   0    0      .30     1.4273e-5     1.010e-6      5.426e-7      .3     1.010e-2
4   0    0      1.0     1.4422e-5     1.021e-6      3.304e-7       1     1.021e-2
5   0    0      2.0     1.4648e-5     1.039e-6      2.856e-7       2     1.039e-2
6   0    0      3.0     1.4883e-5     1.054e-6      4.706e-7       3     1.054e-2
7   0    0      4.0     1.5127e-5     1.071e-6      7.240e-7       4     1.071e-2
8   0    0      5.0     1.5378e-5     1.089e-6      1.725e-6       5     1.089e-2
9   -1
```

Figure A-7. Sample Input File: AM_ACET_POST.IN

```
001080H2O             0       -95.6635  1 2.0 8 1.0

001000H+              1        000.000  1 1.0
011000Na+             1       -105.651 11 1.0
019000K+              1       -113.957 19 1.0

000080OH-            -1        -63.435  1 1.0 8 1.0
000161HSO4-          -1       -304.942 16 1.0 8 4.0 1 1.0
000170Cl-            -1       -52.9550 17 1.0
017080ClO4-          -1         -73.81 17 1.0 8 4.0

000050B(OH)3(aq)      0       -390.810  5 1.0 8 3.0 1 3.0

090000Th++++          4       -284.227 90 1.0
093080Np(V)O2+        1       -369.109 93 1.0 8 2.0
095000Am+++           3       -241.694 95 1.0
095001Am+++F          3       -241.694 95 1.072 1.0

095890AmAc++          2       -395.358 95 1.089 1.0
095891AmAc++F         2        999.999 95 1.089 1.073 1.0

000890Ac-            -1       -147.347 89 1.0
000891Ac-F           -1       -147.347 89 1.071 1.0

000990Ox=            -2         -272.2 99 1.0
001990HOx-           -1        -281.94 99 1.0 1 1.0
001991H2Ox(aq)        0        -284.99 99 1.0 1 2.0

093890NpO2Ac(aq)      0       -519.800 93 1.0 8 2.089 1.0

101990H2Ox.2H2O(s)    0        999.999 99 1.0 1 6.0 8 2.0
111990Na2Ox(s)        0        999.999 99 1.011 2.0

195890AmAc/Am/Ac(s)   0          0.000 73 1.071-1.072-1.0

199002Na+/NpO2+EX               999.999 93-1.011 1.0 8-2.0
199003Na+/Th++++EX              999.999 90-1.011 4.0

111170       Halite            -154.990 17 1. 11 1.
119172      Sylvite            -164.840 19 1. 17 1.

    -1
```

Figure A-8. Sample Input File: AM_ACET_COMP_POST_ABN.DAT

```
 1  NONLIN  V2.0
 2
 3   NONLIN was developed by A.R. Felmy
 4
 5   INPUT     file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_POST.IN;1
 6   GMIN      file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_POST_ABN.GMIN;
 7   OUTPUT    file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_POST_ABN.OUT;1
 8
 9            AQUEOUS SPECIES
10
11      ID       NAME            MOLES          Z    u0rt
12     1080H2O              0.000000000000    0.    -95.663
13    11000Na+              0.000000000000    1.   -105.651
14     1000H+               0.000000000000    1.      0.000
15    95000Am+++            0.000000000000    3.   -241.694
16    95890AmAc++           0.000000000000    2.   -395.358
17      170Cl-              0.000000000000   -1.    -52.955
18      890Ac-              0.000000000000   -1.   -147.347
19            SOLID PHASES
20
21      ID       NAME            MOLES          Z    u0rt
22
23            CONSTRAINT EQUATIONS
24                    0       1       8      11      95      89      17
25   H2O             0.0     2.0     1.0     0.0     0.0     0.0     0.0
26   Na+             1.0     0.0     0.0     1.0     0.0     0.0     0.0
27   H+              1.0     1.0     0.0     0.0     0.0     0.0     0.0
28   Am+++           3.0     0.0     0.0     0.0     1.0     0.0     0.0
29   AmAc++          2.0     0.0     0.0     0.0     1.0     1.0     0.0
30   Cl-            -1.0     0.0     0.0     0.0     0.0     0.0     1.0
31   Ac-            -1.0     0.0     0.0     0.0     0.0     1.0     0.0
32
33   Closed input files GMIN and COMP
34
35   COMP      file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_COMP_POST_ABN.
36   BINARYP   file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_BINARYP.DAT;1
37   TERNARYP  file name is U1:[SCBABB.NONLIN.INPUTFILES]TERNARYP.DAT;1
38   LAMBDA    file name is U1:[SCBABB.NONLIN.INPUTFILES]LAMBDA.DAT;1
39
40          non-ideal electrolyte parameters
41
42          single electrolyte parameters
43   Na+          Cl-              0.07650     0.26640     0.00000     0.00127
44   Na+          Ac-              0.14260     0.22000     0.00000    -0.00629
45   H+           Cl-              0.17750     0.29450     0.00000     0.00080
46   H+           Ac-              0.00000     0.00000     0.00000     0.00000
47   Am+++        Cl-              0.61170     5.40300     0.00000    -0.02840
48   Am+++        Ac-              0.00000     0.00000     0.00000     0.00000
49   AmAc++       Cl-              0.22700     2.15400     0.00000    -0.10200
50   AmAc++       Ac-              0.00000     0.00000     0.00000     0.00000
51
52          ternary electrolyte parameters
53
54                                            Cl-         Ac-
55   Na+          H+               0.03600    -0.00400     0.00000
56   Na+          Am+++            0.00000     0.00000     0.00000
57   Na+          AmAc++           0.00000     0.00000     0.00000
58   H+           Am+++            0.00000     0.00000     0.00000
59   H+           AmAc++           0.00000     0.00000     0.00000
60   Am+++        AmAc++           0.00000     0.00000     0.00000
61
62                                            Na+         H+          Am+++       AmAc++
63   Cl-          Ac-             -0.09000     0.01029     0.00000     0.00000     0.00000
64
65    TOTAL NUMBER OF SPECIES =  7
66    NUMBER OF COMPONENTS    =  7
67    INDEPENDENT CONSTRAINTS =  6
68
```

Figure A-9. Sample Output File: AM_ACET_POST_ABN.OUT (1 of 2)

```
 SOLUBILITY DATA

            input molalities


      Na+          H+          Am+++       AmAc++      Cl-          Ac-
      3.000E-01    1.427E-05   1.010E-06   5.426E-07   3.000E-01    1.010E-02
      1.000E+00    1.442E-05   1.021E-06   3.304E-07   1.000E+00    1.021E-02
      2.000E+00    1.465E-05   1.039E-06   2.856E-07   2.000E+00    1.039E-02
      3.000E+00    1.488E-05   1.054E-06   4.706E-07   3.000E+00    1.054E-02
      4.000E+00    1.513E-05   1.071E-06   7.240E-07   4.000E+00    1.071E-02
      5.000E+00    1.538E-05   1.089E-06   1.725E-06   5.000E+00    1.089E-02

            ADJUSTED PARAMETERS

   DATA SET( 1)

    input     calc       diff
   0.000000000000000E+000   0.000000000000000E+000
   0.000000000000000E+000   0.000000000000000E+000
   0.000000000000000E+000   0.000000000000000E+000
   0.000000000000000E+000   0.000000000000000E+000
   0.000000000000000E+000   0.000000000000000E+000
   0.000000000000000E+000   0.000000000000000E+000

   AVERAGE DEVIATION   =   0.0000E+00

   STANDARD DEVIATION =   0.0000E+00

 FINAL MOLALITIES

 Na+          H+          Am+++       AmAc++      Cl-          Ac-
   3.000E-01   1.427E-05   1.008E-06   5.449E-07   3.000E-01   1.010E-02
   1.000E+00   1.442E-05   1.030E-06   3.219E-07   1.000E+00   1.021E-02
   2.000E+00   1.465E-05   1.020E-06   3.043E-07   2.000E+00   1.039E-02
   3.000E+00   1.488E-05   1.084E-06   4.404E-07   3.000E+00   1.054E-02
   4.000E+00   1.513E-05   1.045E-06   7.496E-07   4.000E+00   1.071E-02
   5.000E+00   1.538E-05   1.093E-06   1.721E-06   5.000E+00   1.089E-02

 FINAL LOG ACTIVITIES

 Na+          H+          Am+++       AmAc++      Cl-          Ac-
  -6.728E-01  -4.958E+00  -7.404E+00  -6.821E+00  -6.758E-01  -2.160E+00
  -1.827E-01  -4.901E+00  -7.715E+00  -7.178E+00  -1.853E-01  -2.207E+00
   1.261E-01  -4.771E+00  -7.842E+00  -7.311E+00   1.237E-01  -2.212E+00
   3.310E-01  -4.625E+00  -7.824E+00  -7.274E+00   3.287E-01  -2.194E+00
   4.960E-01  -4.472E+00  -7.785E+00  -7.202E+00   4.938E-01  -2.160E+00
   6.408E-01  -4.315E+00  -7.669E+00  -7.042E+00   6.385E-01  -2.116E+00

 Calculated Log Activity Coefficients

 Na+          H+          Am+++       AmAc++      Cl-          Ac-
      -0.1500     -0.1130     -1.4077     -0.5573     -0.1529     -0.1643
      -0.1827     -0.0602     -1.7272     -0.6859     -0.1853     -0.2161
      -0.1749      0.0630     -1.8505     -0.7941     -0.1773     -0.2290
      -0.1461      0.2022     -1.8589     -0.9181     -0.1485     -0.2168
      -0.1060      0.3484     -1.8043     -1.0767     -0.1083     -0.1901
      -0.0582      0.4981     -1.7082     -1.2776     -0.0604     -0.1529

 SOLID PHASE NOW IN EQUILIBRIUM

   DATA SET( 1)

     input     calc       diff
**** SINGULAR MATRIX IN DECOMP, ZERO DIVIDE IN SOLVE
```

Figure A-9. Sample Output File: AM_ACET_POST_ABN.OUT (2 of 2)

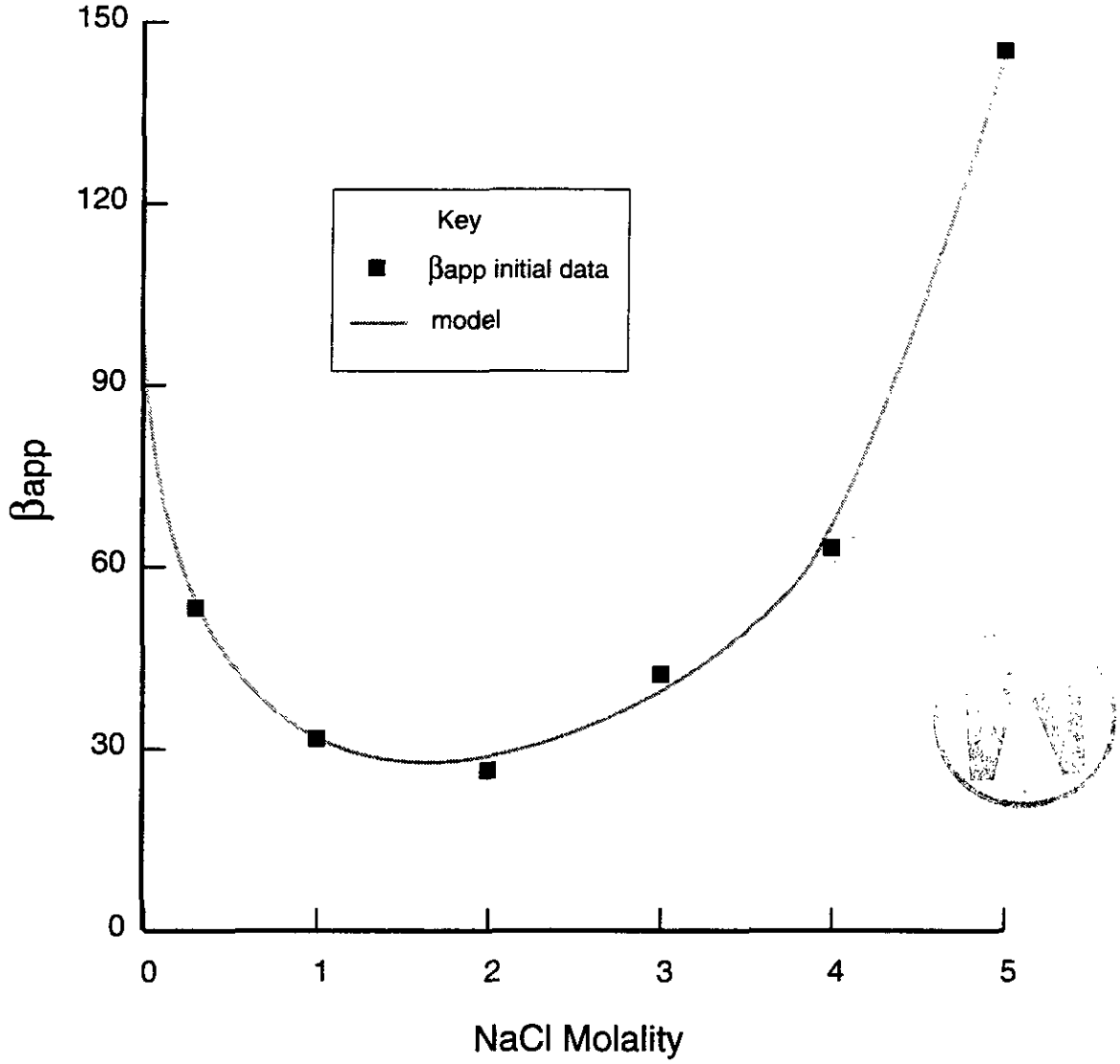


Figure A-10. Apparent stability constant for AmAc in NaCl media: comparison of the model with data.

```
1   0     0     0     0
2   0
3   001080      0.00000000        1   0 H2O
4   011000      0.00000000        2   1 Na+
5   001000      0.00000000        3   2 H+
6   095000      0.00000000        4   3 Am+++
7   095890      0.00000000        5   4 AmAc++
8   000170      0.00000000        6   1 Cl-
9   000890      0.00000000        7   2 Ac-
10  000000
11  195891      0.00000000
12  -1
13  -1
```

Figure A-11. Sample Input File: AM_ACET_POST_NORM.GMIN.

```
001080H2O             0       -95.6635  1 2.0 8 1.0

001000H+              1        000.000  1 1.0
011000Na+             1       -105.651 11 1.0
019000K+              1       -113.957 19 1.0

000080OH-            -1        -63.435  1 1.0 8 1.0
000161HSO4-          -1       -304.942 16 1.0 8 4.0 1 1.0
000170Cl-            -1       -52.9550 17 1.0
017080ClO4-          -1         -73.81 17 1.0 8 4.0

000050B(OH)3(aq)      0       -390.810  5 1.0 8 3.0 1 3.0

090000Th++++          4       -284.227 90 1.0
093080Np(V)O2+        1       -369.109 93 1.0 8 2.0
095000Am+++           3       -241.694 95 1.0
095001Am+++F          3       -241.694 95 1.072 1.0

095890AmAc++          2       -395.358 95 1.089 1.0
095891AmAc++F         2        999.999 95 1.089 1.073 1.0

000890Ac-            -1       -147.347 89 1.0
000891Ac-F           -1       -147.347 89 1.071 1.0

000990Ox=            -2         -272.2 99 1.0
001990HOx-           -1        -281.94 99 1.0 1 1.0
001991H2Ox(aq)        0        -284.99 99 1.0 1 2.0

093890NpO2Ac(aq)      0       -519.800 93 1.0 8 2.089 1.0

101990H2Ox.2H2O(s)    0        999.999 99 1.0 1 6.0 8 2.0
111990Na2Ox(s)        0        999.999 99 1.011 2.0

195890AmAc/Am/Ac(s)   0          0.000 73 1.071-1.072-1.0
195891AmAc/Am/Ac(s)   0          0.000 89 0.095 0.0

199002Na+/NpO2+EX              999.999 93-1.011 1.0 8-2.0
199003Na+/Th++++EX             999.999 90-1.011 4.0

111170       Halite           -154.990 17 1. 11 1.
119172      Sylvite           -164.840 19 1. 17 1.

    -1
```

Figure A-12. Sample Input File: AM_ACET_COMP_POST_NORM.DAT

```
 1    NONLIN   V2.0
 2
 3     NONLIN was developed by A.R. Felmy
 4
 5     INPUT      file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_POST.IN;1
 6     GMIN       file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_POST_NORM.GMIN
 7     OUTPUT     file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_POST_NORM.OUT;
 8
 9              AQUEOUS SPECIES
10
11        ID       NAME            MOLES        Z    u0rt
12       1080H2O              0.000000000000    0.    -95.663
13      11000Na+              0.000000000000    1.   -105.651
14       1000H+               0.000000000000    1.      0.000
15      95000Am+++            0.000000000000    3.   -241.694
16      95890AmAc++           0.000000000000    2.   -395.358
17        170Cl-              0.000000000000   -1.    -52.955
18        890Ac-              0.000000000000   -1.   -147.347
19              SOLID PHASES
20
21        ID       NAME            MOLES        Z    u0rt
22     195891AmAc/Am/Ac(s    0.000000000000    0.       0.000
23
24              CONSTRAINT EQUATIONS
25                     0       1       8      11      95      89      17
26     H2O           0.0     2.0     1.0     0.0     0.0     0.0     0.0
27     Na+           1.0     0.0     0.0     1.0     0.0     0.0     0.0
28     H+            1.0     1.0     0.0     0.0     0.0     0.0     0.0
29     Am+++         3.0     0.0     0.0     0.0     1.0     0.0     0.0
30     AmAc++        2.0     0.0     0.0     0.0     1.0     1.0     0.0
31     Cl-          -1.0     0.0     0.0     0.0     0.0     0.0     1.0
32     Ac-          -1.0     0.0     0.0     0.0     0.0     1.0     0.0
33     AmAc/Am/Ac(s  0.0     0.0     0.0     0.0     0.0     0.0     0.0
34
35     Closed input files GMIN and COMP
36
37     COMP       file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_COMP_POST_NORM
38     BINARYP    file name is U1:[SCBABB.NONLIN.USERGUIDE]AM_ACET_BINARYP.DAT;1
39     TERNARYP   file name is U1:[SCBABB.NONLIN.INPUTFILES]TERNARYP.DAT;1
40     LAMBDA     file name is U1:[SCBABB.NONLIN.INPUTFILES]LAMBDA.DAT;1
41
42             non-ideal electrolyte parameters
43
44             single electrolyte parameters
45   Na+          Cl-              0.07650     0.26640     0.00000     0.00127
46   Na+          Ac-              0.14260     0.22000     0.00000    -0.00629
47   H+           Cl-              0.17750     0.29450     0.00000     0.00080
48   H+           Ac-              0.00000     0.00000     0.00000     0.00000
49   Am+++        Cl-              0.61170     5.40300     0.00000    -0.02840
50   Am+++        Ac-              0.00000     0.00000     0.00000     0.00000
51   AmAc++       Cl-              0.22700     2.15400     0.00000    -0.10200
52   AmAc++       Ac-              0.00000     0.00000     0.00000     0.00000
53
54             ternary electrolyte parameters
55
56                                            Cl-         Ac-
57   Na+          H+               0.03600    -0.00400     0.00000
58   Na+          Am+++            0.00000     0.00000     0.00000
59   Na+          AmAc++           0.00000     0.00000     0.00000
60   H+           Am+++            0.00000     0.00000     0.00000
61   H+           AmAc++           0.00000     0.00000     0.00000
62   Am+++        AmAc++           0.00000     0.00000     0.00000
63
64                                            Na+         H+          Am+++       AmAc++
65   Cl-          Ac-             -0.09000     0.01029     0.00000     0.00000     0.00000
66
67    TOTAL NUMBER OF SPECIES =  8
68    NUMBER OF COMPONENTS    =  7
69    INDEPENDENT CONSTRAINTS =  6
70
71              SOLUBILITY DATA
72
73              input molalities
74
75
76        Na+          H+          Am+++       AmAc++      Cl-         Ac-
77       3.000E-01   1.427E-05   1.010E-06   5.426E-07   3.000E-01   1.010E-02
78       1.000E+00   1.442E-05   1.021E-06   3.304E-07   1.000E+00   1.021E-02
79       2.000E+00   1.465E-05   1.039E-06   2.856E-07   2.000E+00   1.039E-02
80       3.000E+00   1.488E-05   1.054E-06   4.706E-07   3.000E+00   1.054E-02
81       4.000E+00   1.513E-05   1.071E-06   7.240E-07   4.000E+00   1.071E-02
82       5.000E+00   1.538E-05   1.089E-06   1.725E-06   5.000E+00   1.089E-02
83
```

Figure A-13. Sample Output File: AM_ACET_POST_NORM.OUT (1 of 3)

```
 ADJUSTED  PARAMETERS

   DATA SET( 1)

    input     calc       diff
    0.000000000000000E+000   0.000000000000000E+000
    0.000000000000000E+000   0.000000000000000E+000
    0.000000000000000E+000   0.000000000000000E+000
    0.000000000000000E+000   0.000000000000000E+000
    0.000000000000000E+000   0.000000000000000E+000
    0.000000000000000E+000   0.000000000000000E+000

   AVERAGE DEVIATION   =   0.0000E+00

   STANDARD DEVIATION  =   0.0000E+00

  FINAL  MOLALITIES

 Na+          H+           Am+++        AmAc++       Cl-          Ac-
    3.000E-01   1.427E-05   1.008E-06   5.449E-07   3.000E-01   1.010E-02
    1.000E+00   1.442E-05   1.030E-06   3.219E-07   1.000E+00   1.021E-02
    2.000E+00   1.465E-05   1.020E-06   3.043E-07   2.000E+00   1.039E-02
    3.000E+00   1.488E-05   1.084E-06   4.404E-07   3.000E+00   1.054E-02
    4.000E+00   1.513E-05   1.045E-06   7.496E-07   4.000E+00   1.071E-02
    5.000E+00   1.538E-05   1.093E-06   1.721E-06   5.000E+00   1.089E-02

  FINAL  LOG  ACTIVITIES

 Na+          H+           Am+++        AmAc++       Cl-          Ac-
  -6.728E-01  -4.958E+00  -7.404E+00  -6.821E+00  -6.758E-01  -2.160E+00
  -1.827E-01  -4.901E+00  -7.715E+00  -7.178E+00  -1.853E-01  -2.207E+00
   1.261E-01  -4.771E+00  -7.842E+00  -7.311E+00   1.237E-01  -2.212E+00
   3.310E-01  -4.625E+00  -7.824E+00  -7.274E+00   3.287E-01  -2.194E+00
   4.960E-01  -4.472E+00  -7.785E+00  -7.202E+00   4.938E-01  -2.160E+00
   6.408E-01  -4.315E+00  -7.669E+00  -7.042E+00   6.385E-01  -2.116E+00

  Calculated  Log  Activity  Coefficients

 Na+          H+           Am+++        AmAc++       Cl-          Ac-
      -0.1500     -0.1130     -1.4077     -0.5573     -0.1529     -0.1643
      -0.1827     -0.0602     -1.7272     -0.6859     -0.1853     -0.2161
      -0.1749      0.0630     -1.8505     -0.7941     -0.1773     -0.2290
      -0.1461      0.2022     -1.8589     -0.9181     -0.1485     -0.2168
      -0.1060      0.3484     -1.8043     -1.0767     -0.1083     -0.1901
      -0.0582      0.4981     -1.7082     -1.2776     -0.0604     -0.1529

  SOLID  PHASE  NOW  IN  EQUILIBRIUM

   DATA SET( 1)

     input     calc       diff
  projected hessian indefinite
    0.000000000000000E+000   0.000000000000000E+000
  projected hessian indefinite
    0.000000000000000E+000   0.000000000000000E+000
  projected hessian indefinite
    0.000000000000000E+000   0.000000000000000E+000
  projected hessian indefinite
    0.000000000000000E+000   0.000000000000000E+000
  projected hessian indefinite
    0.000000000000000E+000   0.000000000000000E+000
  projected hessian indefinite
    0.000000000000000E+000   0.000000000000000E+000

   AVERAGE DEVIATION   =   0.0000E+00

   STANDARD DEVIATION  =   0.0000E+00
```

Figure A-13. Sample Output File: AM_ACET_POST_NORM.OUT (2 of 3)

```
 FINAL  MOLALITIES

 Na+           H+           Am+++        AmAc++       Cl-          Ac-
    3.000E-01   1.427E-05   1.008E-06   5.449E-07   3.000E-01   1.010E-02
    1.000E+00   1.442E-05   1.030E-06   3.219E-07   1.000E+00   1.021E-02
    2.000E+00   1.465E-05   1.020E-06   3.043E-07   2.000E+00   1.039E-02
    3.000E+00   1.488E-05   1.084E-06   4.404E-07   3.000E+00   1.054E-02
    4.000E+00   1.513E-05   1.045E-06   7.496E-07   4.000E+00   1.071E-02
    5.000E+00   1.538E-05   1.093E-06   1.721E-06   5.000E+00   1.089E-02

 FINAL LOG ACTIVITIES

 Na+           H+           Am+++        AmAc++       Cl-          Ac-
  -6.728E-01  -4.958E+00  -7.404E+00  -6.821E+00  -6.758E-01  -2.160E+00
  -1.827E-01  -4.901E+00  -7.715E+00  -7.178E+00  -1.853E-01  -2.207E+00
   1.261E-01  -4.771E+00  -7.842E+00  -7.311E+00   1.237E-01  -2.212E+00
   3.310E-01  -4.625E+00  -7.824E+00  -7.274E+00   3.287E-01  -2.194E+00
   4.960E-01  -4.472E+00  -7.785E+00  -7.202E+00   4.938E-01  -2.160E+00
   6.408E-01  -4.315E+00  -7.669E+00  -7.042E+00   6.385E-01  -2.116E+00

 Calculated Log Activity Coefficients

 Na+           H+           Am+++        AmAc++       Cl-          Ac-
      -0.1500      -0.1130      -1.4077      -0.5573      -0.1529      -0.1643
      -0.1827      -0.0602      -1.7272      -0.6859      -0.1853      -0.2161
      -0.1749       0.0630      -1.8505      -0.7941      -0.1773      -0.2290
      -0.1461       0.2022      -1.8589      -0.9181      -0.1485      -0.2168
      -0.1060       0.3484      -1.8043      -1.0767      -0.1083      -0.1901
      -0.0582       0.4981      -1.7082      -1.2776      -0.0604      -0.1529

  FINAL L2 NORM OF THE RESIDUALS   0.0000000E+00


 EXIT PARAMETER                    0


  FINAL APPROXIMATE SOLUTION
```

Figure A-13. Sample Output File: AM_ACET_POST_NORM.OUT (3 of 3)

Appendix B - Sample Input File: EXTR_00.GMIN

See Table 7-1 for explanation of this listing.

```
1   0     0     0     0
2   0
3   001080       0.00000000        H2O
4   011000       0.00000000        Na+
5   090000       0.00000000        Th++++
6   001000       0.00000000        H+
7   000080       0.00000000        OH-
8   017080       0.00000000        ClO4-
9   000000
10  199003       0.00000000        Th++++/Na+ extracted
11  -1
12  -1
```

Appendix C - Sample Input File: EXTR_07_EXACT.IN

See Table 7-3 for explanation of this listing.

See key in Figure A-1.

```
1   000007    -120.65        uo[ Th++++/Na+ extracted]
2   010202      1.186        b(0)  Th+++/ClO4-
3   040202    -0.0141        cphi  Th+++/ClO4-
4   -1
5      16    -4
6   1.00E-05          0.000    0.307    2.12E-05          1.00E-07          1.00E-07          0.307
7   1.00E-05          0.000    0.307    2.12E-05          1.00E-07          1.00E-07          0.307
8   1.00E-05          0.000    1.035    5.94E-05          1.00E-07          1.00E-07          1.035
9   1.00E-05          0.000    1.035    5.81E-05          1.00E-07          1.00E-07          1.035
10  1.00E-05          0.000    2.129    1.69E-04          1.00E-07          1.00E-07          2.129
11  1.00E-05          0.000    2.129    1.69E-04          1.00E-07          1.00E-07          2.129
12  1.00E-05          0.000    3.322    3.15E-04          1.00E-07          1.00E-07          3.322
13  1.00E-05          0.000    3.322    3.39E-04          1.00E-07          1.00E-07          3.322
14  1.00E-05          0.000    4.657    9.45E-04          1.00E-07          1.00E-07          4.657
15  1.00E-05          0.000    4.657    9.45E-04          1.00E-07          1.00E-07          4.657
16  1.00E-05          0.000    6.176    1.26E-03          1.00E-07          1.00E-07          6.176
17  1.00E-05          0.000    6.176    1.45E-03          1.00E-07          1.00E-07          6.176
18  1.00E-05          0.000    9.929    1.93E-03          1.00E-07          1.00E-07          9.929
19  1.00E-05          0.000    9.929    2.19E-03          1.00E-07          1.00E-07          9.929
20  1.00E-05          0.000   14.916    2.33E-03          1.00E-07          1.00E-07         14.916
21  1.00E-05          0.000   14.916    2.29E-03          1.00E-07          1.00E-07         14.916
22  -1
23  -1
24
25  mORG              pH        mNa+     mTh++++          mH+               mOH-              mClO4-
```

Appendix D - Sample Input File: SOLUB_00.GMIN

See Table 7-1 for explanation of this listing.

```
1   0     0     0     0
2   0
3   001080       0.00000000        H2O
4   001000       0.00000000        H+
5   000080       0.00000000        OH-
6   000161       0.00000000        HSO4-
7   001991       0.00000000        H2Ox(aq)
8   000000
9   101990       .000000000        H2Ox.2H2O(s)
10  -1
11  -1
```

Appendix E - Sample Input File: SOLUB_01.IN

See Table 7-3 for explanation of this listing.

See key in Figure A-1.

```
1   000006      -10.0          u0(H2C2O4.2H2O(s))
2   -1
3      07    -1
4   0.0       0.0       1.168     8.56E-15          1.168     0.875
5   0.0       0.0       1.965     5.09E-15          1.965     0.653
6   0.0       0.0       2.927     3.42E-15          2.927     0.534
7   0.0       0.0       4.450     2.25E-15          4.450     0.476
8   0.0       0.0       6.660     1.50E-15          6.660     0.432
9   0.0       0.0       9.548     1.05E-15          9.548     0.574
10  0.0       0.0       13.941    7.17E-16          13.941    1.268
11  -1
12  -1
13
14
15  0.0        pH         mH+      mOH-              mHSO4-      mH2Ox
```

Appendix F - Listing of COMP.DAT

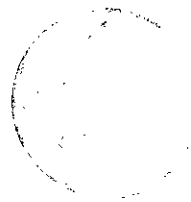
See Table 7-4 for explanation of this listing.

```
1    001080H2O              0       -95.6635  1 2.0 8 1.0
2
3    001000H+               1        000.000  1 1.0
4    011000Na+              1       -105.651 11 1.0
5    019000K+               1       -113.957 19 1.0
6
7    000080OH-             -1        -63.435  1 1.0 8 1.0
8    000161HSO4-           -1       -304.942 16 1.0 8 4.0 1 1.0
9    000170Cl-             -1       -52.9550 17 1.0
10   017080ClO4-           -1         -73.81 17 1.0 8 4.0
11
12   000050B(OH)3(aq)       0       -390.810  5 1.0 8 3.0 1 3.0
13
14   090000Th++++           4       -284.227 90 1.0
15   093080Np(V)O2+         1       -369.109 93 1.0 8 2.0
16   095000Am+++            3       -241.694 95 1.0
17   095001Am+++F           3       -241.694 95 1.072 1.0
18
19   095890AmAc++           2        999.999 95 1.089 1.0
20   095891AmAc++F          2        999.999 95 1.089 1.073 1.0
21
22   000890Ac-             -1       -147.347 89 1.0
23   000891Ac-F            -1       -147.347 89 1.071 1.0
24
25   000990Ox=             -2         -272.2 99 1.0
26   001990HOx-            -1        -281.94 99 1.0 1 1.0
27   001991H2Ox(aq)         0        -284.99 99 1.0 1 2.0
28
29   093890NpO2Ac(aq)       0       -519.800 93 1.0 8 2.089 1.0
30
31   101990H2Ox.2H2O(s)     0        999.999 99 1.0 1 6.0 8 2.0
32   111990Na2Ox(s)         0        999.999 99 1.011 2.0
33
34   195890AmAc/Am/Ac(s)    0          0.000 73 1.071-1.072-1.0
35
36   199002Na+/NpO2+EX               999.999 93-1.011 1.0 8-2.0
37   199003Na+/Th++++EX              999.999 90-1.011 4.0
38
39   111170       Halite            -154.990 17 1. 11 1.
40   119172      Sylvite            -164.840 19 1. 17 1.
41
42       -1
43
```

Appendix G - Listing of BINARYP.DAT

See Table 7-5 for explanation of this listing.

```
1    011000 000170   .0765   .2664    .000 .00127   Na+ - Cl-
2    011000 000161   .0454    .398    .000  .0000   Na+ - HSO4-
3    011000 000080   .0864    .253    .000  .0044   Na+ - OH-
4    011000 017080   .0554  0.2755   .000-.00118   Na+ - ClO4-
5    011000 001990  -.0307   .000     .000   .000   Na+ - HOx-
6    011000 000990   .0028  1.661    .000   .027    Na+ - Ox=
7    011000 000890   .1426   .22      .000-.00629   Na+ - Ac-
8    011000 000891   .1426   .22      .000-.00629   Na+ - Ac-F
9    019000 000170  .04835  .2122    .000-.00084   K+ - Cl-
10   019000 000161  -.0003  .1735    .000   .000    K+ - HSO4-
11   019000 000080   .1298   .320    .000   .0041   K+ - OH-
12   001000 000170   .1775   .2945   .000   .0008   H+ - Cl-
13   001000 000161   .2065   .5556   .000    .000   H+ - HSO4-
14   001000 017080   .1747  0.2931   .000 .00819   H+ - ClO4-
15   090000 000170 1.092    13.7    -160.  -.112    Th++++ - Cl-  Roy et al. 1992
16   090000 017080 1.186    27.3     .000 -.0566   Th++++ - ClO4-  GRC Extr Data
17   093080 000170   .1415   .281    .000   .000    NpO2+ - Cl-   NFRK95
18   093080 017080   .257    .180    .000   .0081   NpO2+ - ClO4- NFRK95
19   095000 000170   .6117  5.403    .000 -.0284   Am+++ - Cl-
20   095001 000170   .6117  5.403    .000 -.0284   Am+++F - Cl-
21   000000
22
23   cation anion    beta0 beta1    beta2   cphi
```



Appendix H - Listing of TERNARYP.DAT

See Table 7-6 for explanation of this listing.

```
1    011000 019000  -.012 000170  -.0018
2    011000 001000   .036 000170   -.004 000161  -.0129 017080  -.0160
3    019000 001000   .005 000170   -.011 000160    .197 000161  -.0265
4    000170 000161  -.006 011000   -.006 001000   .0130
5    000170 000080   -.05 011000   -.006 019000   -.006
6    000170 000890  -.090 011000  .01029
7    000170 000891  -.090 011000  .01029
8    000080 017080 -.0320
9    017080 000890  0.064 011000  -.0072
10   090000 001000   .600
11   090000 011000   .420
12   000000
13
```

Appendix I - Listing of LAMBDA.DAT

See Table 7-7 for explanation of this listing.

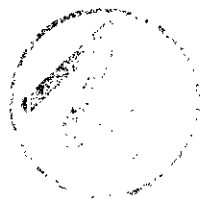
```
1   000050 001000    .000 000170  -.0102
2   000050 019000    -.14
3   000000
```

Appendix J - Sample Output File: EXTR_07_EXACT.OUT

See Table 9-1 for explanation of this listing.

```
 1  NONLIN  V2.0
 2
 3   NONLIN was developed by A.R. Felmy
 4
 5   INPUT     file name is U1:[SCBABB.NONLIN.USERGUIDE]EXTR_07_EXACT.IN;1
 6   GMIN      file name is U1:[SCBABB.NONLIN.USERGUIDE]EXTR_00.GMIN;1
 7   OUTPUT    file name is U1:[SCBABB.NONLIN.USERGUIDE]EXTR_07_EXACT.OUT;1
 8
 9            AQUEOUS SPECIES
10
11      ID       NAME            MOLES        Z    u0rt
12     1080H2O              0.000000000000   0.    -95.663
13    11000Na+              0.000000000000   1.   -105.651
14    90000Th++++           0.000000000000   4.   -284.227
15     1000H+               0.000000000000   1.      0.000
16       80OH-              0.000000000000  -1.    -63.435
17    17080ClO4-            0.000000000000  -1.    -73.810
18            SOLID PHASES
19
20      ID       NAME            MOLES        Z    u0rt
21   199003Na+/Th++++EX    0.000000000000   0.    999.999
22
23            CONSTRAINT EQUATIONS
24                    0      1      8      11      90      17
25   H2O             0.0    2.0    1.0    0.0     0.0     0.0
26   Na+             1.0    0.0    0.0    1.0     0.0     0.0
27   Th++++          4.0    0.0    0.0    0.0     1.0     0.0
28   H+              1.0    1.0    0.0    0.0     0.0     0.0
29   OH-            -1.0    1.0    1.0    0.0     0.0     0.0
30   ClO4-          -1.0    0.0    4.0    0.0     0.0     1.0
31   Na+/Th++++EX    0.0    0.0    0.0    4.0    -1.0     0.0
32
33   Closed input files GMIN and COMP
34
35   COMP      file name is U1:[SCBABB.NONLIN.INPUTFILES]COMP.DAT;3
36   BINARYP   file name is U1:[SCBABB.NONLIN.INPUTFILES]BINARYP.DAT;2
37   TERNARYP  file name is U1:[SCBABB.NONLIN.INPUTFILES]TERNARYP.DAT;1
38   LAMBDA    file name is U1:[SCBABB.NONLIN.INPUTFILES]LAMBDA.DAT;1
39
40          non-ideal electrolyte parameters
41
42          single electrolyte parameters
43   Na+          OH-            0.08640    0.25300    0.00000    0.00440
44   Na+          ClO4-          0.05540    0.27550    0.00000   -0.00118
45   Th++++       OH-            0.00000    0.00000    0.00000    0.00000
46   Th++++       ClO4-          1.18600   27.30000    0.00000   -0.05660
47   H+           OH-            0.00000    0.00000    0.00000    0.00000
48   H+           ClO4-          0.17470    0.29310    0.00000    0.00819
49
50          ternary electrolyte parameters
51
52                                          OH-        ClO4-
53   Na+          Th++++         0.42000    0.00000    0.00000
54   Na+          H+             0.03600    0.00000   -0.01600
55   Th++++       H+             0.60000    0.00000    0.00000
56
57                                          Na+        Th++++      H+
58   OH-          ClO4-         -0.03200    0.00000    0.00000    0.00000
59
60    TOTAL NUMBER OF SPECIES =  7
61    NUMBER OF COMPONENTS    =  6
62    INDEPENDENT CONSTRAINTS =  5
63
64            SOLVENT EXTRACTION DATA
65
```

```
              input molalities


        Na+           Th++++        H+            OH-           ClO4-
        3.070E-01     2.120E-05     1.000E-07     1.000E-07     3.070E-01
        3.070E-01     2.120E-05     1.000E-07     1.000E-07     3.070E-01
        1.035E+00     5.940E-05     1.000E-07     1.000E-07     1.035E+00
        1.035E+00     5.810E-05     1.000E-07     1.000E-07     1.035E+00
        2.129E+00     1.690E-04     1.000E-07     1.000E-07     2.129E+00
        2.129E+00     1.690E-04     1.000E-07     1.000E-07     2.129E+00
        3.322E+00     3.150E-04     1.000E-07     1.000E-07     3.322E+00
        3.322E+00     3.390E-04     1.000E-07     1.000E-07     3.322E+00
        4.657E+00     9.450E-04     1.000E-07     1.000E-07     4.657E+00
        4.657E+00     9.450E-04     1.000E-07     1.000E-07     4.657E+00
        6.176E+00     1.260E-03     1.000E-07     1.000E-07     6.176E+00
        6.176E+00     1.450E-03     1.000E-07     1.000E-07     6.176E+00
        9.929E+00     1.930E-03     1.000E-07     1.000E-07     9.929E+00
        9.929E+00     2.190E-03     1.000E-07     1.000E-07     9.929E+00
        1.492E+01     2.330E-03     1.000E-07     1.000E-07     1.492E+01
        1.492E+01     2.290E-03     1.000E-07     1.000E-07     1.492E+01

     -1.2065E+02   1.1860E+00 -1.4100E-02
                L2 NORM OF THE RESIDUALS  2.3701936E+01



     -1.2065E+02   7.6650E-01 -1.4134E-02
                L2 NORM OF THE RESIDUALS  5.8867175E-01



     -1.2065E+02   7.6650E-01 -1.4134E-02
                L2 NORM OF THE RESIDUALS  5.8867175E-01



             ADJUSTED PARAMETERS
      u0rt(                          Na+/Th++++EX)   -1.2065375E+02
        b0(              Th++++       ClO4-        )    7.6649537E-01
       cmx(              Th++++       ClO4-        )   -1.4134295E-02

     DATA SET( 1)

      input     calc       diff
     1.000000000000000E-005   0.101481694490094
     1.000000000000000E-005   0.101481694490094
     1.000000000000000E-005 -0.220537193518512
     1.000000000000000E-005 -0.242559039934136
     1.000000000000000E-005   6.301298267648374E-002
     1.000000000000000E-005   6.301298267648374E-002
     1.000000000000000E-005 -0.108251784934691
     1.000000000000000E-005 -3.611739799594871E-002
     1.000000000000000E-005   0.242939165971691
     1.000000000000000E-005   0.242939165971691
     1.000000000000000E-005 -5.398818272699338E-002
     1.000000000000000E-005   8.004321603990713E-002
     1.000000000000000E-005 -0.229546862144291
     1.000000000000000E-005 -0.108708180248774
     1.000000000000000E-005   6.078330869018109E-002
     1.000000000000000E-005   4.401442682556691E-002

     AVERAGE DEVIATION   =   1.2496E-01

     STANDARD DEVIATION =   1.4717E-01

    FINAL MOLALITIES

    Na+           Th++++        H+            OH-           ClO4-
      3.070E-01   2.120E-05   1.367E-07   1.367E-07   3.070E-01
      3.070E-01   2.120E-05   1.367E-07   1.367E-07   3.070E-01
      1.035E+00   5.940E-05   1.346E-07   1.346E-07   1.035E+00
```



```
      1.035E+00   5.810E-05   1.346E-07   1.346E-07   1.035E+00
      2.129E+00   1.690E-04   1.157E-07   1.157E-07   2.129E+00
      2.129E+00   1.690E-04   1.157E-07   1.157E-07   2.129E+00
      3.322E+00   3.150E-04   9.326E-08   9.326E-08   3.322E+00
      3.322E+00   3.390E-04   9.327E-08   9.327E-08   3.322E+00
      4.657E+00   9.450E-04   7.150E-08   7.150E-08   4.657E+00
      4.657E+00   9.450E-04   7.150E-08   7.150E-08   4.657E+00
      6.176E+00   1.260E-03   5.191E-08   5.191E-08   6.176E+00
      6.176E+00   1.450E-03   5.194E-08   5.194E-08   6.176E+00
      9.929E+00   1.930E-03   2.303E-08   2.303E-08   9.929E+00
      9.929E+00   2.190E-03   2.303E-08   2.303E-08   9.929E+00
      1.492E+01   2.330E-03   8.007E-09   8.007E-09   1.492E+01
      1.492E+01   2.290E-03   8.007E-09   8.007E-09   1.492E+01

 FINAL LOG ACTIVITIES

 Na+          Th++++       H+           OH-          ClO4-
  -6.693E-01 -5.330E+00 -6.977E+00 -7.024E+00 -6.689E-01
  -6.693E-01 -5.330E+00 -6.977E+00 -7.024E+00 -6.689E-01
  -1.884E-01 -3.547E+00 -6.933E+00 -7.078E+00 -1.879E-01
  -1.884E-01 -3.556E+00 -6.933E+00 -7.078E+00 -1.879E-01
   1.102E-01 -2.229E+00 -6.875E+00 -7.153E+00  1.112E-01
   1.102E-01 -2.229E+00 -6.875E+00 -7.153E+00  1.112E-01
   3.088E-01 -1.509E+00 -6.820E+00 -7.227E+00  3.102E-01
   3.087E-01 -1.478E+00 -6.820E+00 -7.227E+00  3.103E-01
   4.719E-01 -7.038E-01 -6.769E+00 -7.302E+00  4.754E-01
   4.719E-01 -7.038E-01 -6.769E+00 -7.302E+00  4.754E-01
   6.210E-01 -2.366E-01 -6.724E+00 -7.376E+00  6.247E-01
   6.207E-01 -1.795E-01 -6.724E+00 -7.376E+00  6.251E-01
   9.022E-01  8.118E-01 -6.669E+00 -7.511E+00  9.062E-01
   9.019E-01  8.633E-01 -6.669E+00 -7.511E+00  9.065E-01
   1.172E+00  2.017E+00 -6.719E+00 -7.581E+00  1.176E+00
   1.172E+00  2.010E+00 -6.719E+00 -7.581E+00  1.175E+00

 Calculated Log Activity Coefficients

 Na+          Th++++       H+           OH-          ClO4-
      -0.1564      -0.6565      -0.1129      -0.1593      -0.1561
      -0.1564      -0.6565      -0.1129      -0.1593      -0.1561
      -0.2034       0.6797      -0.0622      -0.2074      -0.2028
      -0.2034       0.6797      -0.0622      -0.2074      -0.2028
      -0.2180       1.5430       0.0622      -0.2164      -0.2170
      -0.2180       1.5430       0.0622      -0.2164      -0.2170
      -0.2126       1.9927       0.2105      -0.1970      -0.2112
      -0.2127       1.9919       0.2105      -0.1971      -0.2111
      -0.1962       2.3207       0.3769      -0.1560      -0.1927
      -0.1962       2.3207       0.3769      -0.1560      -0.1927
      -0.1697       2.6630       0.5611      -0.0912      -0.1660
      -0.1700       2.6592       0.5609      -0.0914      -0.1657
      -0.0948       3.5263       0.9687       0.1267      -0.0907
      -0.0950       3.5229       0.9686       0.1266      -0.0904
      -0.0017       4.6499       1.3780       0.5156       0.0019
      -0.0016       4.6503       1.3781       0.5156       0.0018

 SOLVENT EXTRACTION SYSTEM EQUILIBRATED
   u0rt(                          Na+/Th++++EX)  -1.2065375E+02
     b0(             Th++++       ClO4-        )   7.6649537E-01
    cmx(             Th++++       ClO4-        )  -1.4134295E-02

  DATA SET( 1)

    input     calc       diff
  1.000000000000000E-005  0.000000000000000E+000
  1.000000000000000E-005  0.000000000000000E+000
  1.000000000000000E-005  0.000000000000000E+000
  1.000000000000000E-005  0.000000000000000E+000
  1.000000000000000E-005  0.000000000000000E+000
  1.000000000000000E-005  0.000000000000000E+000
  1.000000000000000E-005  0.000000000000000E+000
  1.000000000000000E-005  0.000000000000000E+000
  1.000000000000000E-005  0.000000000000000E+000
```

208	1.000000000000000E-005	0.000000000000000E+000
209	1.000000000000000E-005	0.000000000000000E+000
210	1.000000000000000E-005	0.000000000000000E+000
211	1.000000000000000E-005	0.000000000000000E+000
212	1.000000000000000E-005	0.000000000000000E+000
213	1.000000000000000E-005	0.000000000000000E+000
214	1.000000000000000E-005	0.000000000000000E+000

215

216 AVERAGE DEVIATION = 0.0000E+00

217

218 STANDARD DEVIATION = 0.0000E+00

219

220 FINAL MOLALITIES

221

222 Na+	Th++++	H+	OH-	ClO4-
223 3.070E-01	1.916E-05	1.367E-07	1.367E-07	3.070E-01
224 3.070E-01	1.916E-05	1.367E-07	1.367E-07	3.070E-01
225 1.035E+00	7.409E-05	1.346E-07	1.346E-07	1.035E+00
226 1.035E+00	7.409E-05	1.346E-07	1.346E-07	1.035E+00
227 2.129E+00	1.586E-04	1.157E-07	1.157E-07	2.129E+00
228 2.129E+00	1.586E-04	1.157E-07	1.157E-07	2.129E+00
229 3.322E+00	3.514E-04	9.328E-08	9.328E-08	3.322E+00
230 3.322E+00	3.516E-04	9.328E-08	9.328E-08	3.322E+00
231 4.658E+00	7.374E-04	7.145E-08	7.145E-08	4.657E+00
232 4.658E+00	7.374E-04	7.145E-08	7.145E-08	4.657E+00
233 6.176E+00	1.332E-03	5.192E-08	5.192E-08	6.176E+00
234 6.176E+00	1.336E-03	5.192E-08	5.192E-08	6.176E+00
235 9.927E+00	2.443E-03	2.305E-08	2.305E-08	9.929E+00
236 9.928E+00	2.449E-03	2.304E-08	2.304E-08	9.929E+00
237 1.492E+01	2.190E-03	8.006E-09	8.006E-09	1.492E+01
238 1.492E+01	2.190E-03	8.006E-09	8.006E-09	1.492E+01

239

240 FINAL LOG ACTIVITIES

241

242 Na+	Th++++	H+	OH-	ClO4-
243 -6.693E-01	-5.374E+00	-6.977E+00	-7.024E+00	-6.690E-01
244 -6.693E-01	-5.374E+00	-6.977E+00	-7.024E+00	-6.690E-01
245 -1.885E-01	-3.451E+00	-6.933E+00	-7.078E+00	-1.878E-01
246 -1.885E-01	-3.451E+00	-6.933E+00	-7.078E+00	-1.878E-01
247 1.102E-01	-2.256E+00	-6.875E+00	-7.153E+00	1.112E-01
248 1.102E-01	-2.256E+00	-6.875E+00	-7.153E+00	1.112E-01
249 3.087E-01	-1.462E+00	-6.820E+00	-7.227E+00	3.103E-01
250 3.087E-01	-1.462E+00	-6.820E+00	-7.227E+00	3.103E-01
251 4.724E-01	-8.077E-01	-6.769E+00	-7.302E+00	4.750E-01
252 4.724E-01	-8.077E-01	-6.769E+00	-7.302E+00	4.750E-01
253 6.209E-01	-2.136E-01	-6.724E+00	-7.376E+00	6.249E-01
254 6.209E-01	-2.135E-01	-6.724E+00	-7.376E+00	6.249E-01
255 9.016E-01	9.094E-01	-6.669E+00	-7.511E+00	9.067E-01
256 9.016E-01	9.095E-01	-6.669E+00	-7.511E+00	9.067E-01
257 1.172E+00	1.991E+00	-6.719E+00	-7.581E+00	1.175E+00
258 1.172E+00	1.991E+00	-6.719E+00	-7.581E+00	1.175E+00

259

260 Calculated Log Activity Coefficients

261

262 Na+	Th++++	H+	OH-	ClO4-
263 -0.1564	-0.6565	-0.1129	-0.1593	-0.1561
264 -0.1564	-0.6565	-0.1129	-0.1593	-0.1561
265 -0.2034	0.6791	-0.0623	-0.2075	-0.2027
266 -0.2034	0.6792	-0.0623	-0.2075	-0.2027
267 -0.2180	1.5433	0.0622	-0.2163	-0.2170
268 -0.2180	1.5433	0.0622	-0.2163	-0.2170
269 -0.2127	1.9918	0.2104	-0.1971	-0.2111
270 -0.2127	1.9916	0.2104	-0.1971	-0.2111
271 -0.1958	2.3246	0.3772	-0.1557	-0.1931
272 -0.1958	2.3246	0.3772	-0.1557	-0.1931
273 -0.1698	2.6620	0.5611	-0.0913	-0.1659
274 -0.1698	2.6609	0.5610	-0.0913	-0.1658
275 -0.0952	3.5215	0.9684	0.1263	-0.0902
276 -0.0952	3.5205	0.9684	0.1264	-0.0902
277 -0.0016	4.6508	1.3781	0.5157	0.0017
278 -0.0016	4.6509	1.3781	0.5157	0.0017

```
279
280          FINAL L2 NORM OF THE RESIDUALS  5.8867175E-01
281
282
283          EXIT PARAMETER                        3
284
285
286          FINAL APPROXIMATE SOLUTION
287
288
289          0 0 7  -1.2065375E+02
290          1 2 2   7.6649537E-01
291          4 2 2  -1.4134295E-02
```

Appendix K - Sample Output File: SOLUB_01.OUT

See Table 9-1 for explanation of this listing.

```
 NONLIN  V2.0

  NONLIN was developed by A.R. Felmy

  INPUT     file name is U1:[ SCBABB.NONLIN.USERGUIDE] SOLUB_01.IN;1
  GMIN      file name is U1:[ SCBABB.NONLIN.USERGUIDE] SOLUB_00.GMIN;1
  OUTPUT    file name is U1:[ SCBABB.NONLIN.USERGUIDE] SOLUB_01.OUT;1

            AQUEOUS SPECIES

     ID       NAME            MOLES          Z    u0rt
   1080H2O              0.000000000000    0.     -95.663
   1000H+               0.000000000000    1.       0.000
     80OH-              0.000000000000   -1.     -63.435
    161HSO4-            0.000000000000   -1.    -304.942
   1991H2Ox(aq)         0.000000000000    0.    -284.990
            SOLID PHASES

     ID       NAME            MOLES          Z    u0rt
 101990H2Ox.2H2O(s)    0.000000000000    0.     999.999

            CONSTRAINT EQUATIONS
                    0      1      8     16     99
 H2O              0.0    2.0    1.0    0.0    0.0
 H+               1.0    1.0    0.0    0.0    0.0
 OH-             -1.0    1.0    1.0    0.0    0.0
 HSO4-           -1.0    1.0    4.0    1.0    0.0
 H2Ox(aq)         0.0    2.0    0.0    0.0    1.0
 H2Ox.2H2O(s)     0.0    6.0    2.0    0.0    1.0

  Closed input files GMIN and COMP

  COMP      file name is U1:[ SCBABB.NONLIN.INPUTFILES] COMP.DAT;3
  BINARYP   file name is U1:[ SCBABB.NONLIN.INPUTFILES] BINARYP.DAT;2
  TERNARYP  file name is U1:[ SCBABB.NONLIN.INPUTFILES] TERNARYP.DAT;1
  LAMBDA    file name is U1:[ SCBABB.NONLIN.INPUTFILES] LAMBDA.DAT;1

        non-ideal electrolyte parameters

        single electrolyte parameters
H+          OH-              0.00000    0.00000    0.00000    0.00000
H+          HSO4-            0.20650    0.55560    0.00000    0.00000

        ternary electrolyte parameters

                                        H+
OH-         HSO4-            0.00000    0.00000

        neutral ion parameters
            H2Ox(aq)
H+              0.0000
OH-             0.0000
HSO4-           0.0000
H2Ox(aq)        0.0000

         higher order lambdas

                        OH-          HSO4-
H2Ox(aq)    H+              0.00000    0.00000

 TOTAL NUMBER OF SPECIES =  6
 NUMBER OF COMPONENTS    =  5
 INDEPENDENT CONSTRAINTS =  4

           SOLUBILITY DATA
```

```
66
67              input molalities
68
69
70        H+           OH-          HSO4-        H2Ox(aq)
71         1.168E+00    8.560E-15    1.168E+00    8.750E-01
72         1.965E+00    5.090E-15    1.965E+00    6.530E-01
73         2.927E+00    3.420E-15    2.927E+00    5.340E-01
74         4.450E+00    2.250E-15    4.450E+00    4.760E-01
75         6.660E+00    1.500E-15    6.660E+00    4.320E-01
76         9.548E+00    1.050E-15    9.548E+00    5.740E-01
77         1.394E+01    7.170E-16    1.394E+01    1.268E+00
78
79      -1.0000E+01
80                L2 NORM OF THE RESIDUALS  1.2378927E+03
81
82
83
84      -4.7788E+02
85                L2 NORM OF THE RESIDUALS  2.7255679E+00
86
87
88
89      -4.7788E+02
90                L2 NORM OF THE RESIDUALS  2.7255679E+00
91
92
93
94              ADJUSTED PARAMETERS
95       u0rt(                          H2Ox.2H2O(s))   -4.7787833E+02
96
97      DATA SET( 1)
98
99       input     calc       diff
100     0.000000000000000E+000  -1.30103480373751
101     0.000000000000000E+000 -0.932205339571694
102     0.000000000000000E+000 -0.611447612394127
103     0.000000000000000E+000 -0.249916679321500
104     0.000000000000000E+000  0.325209375816246
105     0.000000000000000E+000  0.889641981011270
106     0.000000000000000E+000    1.87975307818427
107
108      AVERAGE DEVIATION   =   8.8417E-01
109
110      STANDARD DEVIATION =   1.0302E+00
111
112     FINAL MOLALITIES
113
114     H+           OH-          HSO4-        H2Ox(aq)
115       1.168E+00   1.845E-14   1.168E+00   8.750E-01
116       1.965E+00   9.859E-15   1.965E+00   6.530E-01
117       2.927E+00   5.247E-15   2.927E+00   5.340E-01
118       4.450E+00   7.000E-15   4.450E+00   4.760E-01
119       6.660E+00   7.000E-15   6.660E+00   4.320E-01
120       9.548E+00   7.000E-15   9.548E+00   5.740E-01
121       1.394E+01   7.000E-15   1.394E+01   1.268E+00
122
123     FINAL LOG ACTIVITIES
124
125     H+           OH-          HSO4-        H2Ox(aq)
126       7.007E-02 -1.409E+01   7.007E-02 -5.799E-02
127       3.985E-01 -1.444E+01   3.985E-01 -1.851E-01
128       7.056E-01 -1.477E+01   7.056E-01 -2.725E-01
129       1.114E+00 -1.471E+01   1.114E+00 -3.224E-01
130       1.636E+00 -1.477E+01   1.636E+00 -3.645E-01
131       2.265E+00 -1.482E+01   2.265E+00 -2.411E-01
132       3.168E+00 -1.487E+01   3.168E+00   1.031E-01
133
134     Calculated Log Activity Coefficients
135
136     H+           OH-          HSO4-        H2Ox(aq)
```

```
          0.0026      -0.3603       0.0026       0.0000
          0.1051      -0.4330       0.1051       0.0000
          0.2392      -0.4922       0.2392       0.0000
          0.4657      -0.5552       0.4657       0.0000
          0.8128      -0.6145       0.8128       0.0000
          1.2849      -0.6654       1.2849       0.0000
          2.0238      -0.7168       2.0238       0.0000

 SOLID PHASE NOW IN EQUILIBRIUM

  DATA SET( 1)

   input     calc       diff
 0.000000000000000E+000   0.000000000000000E+000
 0.000000000000000E+000   0.000000000000000E+000
 0.000000000000000E+000   0.000000000000000E+000
 0.000000000000000E+000   0.000000000000000E+000
 0.000000000000000E+000   0.000000000000000E+000
 0.000000000000000E+000   0.000000000000000E+000
 0.000000000000000E+000   0.000000000000000E+000

  AVERAGE DEVIATION   =   0.0000E+00

  STANDARD DEVIATION =   0.0000E+00

 FINAL MOLALITIES

 H+            OH-           HSO4-         H2Ox(aq)
   1.168E+00   1.777E-14   1.168E+00   2.280E-01
   1.965E+00   9.589E-15   1.965E+00   2.506E-01
   2.927E+00   7.000E-15   2.927E+00   2.857E-01
   4.450E+00   7.000E-15   4.450E+00   3.691E-01
   6.660E+00   7.000E-15   6.660E+00   5.992E-01
   9.548E+00   7.000E-15   9.548E+00   1.353E+00
   1.394E+01   7.000E-15   1.394E+01   5.061E+00

 FINAL LOG ACTIVITIES

 H+            OH-           HSO4-         H2Ox(aq)
   8.371E-02 -1.410E+01   8.371E-02 -6.319E-01
   4.087E-01 -1.445E+01   4.087E-01 -5.947E-01
   7.133E-01 -1.464E+01   7.133E-01 -5.402E-01
   1.118E+00 -1.471E+01   1.118E+00 -4.312E-01
   1.627E+00 -1.477E+01   1.627E+00 -2.250E-01
   2.210E+00 -1.483E+01   2.210E+00   1.194E-01
   2.828E+00 -1.491E+01   2.828E+00   6.486E-01

 Calculated Log Activity Coefficients

 H+            OH-           HSO4-         H2Ox(aq)
        0.0163      -0.3532       0.0163       0.0102
        0.1153      -0.4288       0.1153       0.0063
        0.2469      -0.4897       0.2469       0.0039
        0.4700      -0.5541       0.4700       0.0017
        0.8038      -0.6163       0.8038      -0.0026
        1.2296      -0.6736       1.2296      -0.0120
        1.6841      -0.7552       1.6841      -0.0556

       FINAL L2 NORM OF THE RESIDUALS  2.7255679E+00


      EXIT PARAMETER                          3


       FINAL APPROXIMATE SOLUTION


       0 0 6  -4.7787833E+02
```

Appendix L - Review Forms

This Appendix contains the review forms for the NONLIN User's Manual.

NOTE: Copies of the User's Manual Reviewer's Forms are available in the Sandia WIPP Central Files.