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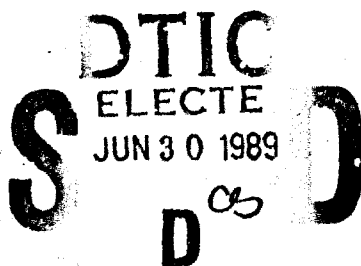
TECHNICAL REPORT

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COMPLEX EQUILIBRIUM CALCULATIONS OF NONIDEAL MULTIPHASE SYSTEMS (CEC-NMS) AND APPLICATIONS TO LIQUID METAL FUEL COMBUSTION

S. H. Chan, P. J. Janke

Prepared for the Department of the Navy
Office of Naval Research
Arlington, VA 22217



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March 15, 1989

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WITH APPLICATIONS TO LIQUID METAL FUEL COMBUSTION

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1. Wisconsin Distinguished Professor and Chairman
2. Graduate student

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ABSTRACT

This technical report summarizes a new chemical equilibrium computer code developed for general reacting systems, and presents equilibrium results for several reacting pairs in liquid metal fuel combustion. The content herein is based on the M.S. dissertation submitted by P.J. Janke, Department of Mechanical Engineering, University of Wisconsin--Milwaukee.

Specifically, the object of this report is to develop a general computer code for calculating complex chemical equilibrium of nonideal, multiphase, electrolytic mixtures. The necessary thermodynamic foundation is provided and thermodynamic potentials which describe the equilibrium state of a system are developed from the fundamental relation using Legendre transforms. For a system at a given temperature and pressure, the Gibbs' potential function reaches a minimum value at equilibrium. The minimization of this function, subject to element and charge conservation constraints, is viewed as a constrained optimization problem, which is solved by the method of Lagrangian multipliers. A new general computer code, called CEC-NMS, has been developed and is presented here for computing chemical equilibria. The evaluation and calculation of necessary program inputs such as thermodynamic data and specifying the relative amounts of reactants are discussed. Equilibrium results, including temperature, density, and species concentrations as a function of mixture fraction are presented for systems using the following reactants:

1. $\text{HCl}_{(g)} - \text{NH}_{3(aq)} - \text{H}_2\text{O}_{(L)}$
2. $\text{Cl}_{2(g)} - \text{Na}_{(L)}$
3. $\text{F}_{2(g)} - \text{Li}_{(L)}$
4. $\text{SF}_{6(g)} - \text{Li}_{(L)}$

Several different modeling techniques are used to accurately estimate the activity coefficients of the species in the above systems. The liquid phase of the electrolytic solution is calculated using a modified Pitzer formulation for multicomponent electrolytes with molecular species. The gas phase of the electrolytic solution is modeled using a pressure-explicit second order virial equation. The pure-component and cross-component second virial coefficients are predicted using O'Connell's generalized method. For the systems containing lithium and sodium, the gas phase is assumed to be ideal, and the activity coefficients of the liquid metal and molten salt comprising the immiscible liquid phases are calculated using the van Laar model.

ACKNOWLEDGMENT

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NOMENCLATURE

Roman

a_i	constant in specific heat polynomial, equations 3.19 and 3.20
a_i	activity of species i , equation 3.30
A_i	constant in the enthalpy of formation, equation 3.38
A_{ki}	value of the subscript to the k th element in the molecular formula of species i , equation 3.1
A_0	natural log based Debye-Huckel parameter, equation 6.3
A_{12}	empirical parameter in the van Laar model, equations 7.1 and 7.2
A'_{12}	empirical parameter in the modified van Laar model, equations 7.5-7.6 and 8.2
b_i	constant in specific heat polynomial, equations 3.19 and 3.20
b_1, b_2	empirical parameters in the van Laar model, equations 7.1-7.4
B	empirical parameter in the modified van Laar model, equations 7.5-7.6 and 8.1
B_k	number of moles of the k th element in the system, equation 3.1
B_i	constant in the enthalpy of formation, equation 3.38
B_m	second virial coefficient of a gaseous mixture, equation 6.4
B_{ij}	pure component and cross component second virial coefficients for pairs of gaseous species, equation 6.6
B_{ij}	term in equation 6.1
B'_{ij}	term in equation 6.1
c_i	constant in specific heat polynomial, equations 3.19 and 3.20
C_i	constant in the enthalpy of formation, equation 3.38
C_m	second virial coefficient of a gaseous mixture, equation 6.4
C_{pi}	heat capacity per unit mole of pure component i , equation 3.19
C_{pi}°	partial molar heat capacity of species i at infinite dilution, equation 3.20
d_i	integration constant in equations 3.21 and 3.22 for enthalpy

D_i	constant in the enthalpy of formation, equation 3.38
D_M	dipole moment of a molecule, Table 6.2
e	electron or charge, Section 6
E_i	integration constant in equation 3.39 for Gibbs free energy of formation
f	mixture fraction, defined in equation 3.41
f	fugacity of a single gas, equation 3.24
f_i	fugacity of species i in a gaseous mixture, equation 3.27
$f_i(\dots)$	function i of a given set of variables, Section 4
f^Y	term in equation 6.1
F	Helmholtz free energy, equation 2.12
G	Gibbs free energy, equation 2.16
ΔG_{fi}°	standard Gibbs free energy of formation at the temperature of the solution
ΔG_{fi}^*	standard Gibbs free energy of formation at the temperature and pressure of the solution
h_i	enthalpy per mole of pure species i , equation 3.17
H	enthalpy, equation 2.14
H_i	partial molar enthalpy of species i in a solution, equation 3.16
H_i°	partial molar enthalpy of species i in a solution of infinite dilution, equation 3.18
ΔH_{fi}°	standard enthalpy of formation of species i from the elements that comprise it, equation 3.36
I	ionic strength of a solution, equation 6.1
L	number of phases in a system, equation 5.2
L	Lagrangian function, equation 3.8
m	number of elements in a system, equation 3.1
m_i	molality of species i in a solution, equation 3.32
M_0	molecular weight of a solvent, equation 3.32

M_i	molecular weight of species i, equation 3.44
M_k	molecular weight of element k, equation 3.44
n	number of species in a system, equation 2.1
N_i	mole numbers of species i, equation 2.1
P	pressure, equation 2.9
r	total number of equations, equation 4.1
R	universal gas constant, equation 3.17
R_D	mean radius of gyration of a molecule, Table 6.2
S	entropy, equation 2.1
T	temperature, equation 2.5
U	internal energy, equation 2.1
v	molar volume of a mixture of gases, equation 6.4
V	volume, equation 2.1
V	specific volume, equation 5.1
V_j	specific volume of phase j, equation 5.2
ΔV_{fi}°	standard volume change for the formation of species i, equation 3.40
X_i	mole fraction of species i in a phase, equation 3.26
x_i	an arbitrary unknown, equation 4.1
Y_k^0	mass fraction of element k in 0 fluid, equation 3.43
Y_k^∞	mass fraction of element k in ∞ fluid, equation 3.43
Y_i^0	mass fraction of species i in 0 fluid, equation 3.44
Y_i^∞	mass fraction of species i in ∞ fluid, equation 3.45
Y_j	mass fraction of phase j, equation 5.2
z_1, z_2	composition variables in the van Laar model defined by equations 7.3 and 7.4
Z_i	ionic charge of species i, equation 6.1

Greek

α	arbitrary constant, equation 2.2
α	void fraction, equation 5.5
B_{ij}^0	binary interaction parameter, equation 6.1
B_{ij}^1	binary interaction parameter, equation 6.1
γ_i	activity coefficient of species i, equation 3.17
δ	denotes an increment in a variable, equation 4.2
Δ	denotes a change in a quantity, equation 3.15
ϵ	some arbitrary small number, equation 4.4
μ_i	chemical potential of species i, equation 2.10
μ_i^0	standard chemical potential of pure species i at the temperature of the solution, equation 3.25
μ_i^*	standard chemical potential of pure species i at the temperature and pressure of the solution, equation 3.28
μ_i^*	standard chemical potential of species i in a hypothetical solution of unit molality at the temperature and pressure of the solution under discussion, equation 3.32
ν_i	stoichiometric coefficients of a reaction, equation 3.37
π_k	the kth Lagrangian multiplier, equation 3.8
ρ	density, equation 5.1
σ_k	dimensionless Lagrangian multiplier, equation 3.13
Σ	summation operator
τ	relaxation factor, equation 4.6
ϕ	conserved property, equation 3.41
Ω_{ij}	binary association parameter, Table 6.3

Others

∂	partial derivative operator, round-d
$ $ $ $	norm operator, equation 4.8

Superscripts

m	iteration number, equation 4.4
p	"product" fluid, equation 3.41
0	"zero" fluid, equation 3.41
∞	"infinity" fluid, equation 3.41
°	standard or reference state (function of T only), equation 3.23
*	standard or reference state (function of T and P), equation 3.28
'	prime, used in equation 6.1 and 7.5

Subscripts

1,2	used to denote components of a binary solution, equation 7.1
aq	aqueous, as in $\text{NH}_3(\text{aq})$
c	crystal, as in $\text{NH}_4\text{Cl}(\text{c})$
f	denotes "formation", equation 3.34
g	gas phase
i	dummy variable for species
j	dummy variable for phases, equation 5.3
k	dummy variable for elements
L	liquid phase
m	denotes "mixture", equation 6.4
p	products, equation 3.15
r	reactants, equation 3.15
s	solid phase
w	denotes "water", equation 6.2
0	denotes "solvent", equation 3.32
ϕ	used in equation 6.3

1. INTRODUCTION

1.1 Definition of Equilibrium

As an introduction to this work, it is useful to present several fundamental definitions. Callen (1985) defines thermodynamic equilibrium as follows:

... in all systems there is a tendency to evolve toward states in which the properties are determined by intrinsic factors and not by previously applied external influences. Such simple terminal states are, by definition, time independent. They are called equilibrium states. (Callen, 1985, p. 13)

In addition, he emphasizes the importance of the concept of equilibrium by calling the determination of equilibrium states "... the single, all-encompassing problem of thermodynamics" (Callen, 1985, p. 26).

The thermodynamic equilibrium of a simple system (i.e., systems that are not acted on by electric, magnetic, or gravitational fields, and are macroscopically homogeneous) requires three distinct kinds of equilibrium (Kuo, 1986, p. 9):

1. Thermal equilibrium - exists when all parts of the system are at the same temperature.
2. Mechanical equilibrium - exists when there are no unbalanced forces within the system.
3. Chemical equilibrium - exists when a system has no tendency to undergo a spontaneous change in chemical composition.

1.2 Applications

The topic of this report is the computation of chemical equilibrium for multiphase systems. Numerous applications exist for chemical equilibrium calculations. Van Zeggeren and Storey (1970) describe four major areas:

1. Determining the specific impulse of a propellant in a rocket motor.
2. Calculation of the properties of explosives.
3. Chemical processing.
4. Calculating the behavior of multiphase biological cell systems.

In addition, Smith and Missen (1982) discuss applications of chemical equilibrium analysis in chemical kinetics, inorganic and organic chemistry, energy conversion, analytical chemistry, and environmental chemistry.

The impetus for this particular foray into the field of chemical equilibrium involves modeling the reaction zone structure of a turbulent, reacting jet discharging into a stagnant bath. As developed by Shearer et al. (1979), Chen and Faeth (1982, 1983) and Chan et al. (1987, 1988), the analytical model assumes local thermodynamic equilibrium at each point in the flow. As an input it requires the calculation of equilibrium compositions for all possible ratios of oxidant to fuel. This model allows the prediction of the concentration of chemical species, velocity, temperature, and mixture density at all points in the flow field. It has been used with reasonable success by this laboratory at the University of Wisconsin--Milwaukee (UWM) in the past (Chan et al., 1987, 1988).

1.3 Computational Methods

Numerous methods have been proposed for computing chemical equilibrium in the last 40 years. These are reviewed by Gautam and Seider (1979), Smith and Missen (1982), van Zeggeren and Storey (1970), and Zeleznik and Gordon (1968). While there are several ways of grouping the approaches, Zeleznik and Gordon (1968) divide the general purpose methods into the equilibrium constant approach and the free energy minimization approach. In the former method chemical reaction equations are written to describe the relevant equilibria.

Equilibrium constants for these equations are calculated which relate the concentrations of the species in the reaction. The resulting system of nonlinear equations may be solved using a variety of techniques. The latter method involves a search for the minimum in the Gibbs free energy of the system. While the equilibrium constant method as formulated by Brinkley (1947) and the free energy minimization method as formulated by White et al. (1958) can be shown to be computationally equivalent (Zeleznik and Gordon, 1960; Smith and Missen, 1982), the latter method eliminates the necessity of writing chemical equations.

1.4 Existing Computer Programs

Several computer programs are available for the solution of general chemical equilibria. Probably the best known is CEC-72 (Gordon and McBride, 1971). This computer code can be used for ideal, multiphase calculations, provided the total mass of the condensed (i.e., liquid and solid) phases are no more than a few percent of the total mass of the system. No provision is made for the use of activity coefficients to describe nonideal mixtures. The thermodynamic state of the system may be specified by assigning temperature and pressure (T,P), enthalpy and Pressure (H,P), entropy and pressure (S,P), temperature and volume (T,V), internal energy and volume (U,V), or entropy and volume (S,V). A data file containing thermodynamic property data for more than 400 chemical species over a temperature range of 300 to 5000 K is provided.

Another popular computer program is SOLGASMIX (Ericksson 1971, 1973, and 1975). This program can be used to calculate equilibria for nonideal, multiphase systems, provided that the activities of the species can be specified on a mole fraction scale (i.e., $\gamma_i \rightarrow 1$ as $X_i \rightarrow 1$, where

γ_i is the activity coefficient and X_i is the mole fraction of species i in the phase). Therefore, it is not applicable to electrolytic solutions, where the activities of the solutes are normally based on molality. The thermodynamic state may be specified by temperature and pressure only. All thermodynamic data must be supplied by the user. An extension of this program by Besmann (1977) uses the ideal gas law to allow the calculation of equilibria at constant total gas volume. Therefore, the thermodynamic state may also be specified by temperature and volume (T,V).

Ericksson (1979) also developed a program called SOLGASWATER, which is designed to be used to calculate multiphase, aqueous equilibria. The system is assumed to have a solvent of unit activity and a constant volume gas phase. Relationships specifying the activity coefficients of the solute species must be provided by the user. Because there is no provision for considering nonideal solvents, accurate predictions of equilibrium compositions are limited to dilute solutions.

Smith and Missen (1982) present two algorithms, BNR and VCS, useful for calculating ideal, multiphase equilibria at a specified temperature and pressure. The BNR program is based on the Rand method (White et al., 1958), and the VCS program is based on a formulation using extent of reaction variables. Thermodynamic data must be supplied by the user for both programs.

Zemaitis et al. (1986) discuss several computer programs that can be used for electrolytic solutions. Generally, the publically available programs are somewhat limited in terms of features and applicability. Several proprietary programs, however, appear to be quite complete and powerful.

1.5 Objectives

Work in this laboratory requires a computer code with a number of features not found (to the authors' knowledge) on existing, publically

available programs. These include the ability to calculate equilibria of electrolytic and non-electrolytic, multiphase, nonideal mixtures at either specified temperature and pressure (T,P) or specified ΔH and pressure ($\Delta H,P$) (i.e., the temperature is determined indirectly by inclusion of an energy equation which contains a specified enthalpy change term - for the adiabatic case, $\Delta H = 0$). Flexibility in the specification of activity coefficients is required, so that they may be written in whatever convention (molality or mole fraction) is relevant to the particular problem.

This report presents the development of such a computer code which utilizes a variation of the direct Gibbs free energy minimization approach first presented by White et al. (1958) while working at Rand Corporation. Section 2 attempts to provide the thermodynamic framework on which a discussion of chemical equilibria can be based. Section 3 presents the analytical derivation of the direct minimization approach. Section 4 describes the numerical technique used to solve the resulting nonlinear equations. The computer code is described in Section 5 and several applications of the program are demonstrated in Sections 6-9.

2. THERMODYNAMIC FUNDAMENTALS

Callen (1985) bases his development of thermodynamic theory on four postulates. We present the first three of his postulates below. The fourth postulate is a restatement of the third law of thermodynamics and is not relevant to this discussion.

2.1 Postulates

The first postulate in Callens' development proposes the existence of the equilibrium state (recall the definition of a simple system given in Chapter 1):

Postulate I. "There exist particular states, (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U , the volume V , and the mole numbers $N_1, N_2, \dots, N_n$ of the chemical components." (Callen, 1985, p. 13)

Several definitions are necessary before proceeding with the next postulate. We define a composite system as two or more simple systems. We further define extensive parameters as those parameters that have values in a composite system equal to the sum of their values in each of the subsystems. The second postulate proposes the existence of entropy and the entropy maximum principle:

Postulate II. "There exists a function (called the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states." (Callen, 1985, p. 27)

The relation that gives the entropy as a function of the extensive parameters is called the fundamental relation. If the fundamental relation of a particular system is known, all possible thermodynamic information about the system can be derived from it. The fundamental relation in entropic form can be written as:

$$S = S(U, V, N_1, N_2, \dots, N_n) \quad (2.1)$$

The third postulate specifies certain properties of entropy:

Postulate III. "The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy." (Callen, 1985, p. 28)

The additivity property of entropy requires that the entropy of a simple system be a homogenous first-order function of the extensive parameters. That is, if all the extensive parameters of a system are multiplied by a constant α , the entropy is multiplied by this same constant:

$$S(\alpha U, \alpha V, \alpha N_1, \dots, \alpha N_n) = \alpha S(U, V, N_1, \dots, N_n) \quad (2.2)$$

2.2 Equations of State

The significance of the differentiability, continuity, and monotonic properties of the entropy are that they allow the entropy function to be inverted with respect to the internal energy. The internal energy is then a single-valued, continuous, and differentiable function of $S, V, N_1, \dots, N_n$. The fundamental equation can then be written in the form:

$$U = U(S, V, N_1, \dots, N_n) \quad (2.3)$$

Computing the first differential:

$$dU = (\partial U / \partial S)_{V,N} dS + (\partial U / \partial V)_{S,N} dV + \sum_{i=1}^n (\partial U / \partial N_i)_{S,V,N} dN_i \quad (2.4)$$

The partial derivatives in the preceding equation occur so frequently that special symbols are used to represent them:

$$(\partial U / \partial S)_{V,N} \equiv T \quad (2.5)$$

$$-(\partial U / \partial V)_{S,N} \equiv P \quad (2.6)$$

$$(\partial U / \partial N_i)_{S, V, N} \equiv \mu_i \quad (2.7)$$

T , P , and μ_i are the temperature, pressure, and chemical potential of the i^{th} component, respectively.

The functional relationships

$$T = T(S, V, N_1, \dots, N_n) \quad (2.8)$$

$$P = P(S, V, N_1, \dots, N_n) \quad (2.9)$$

$$\mu_i = \mu_i(S, V, N_1, \dots, N_n) \quad (2.10)$$

are called equations of state. Since the fundamental equation is homogeneous first order, the equations of state are homogeneous zero order. This means that if we multiply each of the independent extensive parameters by a scalar α , the function is left unchanged:

$$T(\alpha S, \alpha V, \alpha N_1, \dots, \alpha N_n) = T(S, V, N_1, \dots, N_n) \quad (2.11)$$

Parameters for which this is true are said to be intensive parameters.

2.3 Thermodynamic Potentials

A mathematical technique known as the Legendre transformation (Callen, 1985, pp. 137-151) is performed on the energy representation of the fundamental relation (equation 2.3) in order to develop fundamental relations in more convenient forms for particular problems. The Legendre transformed functions are called thermodynamic potentials.

The partial Legendre transform of U that replaces the entropy by the temperature as the independent variable is called the Helmholtz potential (F) or Helmholtz free energy:

$$F = F(T, V, N_1, N_2, \dots, N_n) \quad (2.12)$$

also

$$F = U - TS \quad (2.13)$$

As a result of the entropy maximum principle stated in postulate II, it can be shown that the Helmholtz potential of a system at constant temperature is minimized at equilibrium.

The partial Legendre transform of U that replaces the volume by the pressure as an independent variable is called the enthalpy (H):

$$H = H(S, P, N_1, N_2, \dots, N_n) \quad (2.14)$$

also

$$H = U + PV \quad (2.15)$$

The enthalpy of a system at constant pressure is minimized at equilibrium.

The partial Legendre transform of U that simultaneously replaces the entropy by the temperature and the volume by the pressure as independent variables is called the Gibbs potential (G) or Gibbs free energy:

$$G = G(T, P, N_1, N_2, \dots, N_n) \quad (2.16)$$

also

$$G = U - TS + PV \quad (2.17)$$

The equilibrium state of a system at constant temperature and pressure is the state in which the Gibbs potential is minimized.

The homogeneous first-order property of the fundamental relation described above permits equation 2.3 to be written in a different form, known as the Euler relation (Callen, 1985, p. 59):

$$U = TS - PV + \mu_1 N_1 + \dots + \mu_n N_n \quad (2.18)$$

Substituting the Euler relation into equation 2.17, we get

$$G = \mu_1 N_1 + \mu_2 N_2 + \dots + \mu_n N_n$$

or, in more compact notation

$$G = \sum_{i=1}^n \mu_i N_i \quad (2.19)$$

Therefore the Gibbs potential for a multicomponent system is related to the chemical potentials of the individual components.

3. FORMULATION OF THE DIRECT MINIMIZATION TECHNIQUE

As shown in Section 2, the condition for chemical equilibrium at constant temperature and pressure is the minimization of the Gibbs potential. This minimization is subject to the element abundance constraints (conservation of chemical elements making up the species of the system).

3.1 Constraint Equations

The constraining element abundance equations may be written as

$$\sum_{i=1}^n A_{ki} N_i = B_k; \quad k = 1, 2, \dots, m$$

or, equivalently

$$\sum_{i=1}^n A_{ki} N_i - B_k = 0; \quad k = 1, 2, \dots, m \quad (3.1)$$

where A_{ki} is the value of the subscript to the k th element in the molecular formula of species i ; N_i is the number of moles of species i ; B_k is the fixed number of moles of the k th element in the system (determined from the initial conditions); m is the number of elements; and n is the number of species (Smith and Missen, 1982, p. 15).

When ions are present, we must add a charge balance equation (conservation of electrons) to the elemental abundance equations. This equation can be written as

$$\sum_{i=1}^n A_{m+1,i} N_i - B_{m+1} = 0; \quad k = m + 1 \quad (3.2)$$

where the coefficients $A_{m+1,i}$, $i = 1, \dots, n$, are the charge of the i th specie. For molecular species, $A_{m+1,i} = 0$; for an ion with a +2 charge,

$A_{m+1,i} = 2$; for an ion with a -1 charge, $A_{m+1,i} = -1$, etc. Since the overall charge of the mixture is zero, $B_{m+1} = 0$. The complete set of constraint equations are

$$\sum_{i=1}^n A_{ki} N_i - B_k = 0; \quad k = 1, 2, \dots, m+1 \quad (3.3)$$

These equations can also be written in matrix form as

$$[A] [N] = [B] \quad (3.4)$$

where $[A]$ is the formula matrix, $[N]$ is the species-abundance vector, and $[B]$ is the element abundance vector (Smith and Missen, 1982, p. 16). The matrices may be written in detail as

$$[A] = \begin{bmatrix} A_{11} & A_{12} & \dots & A_{1n} \\ A_{21} & A_{22} & & \\ \cdot & & & \\ \cdot & & & \\ A_{m+1,1} & & & A_{m+1,n} \end{bmatrix} \quad (3.5)$$

$$[N] = \begin{bmatrix} N_1 \\ N_2 \\ \cdot \\ \cdot \\ N_n \end{bmatrix} \quad (3.6) \quad \text{and} \quad [B] = \begin{bmatrix} B_1 \\ B_2 \\ \cdot \\ \cdot \\ B_{m+1} \end{bmatrix} \quad (3.7)$$

The formula matrix $[A]$ must be checked to ensure that it does not contain any linearly dependent rows. If any of the rows are linearly dependent, a singular coefficient matrix will result (Smith and Missen, 1982, p. 213). The offending rows must be identified and eliminated. One technique is to use Gauss-Jordan reduction to reduce the left side of $[A]$ to unit matrix form

(Smith and Missen, 1982, p. 24). Linearly dependent rows will appear as a zero vector and may be removed from the system.

3.2 Deriving the Lagrangian Function

We are now ready to derive the equations used in the direct minimization technique. The extremum function G must be minimized, subject to the side conditions of equation 3.3. This type of constrained optimization problem can be solved using the method of Lagrange multipliers (for a brief review of the method, see van Zeggeren and Storey, 1970, p. 158). The Lagrangian function L is defined as:

$$L = G + \sum_{k=1}^{m+1} \pi_k \left(\sum_{i=1}^n A_{ki} N_i - B_k \right) \quad (3.8)$$

where π_k are Lagrangian multipliers. Substituting in equation 2.19 for G , we get:

$$L = \sum_{i=1}^n \mu_i N_i + \sum_{k=1}^{m+1} \pi_k \left(\sum_{i=1}^n A_{ki} N_i - B_k \right) \quad (3.9)$$

Taking the derivative and setting equal to zero:

$$dL = \sum_{i=1}^n (\partial L / \partial N_i) dN_i + \sum_{k=1}^{m+1} (\partial L / \partial \pi_k) d\pi_k = 0 \quad (3.10)$$

Then, since $N_1, N_2, \dots$; and $\pi_1, \pi_2, \dots$; are independent, the corresponding partial derivatives must also be equal to zero

$$(\partial L / \partial N_i)_{N, \pi} = \mu_i + \sum_{k=1}^{m+1} A_{ki} \pi_k = 0; \quad i = 1, \dots, n \quad (3.11)$$

$$(\partial L / \partial \pi_k)_{N, \pi} = \sum_{i=1}^n A_{ki} N_i - B_k = 0 \quad k = 1, \dots, m+1 \quad (3.12)$$

Dividing equation 3.11 by RT to and defining $\sigma_k \equiv \pi_k/RT$, we then have the set of equations

$$\mu_i/RT + \sum_{k=1}^{m+1} A_{ki}\sigma_k = 0; \quad i = 1, \dots, n \quad (3.13)$$

and the original conservation equations

$$\sum_{i=1}^n A_{ki}N_i - B_k = 0; \quad k = 1, \dots, m+1 \quad (3.14)$$

a total of $n + m + 1$ equations. For equilibrium conditions at a specified temperature and pressure (T, P), these equations can be solved for the $n + m + 1$ unknowns N_i ; $i = 1, 2, \dots, n$ and σ_k ; $k = 1, 2, \dots, m+1$.

For equilibrium conditions at a specified enthalpy and pressure ($\Delta H, P$), the final mixture temperature becomes an unknown and we must add another equation to the above set. This equation is called the energy equation and can be written as

$$H_p(T, P, N_1, \dots)_p = H_r(T, P, N_1, \dots)_r + \Delta H \quad (3.15)$$

where H_r is the total enthalpy of the reactants, H_p is the total enthalpy of the equilibrium products and ΔH is some specified enthalpy change. The temperature is solved by iteration like any of the other unknowns. In many cases the enthalpy change may be due to heat transfer; for the adiabatic case, $\Delta H = 0$.

The set of equations 3.13, 3.14, and 3.15 contain several parameters that we must derive expressions for. These include the chemical potential of each species (μ_i), the product and reactant enthalpy (H_p, H_r), and the number of moles of each element in the system (B_k).

3.3 Enthalpy

The total enthalpy of a mixture (whether it be a mixture of products or a mixture of reactants) may be calculated from

$$H = \sum_{i=1}^n H_i N_i \quad (3.16)$$

where H_i is the partial molal (or molar) enthalpy of species i . The partial molar enthalpies of the species can be calculated from one of the following equations depending on the convention used to specify the activity coefficients of the species (Denbigh, 1981, p. 128 and p. 279). For the convention $\gamma_i \rightarrow 1$ as $X_i \rightarrow 1$, then

$$H_i = h_i - RT^2(\partial \ln \gamma_i / \partial T) \quad (3.17)$$

where h_i is the enthalpy per mole of the pure species i . For the convention $\gamma_i \rightarrow 1$ as $X_i \rightarrow 0$ and the convention $\gamma_i \rightarrow 1$ as $m_i \rightarrow 0$, then

$$H_i = H_i^\circ - RT^2(\partial \ln \gamma_i / \partial T) \quad (3.18)$$

where H_i° is the partial molar enthalpy of species i at infinite dilution. Generally, the partial derivatives in the above equations are calculated numerically by perturbing the appropriate function with respect to temperature. Of course, for an ideal solution, the activity coefficients are always equal to one, and the second term in each of the above equations will disappear.

The temperature dependence of h_i and H_i° can be calculated from specific heat data. Experimental data for the specific heat of a substance can be curve-fit to a polynomial of the form

$$C_{pi} = a_i + b_i T + c_i T^2 \quad (3.19)$$

where C_{pi} is heat capacity per unit mole of the pure component i , or

$$C_{pi}^\circ = a_i + b_i T + c_i T^2 \quad (3.20)$$

where C_{pi}° is the partial molar heat capacity of species i at infinite dilution. Using either the equation $dh_i = C_{pi} dT$, or the equation $dH_i^\circ = C_{pi}^\circ dT$, the polynomial can be integrated to get the enthalpy of the species as a function of temperature:

$$h_i = \int C_{pi} dT + \text{constant}$$

$$H_i^\circ = \int C_{pi}^\circ dT + \text{constant}$$

or

$$h_i = a_i T + b_i T^2/2 + c_i T^3/3 + d_i \quad (3.21)$$

$$H_i^\circ = a_i T + b_i T^2/2 + c_i T^3/3 + d_i \quad (3.22)$$

The integration constant d_i can be calculated if the enthalpy is known at any temperature within the range of applicability of the equation.

3.4 Chemical Potential

From Denbigh (1981) the chemical potential for a single perfect gas is defined as follows:

$$\mu(T, P) = \mu^\circ(T) + RT \ln P \quad (3.23)$$

where $\mu^\circ(T)$ is the standard chemical potential (or Gibbs free energy per mole) at temperature T and one atmosphere pressure; P is the pressure in atmospheres, and R is the universal gas constant.

For a single imperfect gas

$$\begin{aligned}\mu(T,P) &= \mu^\circ(T) + RT \ln f, \\ f &= \gamma P, \\ \gamma &\rightarrow 1 \text{ as } P \rightarrow 0\end{aligned}\tag{3.24}$$

where f is the fugacity of the gas, γ is the fugacity coefficient, and $\mu^\circ(T)$ is the chemical potential of the gas at unit fugacity. Since γ is very nearly 1 at $P = 1$, the numerical value for $\mu^\circ(T)$ is essentially the same as in equation 3.23. Note that for a perfect gas, $\gamma = 1$ and equation 3.24 reduces to equation 3.23.

For a perfect gas mixture

$$\mu_i(T,P,X_i) = \mu_i^\circ(T) + RT \ln P_i \tag{3.25}$$

where $\mu_i^\circ(T)$ is the standard chemical potential of gas i in its pure state at atmospheric pressure (exactly the same as $\mu_i^\circ(T)$ in equation 3.23). X_i is the mole fraction of component i in the gaseous mixture defined by

$$X_i = N_i / \sum_{i=1}^{n_{\text{gas}}} N_i \tag{3.26}$$

and P_i is the partial pressure of gaseous species i defined by $P_i = X_i P$.

For an imperfect gas mixture

$$\begin{aligned}\mu_i(T,P,X_i) &= \mu_i^\circ(T) + RT \ln f_i \\ f_i &= \gamma_i X_i P\end{aligned}\tag{3.27}$$

where f_i is the fugacity of species i , γ_i is the fugacity coefficient of species i in the gaseous mixture, and $\mu_i^\circ(T)$ has the same value as in

equation 3.24. Once again, for an ideal gaseous mixture $\gamma_i = 1$ and equation 3.27 reduces to equation 3.26.

The chemical potential for condensed phase solutions is defined similarly. When no distinction is made between the solvent and solutes in a solution, the Raoult convention is commonly used for all species in that solution. When a distinction is made between solvent and solutes (e.g., aqueous solutions), the Henry convention is commonly used for the solute species and the Raoult convention for the solvent species (Smith and Missen, 1982, p. 52).

For a Raoult's law ideal solution

$$\mu_i(T, P, X_i) = \mu_i^*(T, P) + RT \ln X_i \quad (3.28)$$

where $\mu_i^*(T, P)$ is the chemical potential of pure species i at the temperature and pressure of the solution.

For a solute following the Henry's law convention

$$\mu_i(T, P, X_i) = \mu_i^*(T, P) + RT \ln X_i \quad (3.29)$$

where $\mu_i^*(T, P)$ is the chemical potential of solute species i in an infinitely dilute solution and X_i is the mole fraction of the i th liquid species in the particular liquid phase.

For a nonideal solution

$$\mu_i(T, P, X_i) = \mu_i^*(T, P) + RT \ln a_i \quad (3.30)$$

where a_i is the activity of species i in the solution. For non-electrolytic solutions the activity can be written as

$$a_i = \gamma_i X_i \quad (3.31)$$

where γ_i is the activity coefficient of species i in the solution which accounts for any deviation from ideality. Note that for an ideal solution, $\gamma_i = 1$. For a species which approaches Raoult's law, $\gamma_i \rightarrow 1$ as $X_i \rightarrow 1$. For a solute species which exhibits Henry's law behavior, $\gamma_i \rightarrow 1$ as $X_i \rightarrow 0$.

In some cases the amount of solute is specified on the molality scale. Then

$$\begin{aligned} \mu_i(T, P, m_i) &= \mu_i^*(T, P) + RT \ln a_i \\ \gamma_i &\rightarrow 1 \text{ as } m_i \rightarrow 0 \end{aligned} \quad (3.32)$$

where $a_i = \gamma_i m_i$ and $m_i = 1000 N_i / (M_0 N_0)$. M_0 is the molecular weight of the solvent and N_0 is the number of moles of the solvent. $\mu_i^*(T, P)$ is the chemical potential of the solute in a hypothetical ideal solution of unit molality at the same temperature and pressure as the solution under discussion (Denbigh, 1981, p. 276).

The chemical potential of a single species phase such as a pure solid is written as

$$\mu_i(T, P) = \mu_i^*(T, P) \quad (3.33)$$

where $\mu_i^*(T, P)$ is the chemical potential of the pure species i at the temperature and pressure of the phase. All of the above specifications for chemical potential contain a standard reference potential for that species. It is necessary to assign a numerical value to that term. According to van Zeggeren and Storey, (1970), p. 31, we may set

$$\mu_i^\circ(T) = \Delta G_{fi}^\circ(T) \quad (3.34)$$

where $\Delta G_{fi}^{\circ}(T)$ is the standard Gibbs free energy of formation of the pure species (or ideal one molal solution, whichever the case may be) at temperature T . Similarly, for reference potentials that are a function of pressure

$$\mu_i^*(T,P) = \Delta G_{fi}^*(T,P) \quad (3.35)$$

where $\Delta G_{fi}^*(T)$ is the standard Gibbs free energy of formation of species i at temperature T and pressure P . These quantities can be found tabulated for a wide range of species in the literature e.g., Wagman et al. (1968) and JANAF (1971). If it is only available at one temperature, values at other temperatures can be calculated from enthalpy data using a form of the van't Hoff equation (Denbigh, 1981, p. 143):

$$[\partial(-\Delta G_{fi}^{\circ}/T)/\partial T]_P = \Delta H_{fi}^{\circ}/T^2 \quad (3.36)$$

where the enthalpy of formation ΔH_{fi}° represents the enthalpy change occurring when species i is formed from the elements comprising it. For a solvent, a gas or a Raoult's law solute, ΔH_{fi}° may be calculated from the enthalpy per mole of the pure component, h_i (equation 3.21), and enthalpy per mole of the elements comprising it

$$\Delta H_{fi}^{\circ} = h_i - \sum_r \nu_j h_j \quad (3.37a)$$

where h_j and ν_j are the enthalpy and the stoichiometric coefficient of the j th element in the formation reaction. For a Henry's law solute, ΔH_{fi}° may be calculated from the partial molar enthalpy of the species at infinite dilution, H_i° (equation 3.22), and the enthalpy per mole of the reference elements:

$$\Delta H_{fi}^{\circ} = H_i^{\circ} - \sum_r \nu_j h_j \quad (3.37b)$$

Assuming that the enthalpies of the elements, h_j , are fitted to the same type of function as the species formed (given by equations 3.21 and 3.22), we have

$$\Delta H_{fi}^{\circ} = A_i T + B_i T^2/2 + C_i T^3/3 + D_i \quad (3.38)$$

where $A_i \equiv a_i - \sum \nu_j a_j$, $B_i \equiv b_i - \sum \nu_j b_j$, etc. Integrating equation 3.36,

$$-\Delta G_{fi}^{\circ}/T = \int (A_i/T + B_i/2 + C_i T/3 + D_i/T^2) dT + \text{constant}$$

Finally,

$$\Delta G_{fi}^{\circ} = A_i T \ln(T) - B_i T^2/2 - C_i T^3/6 + D_i + E_i T \quad (3.39)$$

Since most compilations list the Gibbs free energy of formation at a pressure of one atmosphere only, we similarly can calculate values at other pressures using (Denbigh, 1981, p. 300):

$$[\partial(\Delta G_{fi}^{\circ}/T)/\partial P]_T = \Delta V_{fi}^{\circ} \quad (3.40)$$

where ΔV_{fi}° is the standard volume change for the formation of species i , analogous to ΔH_{fi}° and ΔG_{fi}° .

3.5 Specifying Amounts of Reactants

The relative amounts of reactants present can be specified by a parameter called the mixture fraction (Spalding, 1979, ch. 6), usually denoted by the symbol f . Suppose we divide the components of the reactants into two portions: the "0" (zero) fluid and the " ∞ " (infinity) fluid. The fluid resulting from the mixing of the 0 fluid and the ∞ fluid will be called the

"p" (product) fluid. For any conserved property ϕ , the mixture fraction is defined as

$$f \equiv (\phi^p - \phi^\infty) / (\phi^0 - \phi^\infty) \quad (3.41)$$

Usually, the fluid state at ∞ and 0 is known, and we wish to determine ϕ^p at a given mixture fraction. Rewriting equation 3.41, we get

$$\phi^p = f\phi^0 + (1 - f)\phi^\infty \quad (3.42)$$

Therefore, for $f = 1$, $\phi^p = \phi^0$, and for $f = 0$, $\phi^p = \phi^\infty$. If we exclude nuclear reactions, then Y_k , the mass fraction of element k in a mixture of compounds, is a conserved property (Kays and Crawford, 1980, p. 344). Then we can write

$$Y_k = fY_k^0 + (1 - f)Y_k^\infty; \quad k = 1, 2, \dots, m \quad (3.43)$$

where

$$Y_k^0 = \sum_{i=1}^n Y_i^0 (M_k/M_i) A_{ki}; \quad k = 1, 2, \dots, m \quad (3.44)$$

$$Y_k^\infty = \sum_{i=1}^n Y_i^\infty (M_k/M_i) A_{ki}; \quad k = 1, 2, \dots, m \quad (3.45)$$

Y_i^0 , Y_i^∞ , are the mass fraction of species i in the 0 fluid and ∞ fluid, respectively; M_k and M_i are the molecular weights of element k and species i respectively; and A_{ki} are the number of moles of element k in species i (defined previously).

The number of moles of element k in the system, B_k , can be written as

$$B_k = Y_k^p / M_k; \quad k = 1, 2, \dots, m \quad (3.46)$$

Using equation 3.43, we get

$$B_k = (fY_k^0 + (1 - f) Y_k^\infty)/M_k; \quad k = 1, 2, \dots, m$$

or

$$B_k = f \sum_{i=1}^n A_{ki} Y_i^0/M_i + (1 - f) \sum_{i=1}^n A_{ki} Y_i^\infty/M_i; \quad k = 1, 2, \dots, m \quad (3.47)$$

Equation 3.47 can be used to calculate the components of the B vector when the mixture fraction f , the mass fractions of all species in the 0 fluid state Y_i^0 and in the ∞ fluid state Y_i^∞ are specified. For the B vector, the computer code developed in later section take the mass of the mixture as one kg such that B_k can then be interpreted as the number of moles of k th element in a unit kg mass of mixture.

4. NUMERICAL METHOD

4.1 Newton-Raphson Technique

The system of nonlinear equations set up by the direct minimization technique in Section 3 can be solved using Newton-Raphson iteration (Gerald and Wheatley, 1984, pp. 135-137). The set of $r = n + m + 1$ equations to be solved can be written in the following form:

$$\begin{aligned} f_1 (\underline{X}_1, \underline{X}_2, \dots, \underline{X}_r) &= 0 \\ f_2 (\underline{X}_1, \underline{X}_2, \dots, \underline{X}_r) &= 0 \\ &\vdots \\ f_r (\underline{X}_1, \underline{X}_2, \dots, \underline{X}_r) &= 0 \end{aligned} \tag{4.1}$$

where $\underline{X}_1, \underline{X}_2, \dots, \underline{X}_r$ are the roots of the equations. The relationship between any $f_i (X_1 + \delta X_1, X_2 + \delta X_2, \dots)$ and $f_i (X_1, X_2, \dots)$ where $\delta X_1, \delta X_2, \dots, \delta X_r$ denote arbitrary increments in $X_1, X_2, \dots, X_r$ is given by Taylor's Expansion (Callen, 1985, p. 474):

$$\begin{aligned} f_i (X_1 + \delta X_1, X_2 + \delta X_2, \dots) &= f_i (X_1, X_2, \dots) + \\ &+ (\partial f_i / \partial X_1) \delta X_1 + (\partial f_i / \partial X_2) \delta X_2 + \dots] \\ &+ (1/2) [(\partial^2 f_i / \partial X_1^2) \delta X_1^2 + \dots] \\ &+ \dots; \end{aligned} \tag{4.2}$$

$i = 1, 2, \dots, r$

If we define $\delta X_i = \underline{X}_i - X_i$, where $\underline{X}_i$ and X_i are the true and guessed roots, respectively, so that

$$f_i (X_1 + \delta X_1, X_2 + \delta X_2, \dots) = f_i (\underline{X}_1, \underline{X}_2, \dots) = 0; \quad i = 1, 2, \dots, r \tag{4.3}$$

we could solve the above set of equations for the δX_i and calculate the roots $\underline{X}_i$ from $\underline{X}_i = X_i + \delta X_i$. In practice, if the initial estimates X_i are near enough to the solution, we can truncate the series after the first order terms and get an approximation X^{m+1} to the final solution $\underline{X}_i$:

$$f_i (X_1^{m+1}, X_2^{m+1}, \dots) = 0 = f_i (X_1^m, X_2^m, \dots) + [\partial f_i / \partial X_1] \delta X_1 + \dots]$$

or

$$\begin{aligned} -f_i (X_1^m, X_2^m, \dots) &= (\partial f_i / \partial X_1) \delta X_1 + (\partial f_i / \partial X_2) \delta X_2 + \dots; \\ i &= 1, 2, \dots, r \end{aligned} \quad (4.4)$$

where $X^{m+1} = X^m + \delta X$. This set of linear equations is solved using Gaussian elimination (Gerald and Wheatley, 1984, p. 91) for the unknowns δX_i . The new approximations are calculated from $X^{m+1} = X^m + \delta X$ and the procedure is repeated until $(\delta X_i)_{\max} < \epsilon_1$ or $f (X_1^m, X_2^m, \dots)_{\max} < \epsilon_2$, where ϵ_1 and ϵ_2 are some small numbers (1.E-6 and 5.E-5 respectively, in this case).

In order to solve the above set of equations we must calculate the partial derivatives appearing on the right sides. Rather than derive an expression for the partial derivatives by hand, it is easier to approximate the partials numerically. This is done by recalculating the function with a small perturbation to each of the variables in turn (Gerald and Wheatley, 1984, p. 137):

$$\begin{aligned} \partial f_1 / \partial X_1 &\approx [f_1 (X_1 + \delta, X_2, \dots) - f_1 (X_1, X_2, \dots)] / \delta \\ \partial f_1 / \partial X_2 &\approx [f_1 (X_1, X_2 + \delta, \dots) - f_1 (X_1, X_2, \dots)] / \delta \\ &\vdots \\ \partial f_1 / \partial X_r &\approx [f_1 (X_1, \dots, X_r + \delta) - f_1 (X_1, \dots, X_r)] / \delta \end{aligned} \quad (4.5)$$

Thus, the solution to the set of nonlinear equations is approximated by solving the linear set of equations. Each successive approximation generates a set of solutions closer and closer to the final solution.

4.2 Relaxation Factor

Certain modifications to this technique are necessary in order to improve the stability of the iteration. A step-size parameter (or relaxation factor) τ can be introduced as follows:

$$X_i^{m+1} = X_i^m + \tau \delta X_i \quad (4.6)$$

where $0 < \tau \leq 1$. Poor initial guesses can lead to a large negative correction which could cause the number of moles of a species to become negative. We choose the relaxation factor to ensure that the mole numbers of all the species remain positive throughout the iteration process (non-negativity constraint). We start the process with $\tau = 1$ and find the maximum value for τ less than one that will ensure that all of the new mole number estimates will be positive. The algorithm used is

Start with $\tau = 1$

For $i = 1, 2, \dots, n$

If $\delta X_i < 0$, Then

$$\tau_{\max} = \min (\tau, -X_i^m (1 - c) / \delta X_i)$$

(4.7)

$$\tau = \tau_{\max}$$

Next i

where c is some small number (0.01 in this case). Note that there is no such non-negativity constraint on the Lagrangian multipliers. The Euclidean norm of the error vector is defined as (Gerald and Wheatley, 1984, p. 115):

$$|| f^m ||_e = [\sum_{i=1}^r f_i (x_1^m, x_2^m, \dots)^2]^{0.5} \quad (4.8)$$

As long as the Newton-Raphson corrections decrease the norm of the error vector (i.e., the iteration is converging) τ is set equal to $\tau_{\max}$. If for any iteration $m + 1$, the norm is greater than the norm calculated at the previous step, i.e.

$$|| f^{m+1} || > || f^m || \quad (4.9)$$

the relaxation factor is reduced by setting τ equal to $0.7\tau_{\max}$ and the norm at the $m + 1$ step is recalculated (see Prausnitz et al., 1980, p. 116). This reduction of τ is repeated until the norm decreases (in which case the iteration proceeds), or until τ becomes too small, say 0.01, (in which case τ is just set equal to $\tau_{\max}$ and the iteration is allowed to take a step which increases the norm of the error vector).

4.3 Species Present in Small Amounts

When a species in a multispecies phase is present in a very small amount, it forces the step-size parameter to become very small, slowing the convergence of the algorithm. The species must then be removed from the main calculation. After convergence is achieved with this species removed, the amount of the species present may be calculated from (Smith and Missen, 1982, pp. 217-218):

$$x_i = \exp \left(- \mu_i^* / RT - \sum_{k=1}^{m+1} A_{ki} \sigma_k \right) \quad (4.10)$$

This equation, of course, is only valid if the species is indeed present in a very small amount at equilibrium. Note that during the course of iteration, a species may be erroneously removed (especially if poor initial estimates are

given). If so, equation 4.10 provides a means of checking if any other species should have been included in the main calculation.

An equation similar to that given above may be used to determine if a single species phase (such as a pure solid species) should be included in the calculation. Equilibrium may at first be calculated with only multispecies phases present, then the following test may be made to determine if the conditions are favorable for the formation of a single species phase (Smith and Missen, 1982, p. 59):

$$\mu_i^*/RT + \sum_{k=1}^{m+1} A_{ki} \sigma_k < 0 \quad (4.11)$$

If the quantity given above is less than zero, the single species phase in question should be added to the system and equilibrium recalculated. If the quantity is exactly zero, the phase is at incipient formation. If the quantity is greater than zero, the phase should not be included. A similar test may be used for multispecies phases, as well (Smith and Missen, 1982, p. 59).

5. COMPUTER PROGRAM

The equations developed in the previous sections have been implemented in a computer program called CEC-NMS (Complex Equilibrium Calculations of Nonideal, Multiphase Systems). For a listing of the program, see the appendix. The program is written in Fortran 77 and is approximately 1300 lines long, including a generous number of comment cards. CEC-NMS consists of a main program unit and 9 primary subroutines. Additional subroutines to calculate the activity coefficients for nonideal solutions may also be present, depending on the particular system.

5.1 Main

The main program unit performs several functions:

1. Declare and initialize variables.
 2. Set up chemical system (species symbols, molecular weight, species coefficient matrix, etc.).
 3. Open output file and read in data for calculation point.
 4. Call subroutine GUESS to provide initial estimates.
 5. Calculate reactant enthalpy.
 6. Call subroutine NLSYST, the Newton-Raphson equation solver.
 7. Print out error messages, if any.
 8. Call subroutines PREOUT and OUTPUT to print out results.
 9. Return to step 3 and read in data for the next calculation point.
- Stop program execution after last data point.

5.2 Gcal

Subroutine GCAL calculates the standard Gibbs potential of each species in the system at a given temperature. In the present form, equation 3.39 is used. The user must supply the coefficients A_i , B_i , etc.

5.3 Hcal

Subroutine HCAL calculates the partial molar enthalpy of the species in solution (H_i in equation 3.16) using equations 3.17-18 and 3.21-22. The user must supply the coefficients a_i , b_i , etc. Later versions of the program combine subroutine GCAL and subroutine HCAL into one subroutine called HSGCAL.

5.4 Preout

Subroutine PREOUT calculates the number of moles of any species which have been removed from the main calculation using equation 4.10. Also calculated are various mass and mole fractions, the mixture density, and the mixture void fraction (volume fraction of gas phase present). The mixture density, ρ [kg/m^3], is defined as

$$\rho \equiv 1/V \quad (5.1)$$

where V is the specific volume of the mixture [m^3/kg]. The specific volume of a mixture of L phases may be expressed as

$$V = \sum_{j=1}^L Y_j V_j \quad (5.2)$$

or

$$V = \sum_{j=1}^L Y_j / \rho_j \quad (5.3)$$

where V_j , ρ_j , and Y_j are the specific volume, density, and mass fraction of phase j in the total mixture, respectively. Substituting equation 5.3 into 5.1, we have

$$\rho = 1 / \left(\sum_{j=1}^L Y_j / \rho_j \right) \quad (5.4)$$

The void fraction of the mixture is defined as

$$\alpha \equiv V_{\text{gas}}/V \quad (5.5)$$

or

$$\alpha = \left(\sum_{j=1}^{n_{\text{gas}}} Y_j / \rho_j \right) / \left(\sum_{j=1}^n Y_j / \rho_j \right) \quad (5.6)$$

5.5 Output

Subroutine OUTPUT sends detailed results for a calculation point to the line printer and abridged results to a file. The file is later used to plot the results.

5.6 Guess

Subroutine GUESS provides initial estimates needed to begin the iteration at each calculation point. The user must provide these estimates for every species. Fortunately, CEC-NMS has converged quite well for all test systems with rather arbitrary initial guesses.

5.7 Nlsyst

Subroutine NLSYST solves the system of nonlinear equations by a step-limited Newton-Raphson technique. The subroutine performs the following functions:

1. Declare and initialize variables.
2. Begin calculations with only multispecie phase present. Single species phases will be added one at a time after convergence is achieved with only multispecies phases present.
3. Call subroutine FCN to calculate function values.
4. Remove any specie or phase that is present in a very small amount (i.e., less than 10^{-10}).

5. Remove any specie that is causing convergence problems (i.e., if convergence is not achieved within 20 iterations since the last species was removed, remove the species in the system that is present in the least amount).
6. Check if function values meet the F-tolerance.
7. Calculate the partial derivative matrix.
8. Call subroutine SCALE to scale the matrix.
9. Call subroutine ELIM to solve the matrix.
10. Calculate the maximum relaxation factor that will ensure that the mole numbers of all species remain positive.
11. Reduce the relaxation factor if such a reduction will reduce the Euclidean norm of the vector.
12. Calculate new estimates for the unknowns.
13. Check if X-tolerance is met.
14. After convergence is achieved with only multispecies phases present, check if any of the single species phases will reduce the Gibbs free energy of the system using equation 4.11. Recalculate the equilibrium with each new phase added in turn.

5.8 Elim

Subroutine ELIM solves the partial derivative matrix generated by NLSYST (the set of equations 4.4) using Gaussian elimination.

5.9 Scales

This subroutine scales the values of the partial derivative matrix so that the largest element in each row is unity.

5.10 Fcn

Subroutine FCN calculates the function values (the f_i in equations 4.4) of the system of nonlinear equations. The following calculations are performed:

1. Shift the X-vector if any species have been removed.
2. Calculate the enthalpy of the mixture by calling subroutine HCAL.
3. Calculate the standard Gibbs free energy of the species by calling subroutine GCAL.
4. Calculate the mole fractions of each species.
5. Calculate the chemical potential of each species using equations 3.25, 3.27, 3.28, 3.30, or 3.32.
6. Calculate the functions using equations 3.13-15.
7. Shift F-vector for any removed species.

5.11 Activ

Optional user supplied subroutines ACTIV1, ACTIV2, etc. are used to calculate the activity coefficients of multispecies phase 1, phase 2, etc.

6. APPLICATION TO AN ELECTROLYTIC SYSTEM

In the course of study of the structure of chemically reacting jets it became necessary to compute the equilibrium compositions for a mixture of aqueous ammonia (NH_3) solution and hydrogen chloride gas (HCl) (Chan et al., 1987). These reactants form a multicomponent electrolytic solution containing ions and molecules dissolved in water.

The initial compositions of the reactants are specified by the mixture fraction f (see equation 3.41) and the mass fractions of species in 0 and ∞ fluid streams, Y_i^0 and Y_i^∞ . The 0 and ∞ fluids were defined to be pure HCl(g) , ($Y_i^0 = 1$), and aqueous ammonia solution ($Y_{\text{NH}_3(\text{aq})}^\infty$), respectively. The initial concentration of the aqueous ammonia solution ($Y_{\text{NH}_3(\text{aq})}^\infty$) varies from 0-30% by mass. The relative amount of HCl to ammonia solution ranged from 0-100% (i.e., the mixture fraction ranged from 0 to 1).

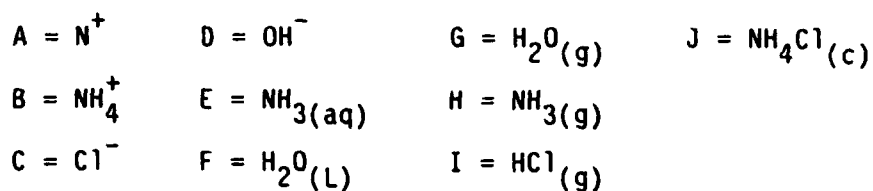
The system under consideration was assumed to contain the following species in the liquid phase: H^+ , NH_4^+ , Cl^- , $\text{NH}_3(\text{aq})$, OH^- and $\text{H}_2\text{O}(\text{L})$. The chemical potential of the solutes were expressed using equation 3.32. the chemical potential of water (the solvent) was expressed using equation 3.30. The gas phase (when present) was assumed to consist of $\text{H}_2\text{O}(\text{g})$, $\text{NH}_3(\text{g})$, and $\text{HCl}(\text{g})$. The chemical potentials of the gaseous species were expressed using equation 3.27. A solid phase consisting of $\text{NH}_4\text{Cl}(\text{c})$ appears at high concentrations of NH_4^+ and Cl^- . The chemical potential of the pure solid phase was expressed using equation 3.33.

6.1 Species Coefficient Matrix

The formula matrix $[A]$ of the system is written as

	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)	(I)	(J)
Cl	0	0	1	0	0	0	0	0	1	1
H	1	4	0	1	3	2	2	3	1	4
N	0	1	0	0	1	0	0	1	0	1
O	0	0	0	1	0	1	1	0	0	0
e	1	1	-1	-1	0	0	0	0	0	0

where



and

Cl = chlorine

H = hydrogen

N = nitrogen

O = oxygen

e = electron

Performing Gauss-Jordan reduction we obtain

	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)	(I)	(J)
H	1	0	0	0	-1	1	1	-1	1	0
N	0	1	0	0	1	0	0	1	0	1
Cl	0	0	1	0	0	0	0	0	1	1
O	0	0	0	1	0	1	1	0	0	0
e	0	0	0	1	0	1	1	0	0	0

We see that row 4 and row 5 are, in fact, the same equation. Therefore, we eliminate row 5, the charge balance equation, as it is redundant. The final revised formula matrix is

	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)	(I)	(J)
Cl	0	0	1	0	0	0	0	0	1	1
H	1	0	0	0	-1	1	1	-1	1	0
N	0	1	0	0	1	0	0	1	0	1
O	0	0	0	1	0	1	1	0	0	0

Therefore, for constant temperature and pressure equilibrium, there are a total of 14 unknowns - the mole numbers of 10 species and the Lagrangian multipliers for 4 constraint equations. Note that if during the course of computation, any species is eliminated from consideration, we must check to see that all of the rows in the matrix are still independent.

6.2 Calculation of Thermodynamic Data

The thermodynamic data necessary for this system was obtained from a variety of sources. C_p° , ΔH_f° , and ΔG_f° for the ions at 298.15 K is from Wagman et al. (1968). $\Delta H_f^\circ(T)$ for $\text{NH}_3(\text{aq})$ was curve-fit from experimental data found in Washburn (1930). The polynomial constants for the specific heat of the gases were obtained from Reynolds and Perkins (1984). Thermodynamic data for $\text{NH}_4\text{Cl}_{(\text{c})}$ is from the JANAF Thermochemical Tables (1971). The computer program used to calculate the constants A_i , B_i , C_i , D_i , and E_i of equation 3.38 and 3.39 is listed in Appendix A.

6.3 Activity Coefficients in the Liquid Phase

The activity coefficients of the species in the liquid phase were approximated using a theoretical model developed by Edwards et al. (1978). The Edwards model is based on formalism set forth by Pitzer in a series of papers (1973, 1974). Edwards, however, neglects all ternary interaction parameters. Their justification for this simplification is that sufficient

ternary experimental data is rarely available to fix ternary parameters. Therefore, the model relies instead on only binary parameters to describe the interactions between the species in solution. Edwards also extended the equations to weak electrolytes and molecular species by defining parameters for ion-molecule and molecule-molecule interactions as well as the Pitzer ion-ion interactions.

It should be noted that Zemaitis et al. (1986) provides an excellent summary of the most recent modeling techniques for determining the activity coefficients in electrolytic solutions. Included are chapters on single and multicomponent strong electrolytes, strongly complexing compounds, weak electrolytes and molecular species. The equations Edwards used for the activity coefficient of a solute are (Zemaitis et al., 1986, pp. 503):

$$\ln \gamma_i = Z_i^2 f^Y + 2 \sum_{j=1}^{ns} m_j B_{ij} + Z_i^2 \sum_{j=1}^{ns} \sum_{k=1}^{ns} m_j m_k B'_{jk} \quad (6.1)$$

where

$$f^Y = -A_\phi \left[\sqrt{I} / (1 + 1.2\sqrt{I}) + (2/1.2) \ln (1 + 1.2\sqrt{I}) \right]$$

$$B_{ij} = B_{ij}^\circ + (\beta_{ij}^1/2I) [1 - (1 + 2\sqrt{I}) \exp(-2\sqrt{I})]$$

$$B'_{ij} = (\beta_{ij}^1/4I^2) [-1 + (1 + 2\sqrt{I} + 2I) \exp(-2\sqrt{I})]$$

$$A_\phi = \text{natural log based Debye-Huckel constant (see equation 6.3)}$$

$$I = \text{ionic strength of the solution}$$

$$\equiv 0.5 \sum_{i=1}^{ns} Z_i^2 m_i$$

and where

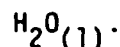
Z_i = ionic charge of species i

m_i = molality of species i

β_{ij}° = binary interaction parameter

β_{ij}^1 = binary interaction parameter

ns = number of solutes in the solution. Note that this does not include



The activity of water is expressed as (Zemaitis et al., 1986, pp. 504):

$$\ln a_w = M_w \{ 2A_\phi I^{3/2} / (1 + 1.2\sqrt{I}) - \sum_{i=1}^{ns} \sum_{j=1}^{ns} m_i m_j [\beta_{ij}^\circ + \beta_{ij}^1 \exp(-2\sqrt{I})] - \sum_{i=1}^{ns} m_i \} \quad (6.2)$$

The Debye-Huckel parameter for aqueous electrolytic systems is calculated from (Chen et al., 1982):

$$\begin{aligned} A_\phi = & - 61.44534 \exp [(T - T^\circ)/T^\circ] \\ & + 2.864468 [\exp (T - T^\circ)/T^\circ]^2 \\ & + 183.5379 \ln (T/T^\circ) - 0.6820223 (T - T^\circ) \\ & + 0.0007875695 (T^2 - (T^\circ)^2) + 58.95788 (T^\circ/T) \end{aligned} \quad (6.3)$$

where $T^\circ = 273.15$ K. The estimated values for the binary interaction parameters used in this study along with the source are shown in Table 1. Note that, as suggested by Edwards, like charge ionic interactions are ignored, as well as the β_{ij}^1 term for interactions involving molecules.

Table 6.1 Binary Interaction Parameters for the $\text{NH}_3\text{-HCl-H}_2\text{O}$ System

Binary Pair	B_{ij}°	Source	B_{ij}^1	Source
$\text{H}^+ - \text{H}^+$	0	(e)	0	(e)
$\text{H}^+ - \text{NH}_4^+$	0	(e)	0	(e)
$\text{H}^+ - \text{Cl}^-$	0.1775	(a)	0.2945	(a)
$\text{H}^+ - \text{OH}^-$	0.208	(b)	$0.018 + 3.06B_{ij}^\circ$	(b,c)
$\text{H}^+ - \text{NH}_3(\text{aq})$	0.015	(b,c,d)	0	(b,c,d)
$\text{NH}_4^+ - \text{NH}_4^+$	0	(e)	0	(e)
$\text{NH}_4^+ - \text{Cl}^-$	0.0522	(a)	0.1918	(a)
$\text{NH}_4^+ - \text{OH}^-$	0.06	(b)	$0.018 + 3.06B_{ij}^\circ$	(b,c)
$\text{NH}_4^+ - \text{NH}_3(\text{aq})$	0.0117	(b)	-0.020	(b)
$\text{Cl}^- - \text{Cl}^-$	0	(e)	0	(e)
$\text{Cl}^- - \text{OH}^-$	0	(e)	0	(e)
$\text{Cl}^- - \text{NH}_3(\text{aq})$	0	N/A	0	N/A
$\text{OH}^- - \text{OH}^-$	0	(e)	0	(e)
$\text{OH}^- - \text{NH}_3(\text{aq})$	0.227	(b,c)	0	(b,c)
	$- 1.47\text{E-}3\text{T}$			
	$+ 2.6\text{E-}6\text{T}^2$			
$\text{NH}_3(\text{aq}) - \text{NH}_3(\text{aq})$	- 0.026	(b,c)	0	(b,c)
	$+12.29/\text{T}$			

(a) Pitzer, 1979

(b) Maurer, 1980

(c) Edwards et al., 1975

(d) Edwards et al., 1978

(e) Interactions between like-charged ions are neglected.

In order to determine the accuracy of Edwards' formulation for the species under consideration in this study, a comparison was made of the theoretically derived and experimentally measured activity coefficients for two strong electrolytes. Figures 6.1 and 6.2 show a comparison of activity coefficients calculated using Edwards model with experimental data for hydrochloric acid at 25° C and 50° C respectively. Figure 6.3 shows the same comparison for aqueous solutions of $\text{NH}_4\text{Cl}_{(\text{aq})}$ at 25° C. In all cases the agreement is extremely good at low to medium concentrations, but significant deviations are present at high concentrations. This may be due to the fact that the binary interaction parameters for these strong electrolytes are generally fit to experimental data of no greater than 6 molal concentration. Predicted results exhibiting similar deviation at high concentration for the activity coefficient of hydrochloric acid have been obtained by Zemaitis (1986) using several state-of-the-art theoretical models, including Pitzers' original formulation. Clearly the art of modeling strong electrolytes is not developed to the point where solutions at high concentrations can be predicted accurately.

6.4 Activity Coefficients in the Gas Phase

The gas phase was assumed to be non-ideal due to the highly polar nature of the molecules present. As suggested by Prausnitz et al. (1980) the virial equation was chosen as the mechanical equation of state. The virial equation obtained from a power series expansion of pressure can be written as:

$$Pv/RT = 1 + B_m P/RT + C_m (P/RT)^2 + \dots \quad (6.4)$$

where v is the molar volume of the mixture, and B_m and C_m are the second and third virial coefficients for the gaseous mixture, respectively. At low

to moderate densities, the virial equation may be truncated after the second term:

$$Pv/RT \approx 1 + B_m P/RT \quad (6.5)$$

According to Prausnitz et al. (1980, p. 28) the virial coefficient for a mixture may be calculated from the individual virial coefficients of the components by the following relation:

$$B_m(T, x_1, x_2, \dots, x_{ngas}) = \sum_{i=1}^{ngas} \sum_{j=1}^{ngas} x_i x_j B_{ij}(T) \quad (6.6)$$

The B_{ij} are the individual pure component (i equal j) and cross component (i not equal j) second virial coefficients. The activity coefficients may be obtained from:

$$\ln \gamma_i = (2 \sum_{j=1}^{ngas} x_j B_{ij} - B_m) P/RT \quad (6.7)$$

The method of Hayden and O'Connell (1975) was used to calculate the B_{ij} . The necessary input parameters for each component are: critical temperature T_c , critical pressure P_c , dipole moment D_M , and mean radius of gyration R_D . In addition, an association parameter Ω_{ij} is needed for each binary pair. These parameters are given for a large number of species by Prausnitz et al. (1980) pp. 145-178. The values used in this study are presented in Tables 6.2 and 6.3. Prausnitz also presents the numerous equations (approximately 30) necessary to calculate the B_{ij} (pp. 130-133). They will not be repeated here.

Table 6.2. Molecular Species Data for Virial Model

Species	T_c (K)	P_c (bar)	R_D (angstrom)	D_M (Debye)
H ₂ O	647.37	221.20	0.615	1.83
NH ₃	405.54	112.80	0.853	1.47
HCl	324.54	82.60	0.299	1.07

Table 6.3. Binary Association Parameter Ω_{ij} for Virial Model

$i \backslash j$	H ₂ O(g)	NH ₃ (g)	HCl(g)
H ₂ O(g)	1.70	0.0	1.38
NH ₃ (g)	0.20	0.0	2.20
HCl(g)	0.0	0.0	0.0

In order to check the accuracy of the model, the virial coefficient of steam was calculated using Hayden and O'Connells' method (Figure 6.4). The results are identical with those presented by Prausnitz et al. (1980), p. 30. In addition, the specific volume of steam was calculated from the virial equation as follows

$$v = RT/P + B_m \quad (6.8)$$

These results, along with results using the ideal gas equation, are compared against experimental results in Figure 6.5. The agreement near the boiling temperature is noticeably better with the virial equation.

6.4 Binary System Equilibrium Calculations

Using these activity coefficient relationships, the computer program was tested for three binary systems in which experimental data was available. Figure 6.6 shows predicted and experimental solubility data for the $\text{NH}_4\text{Cl-H}_2\text{O}$ system. Agreement is good at lower temperatures, but deviates significantly at higher temperatures. It is felt that this deviation at high temperatures may be due to the variation of the partial molar specific heat of NH_4^+ and Cl^- with temperature. Values for these ions were only available at 298.15 K. Figures 6.7 and 6.8 show predicted and experimental boiling diagrams for the $\text{NH}_3\text{-H}_2\text{O}$ system and for the $\text{HCl-H}_2\text{O}$ system, respectively. It can be seen that the agreement for the weak electrolyte, $\text{NH}_3(\text{aq})$, is excellent, while the agreement for the strong electrolyte, $\text{HCl}(\text{aq})$, is only fair. This discrepancy is a direct result of the inability of the activity coefficient model for $\text{HCl}(\text{aq})$ to accurately predict solution behavior at extremely high concentrations.

6.6 Equilibrium Calculations for HCl-NH₃-H₂O System

Basically encouraged by the test cases, the computer program was used to predict the equilibrium compositions of the complete HCl-NH₃-H₂O ternary system. The version of the computer program used for this calculation is listed in Appendix A. Results for 0%, 10%, 20%, and 30% concentrations of ammonia in water are shown in Figures (6.9-16). Mixture density, temperature, phase and species mass fractions and the void fraction (volume fraction of the gas phase) are plotted against mixture fraction, f . Calculations presented in this form (using mixture fraction to specify the relative amount of reactants) can be used directly in the reaction zone modeling technique used by this lab (Chan et al., 1987-1988). Overall, these results are fairly close to those obtained by previous methods for this system (Chan et al., 1987-1988). The primary difference is that the modeling techniques described in this report were able to predict the formation of a solid phase, $\text{NH}_4\text{Cl}_{(c)}$.

FIGURE 6.1 MEAN ACTIVITY COEFFICIENT, HCL AT 25 DEG. C

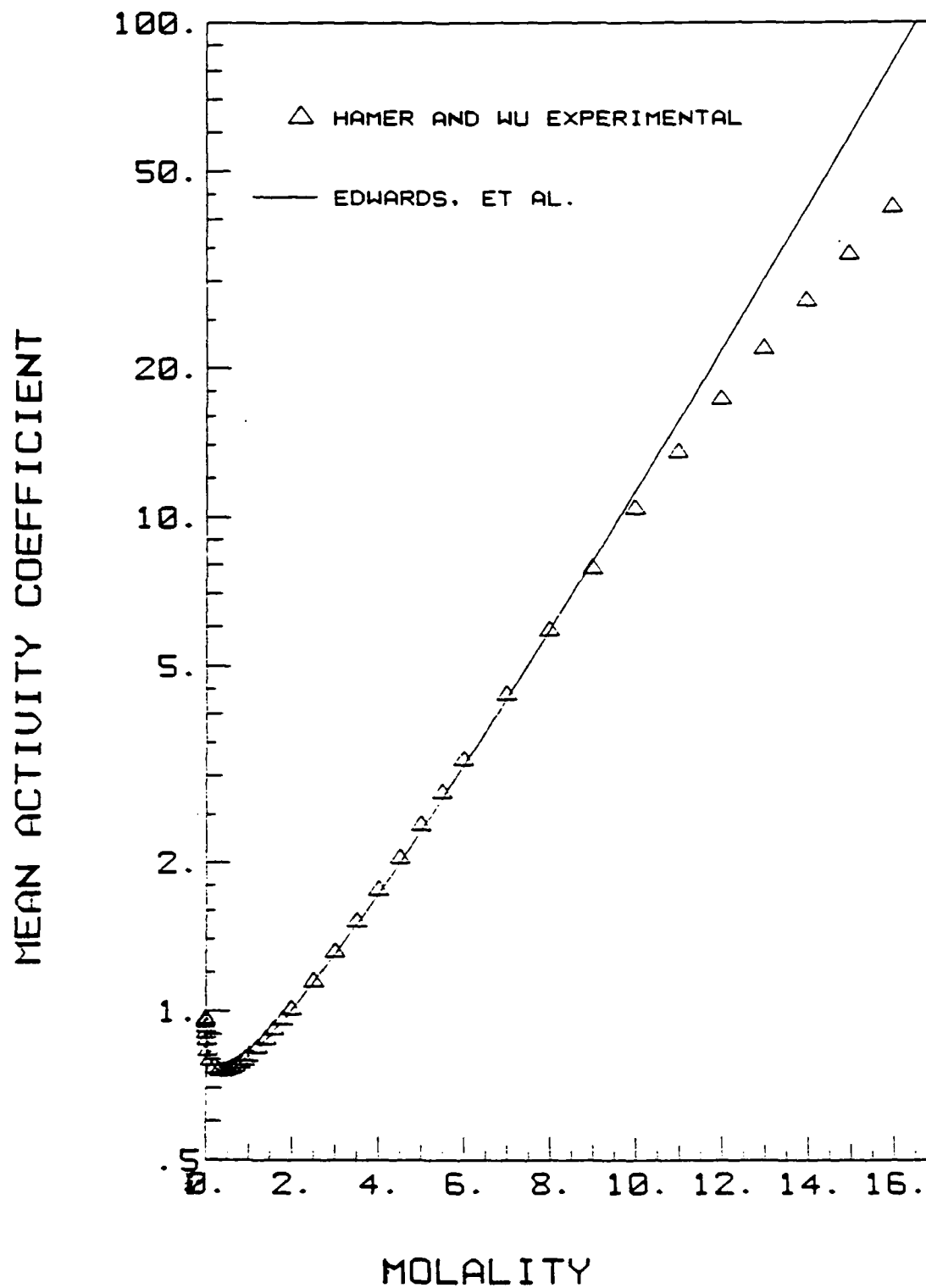


FIGURE 6.2 MEAN ACTIVITY COEFFICIENT, HCL AT 50 DEG. C

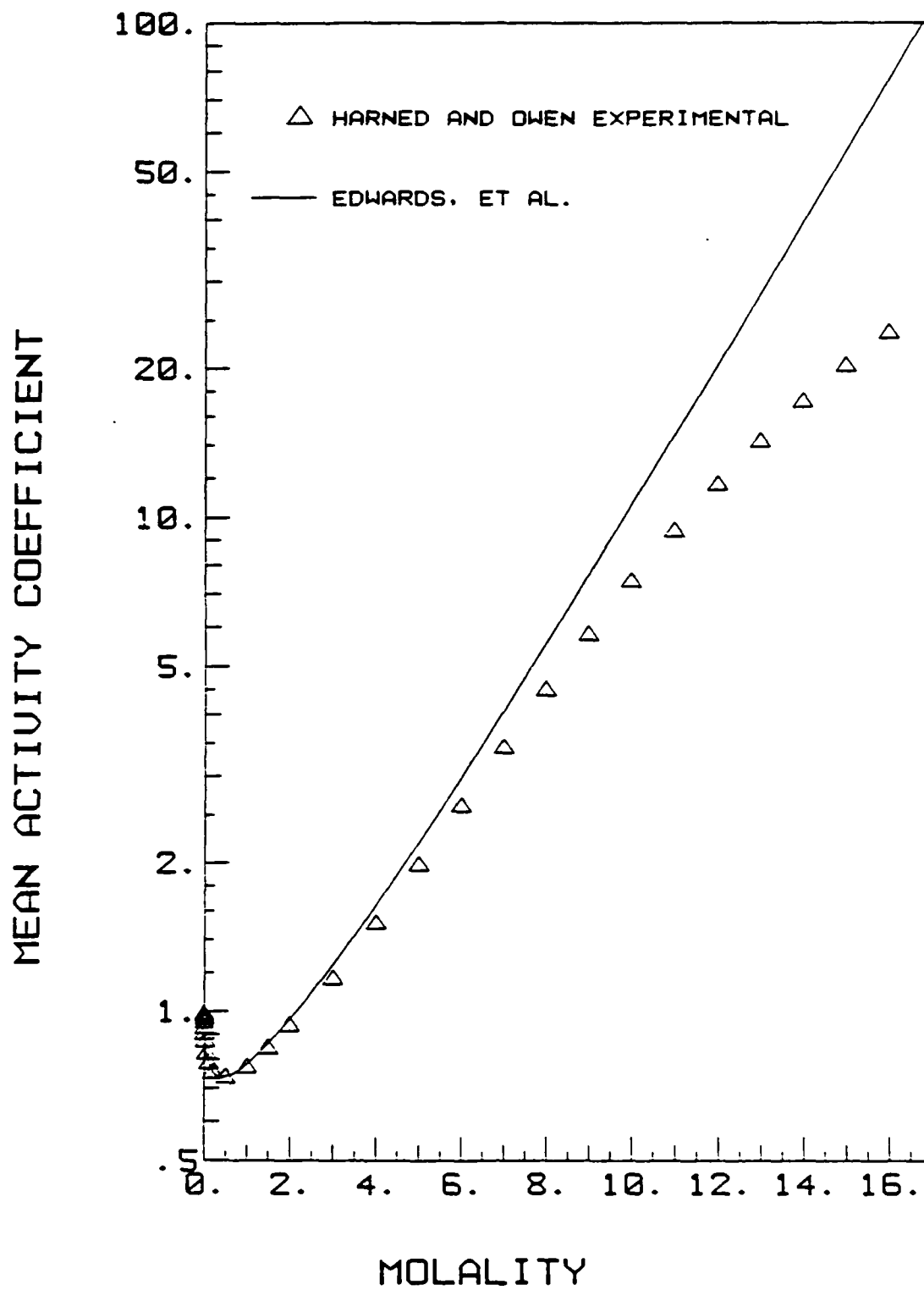


FIGURE 6.3 MEAN ACTIVITY COEFFICIENT, NH_4Cl AT 25 DEG. C

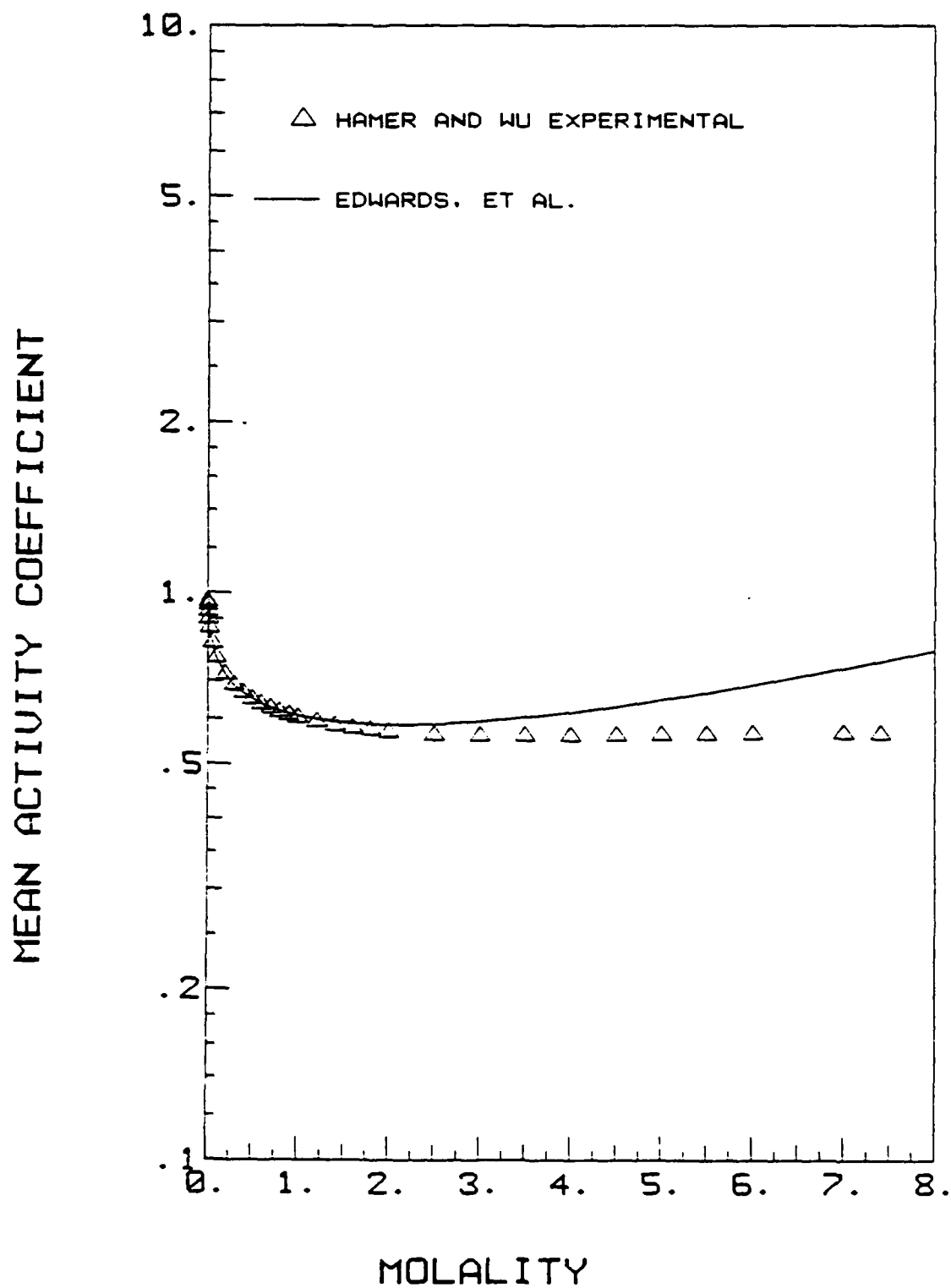


FIGURE 6.4 SECOND VIRIAL COEFFICIENT FOR STEAM

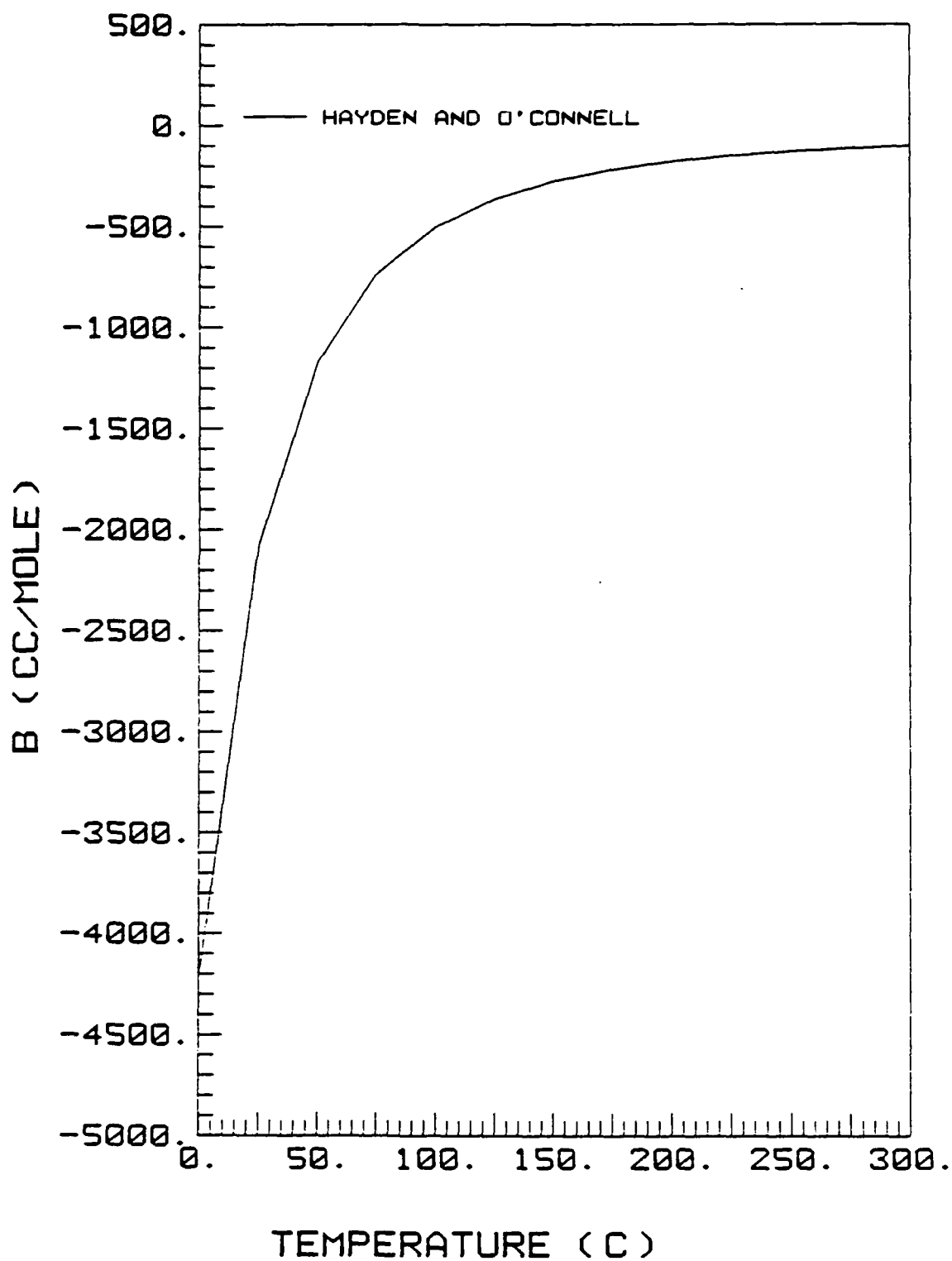


FIGURE 6.5 SPECIFIC VOLUME OF STEAM AT 0.1 MPa

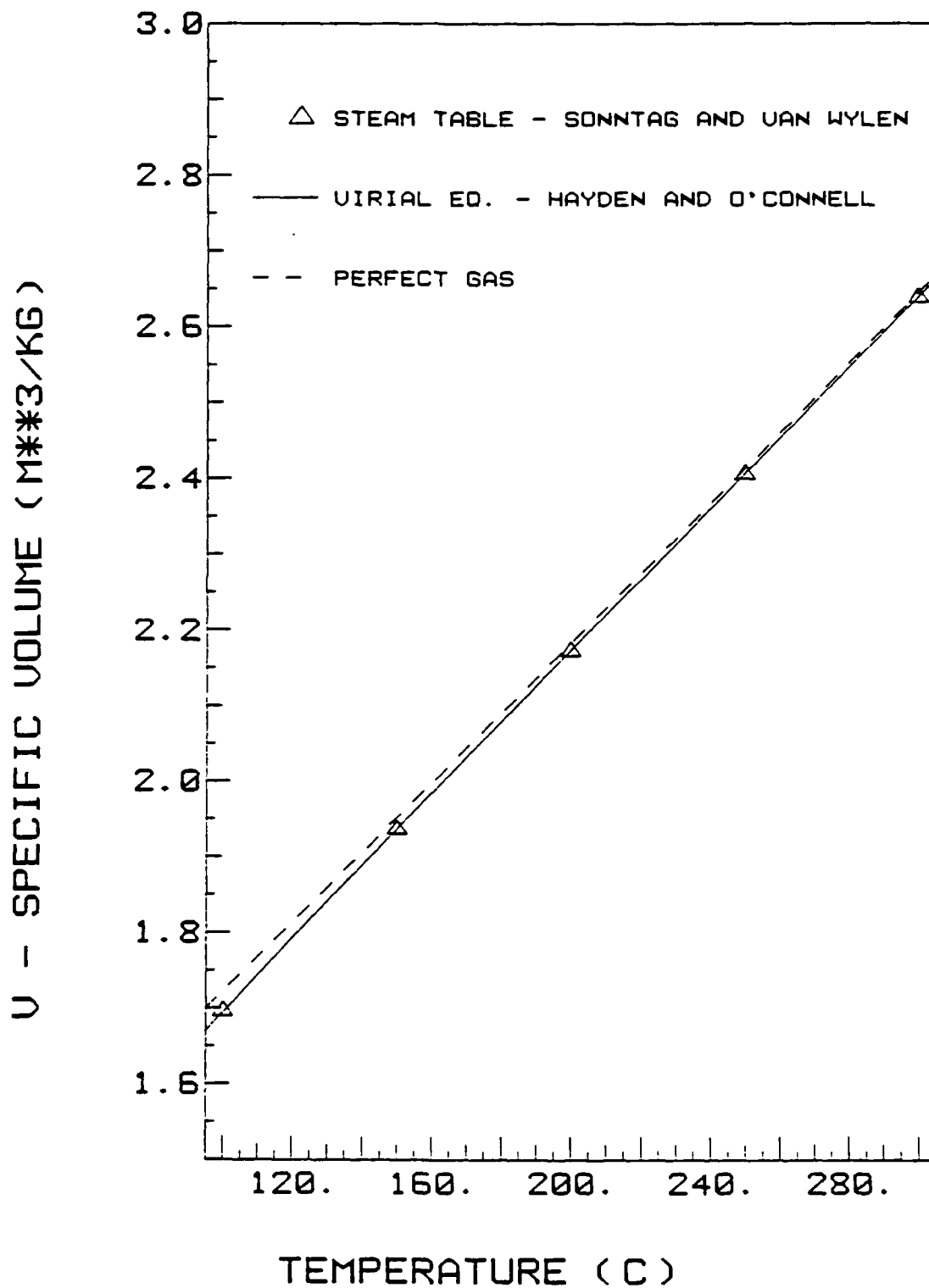
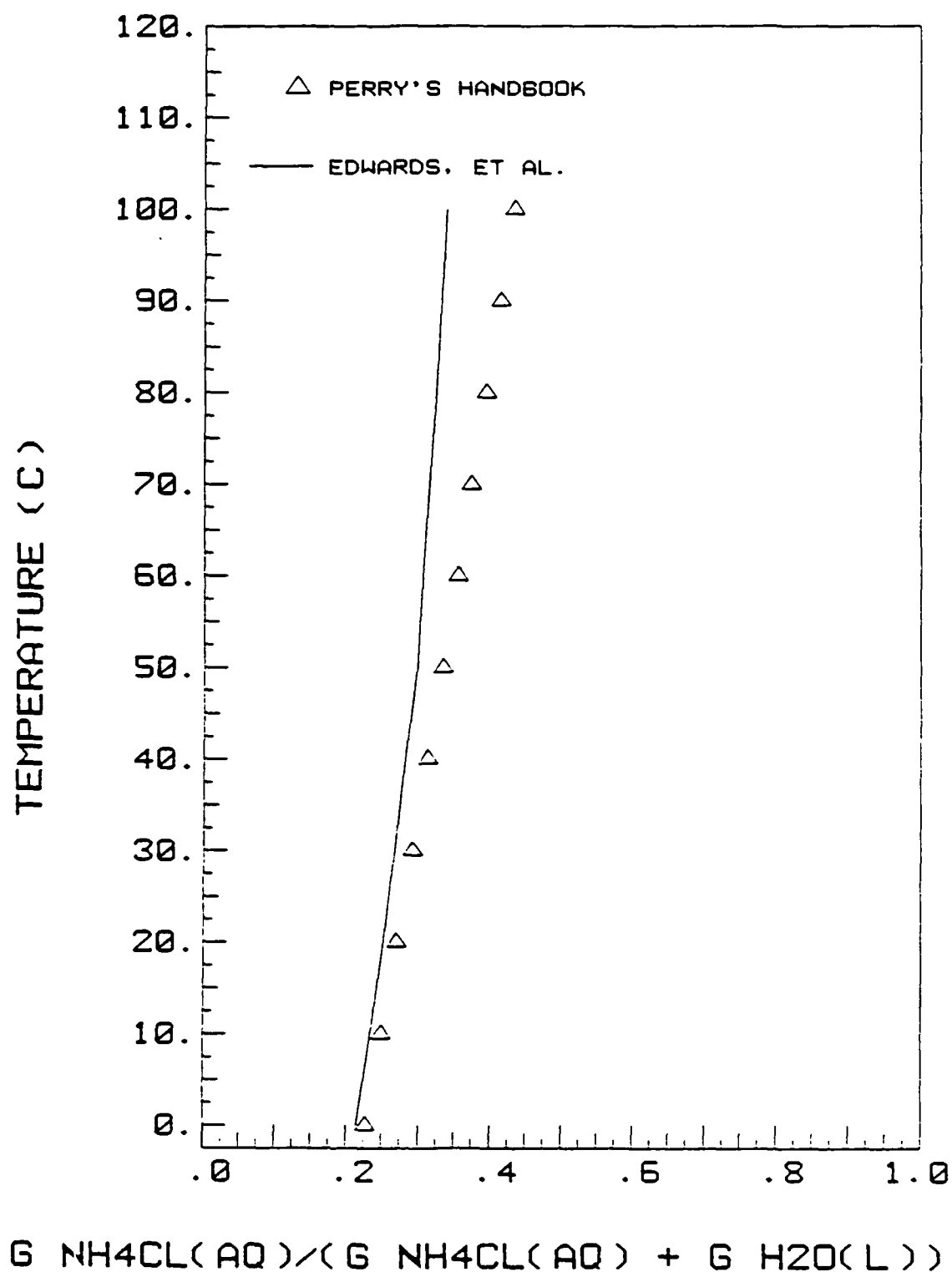


FIGURE 6.6 SOLUBILITY OF $\text{NH}_4\text{CL}(\text{C})$ IN $\text{H}_2\text{O}(\text{L})$, 1 ATM



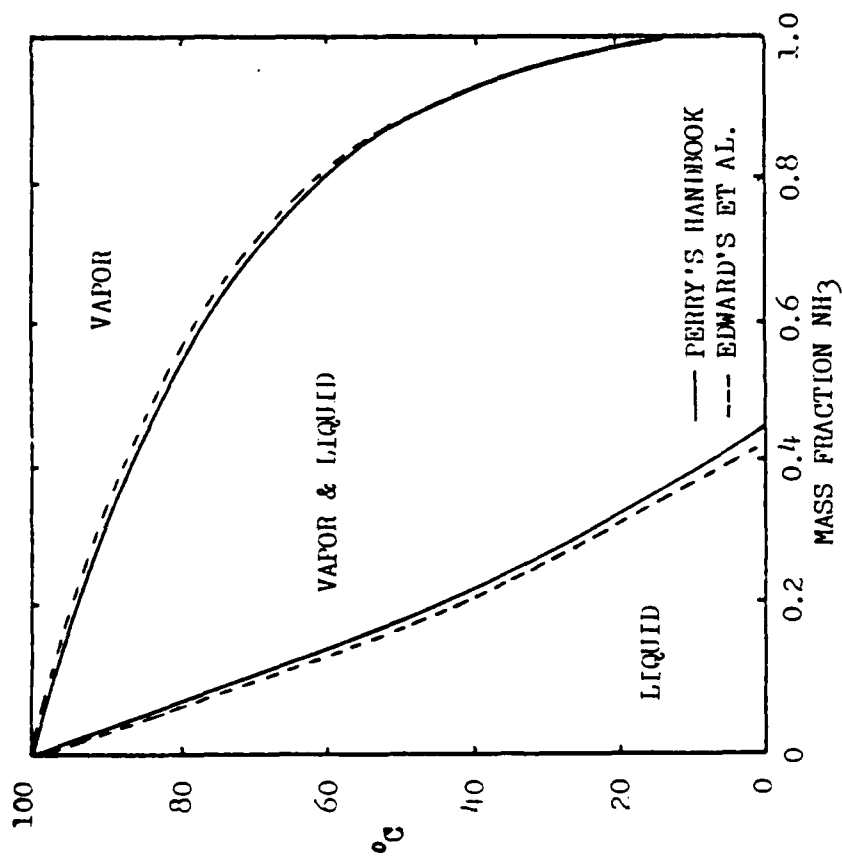


FIGURE 6.7 BINARY PHASE DIAGRAM, $\text{NH}_3\text{-H}_2\text{O}$ SYSTEM AT 1 ATM.

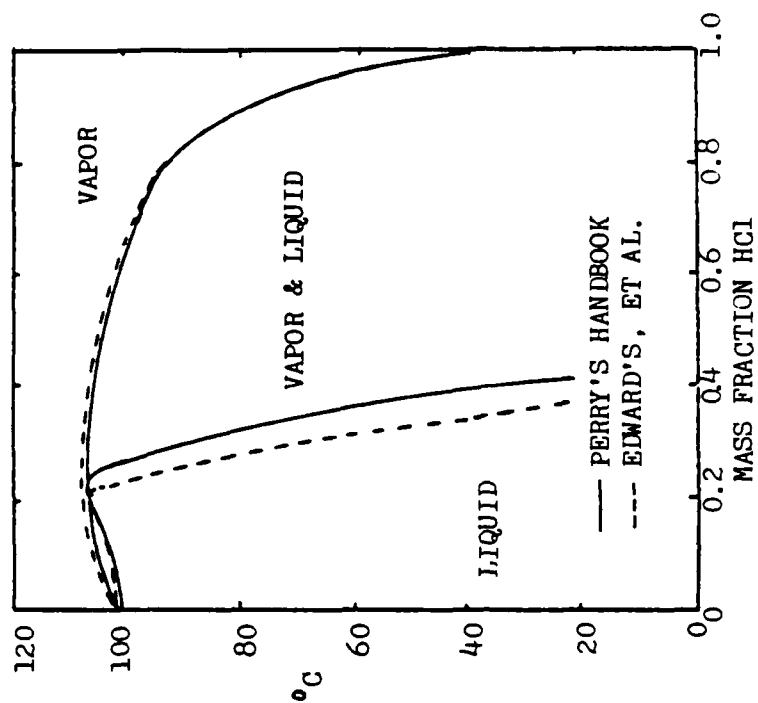


FIGURE 6.8 BINARY PHASE DIAGRAM, $\text{HCl-H}_2\text{O}$ SYSTEM AT 1 ATM.

FIGURE 6.9 PURE $H_2O(L) + HCl(G)$, $T_{INF}=T_0=298K$, 1 ATM

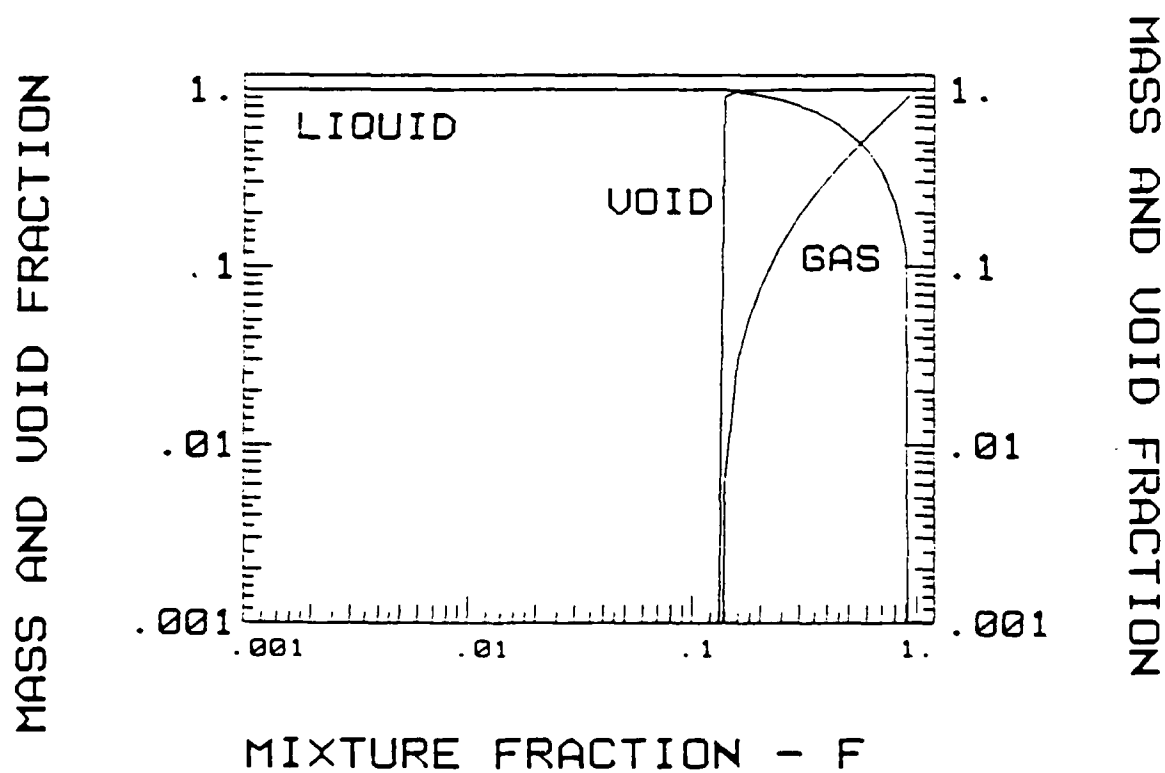
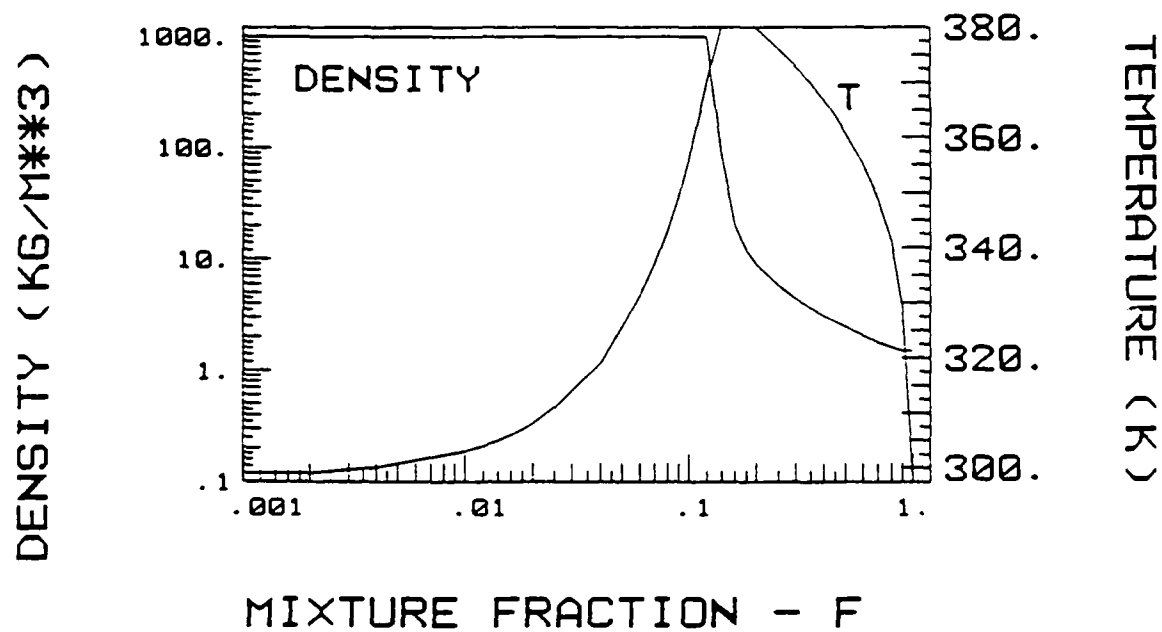
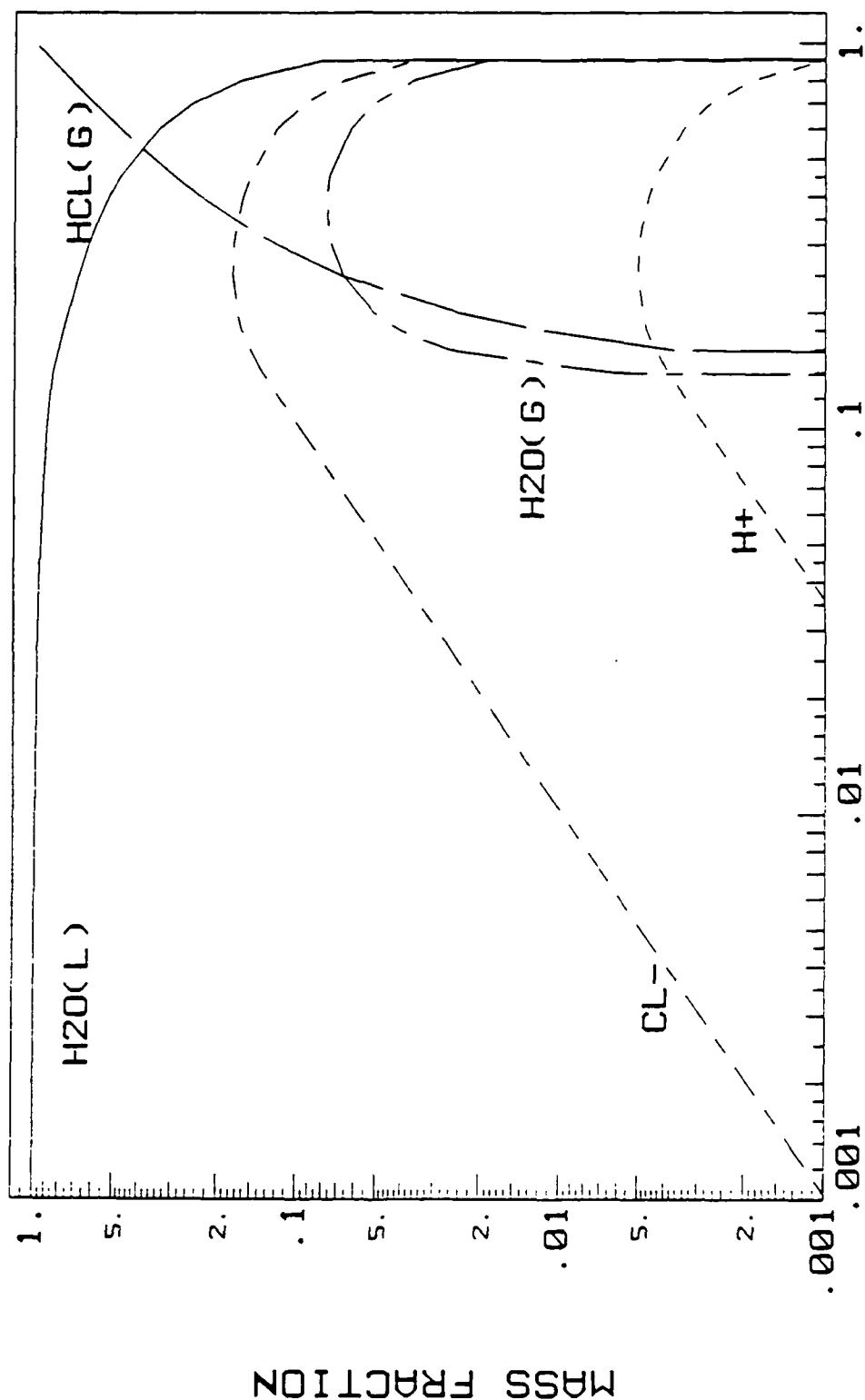


FIGURE 6.10 PURE $\text{H}_2\text{O}(\text{L}) + \text{HCL}(\text{G})$, $T_{\text{INF}} = T_0 = 298\text{K}$, 1 ATM



MIXTURE FRACTION - F

FIGURE 6.11 10/ NH₃(AD) + HCL(G), T_{INF}=T₀=298K, 1 ATM

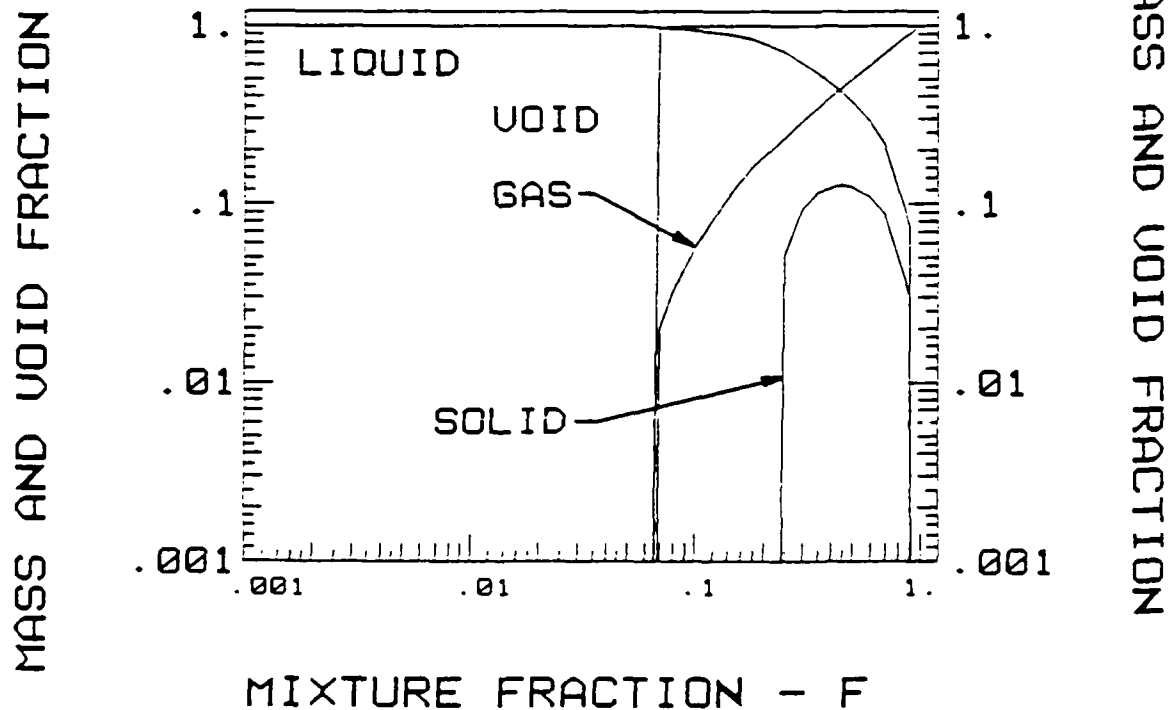
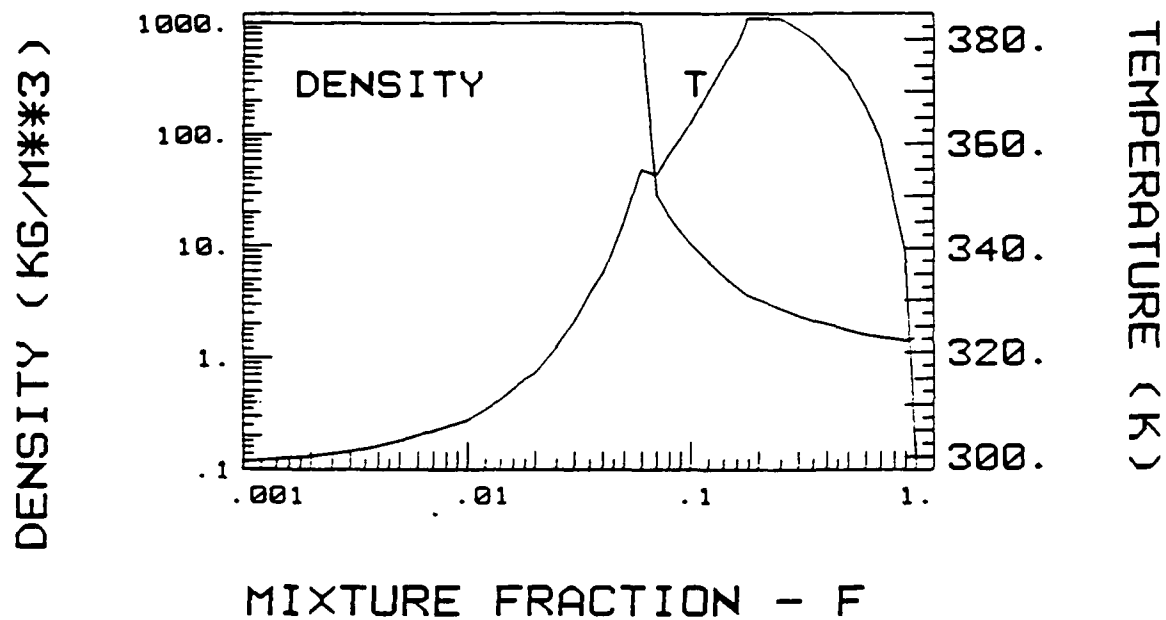
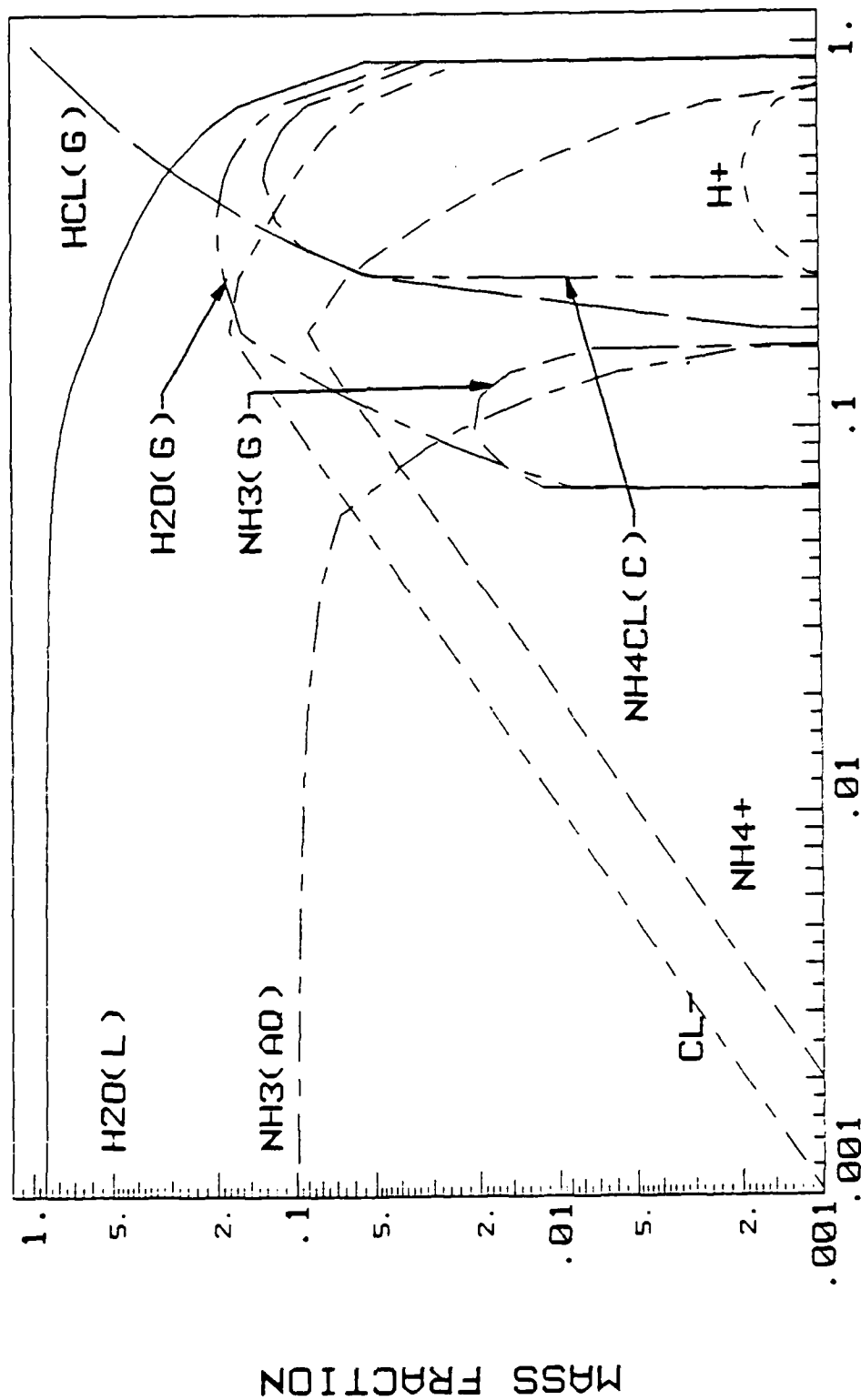


FIGURE 6.12 10% NH₃(A0) + HCL(G), TINF=T0=298K, 1 ATM



MIXTURE FRACTION - F

FIGURE 6.13 20% NH₃(AQ) + HCL(G), T_{INF}=T₀=298K, 1 ATM

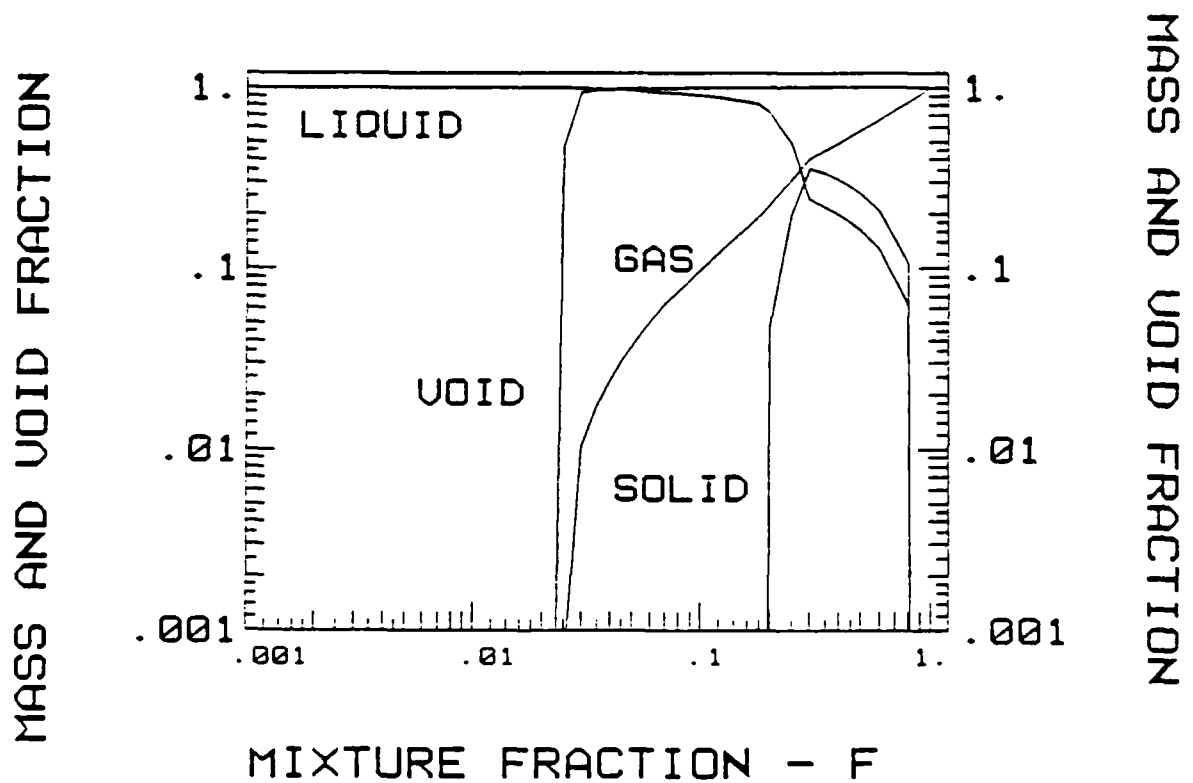
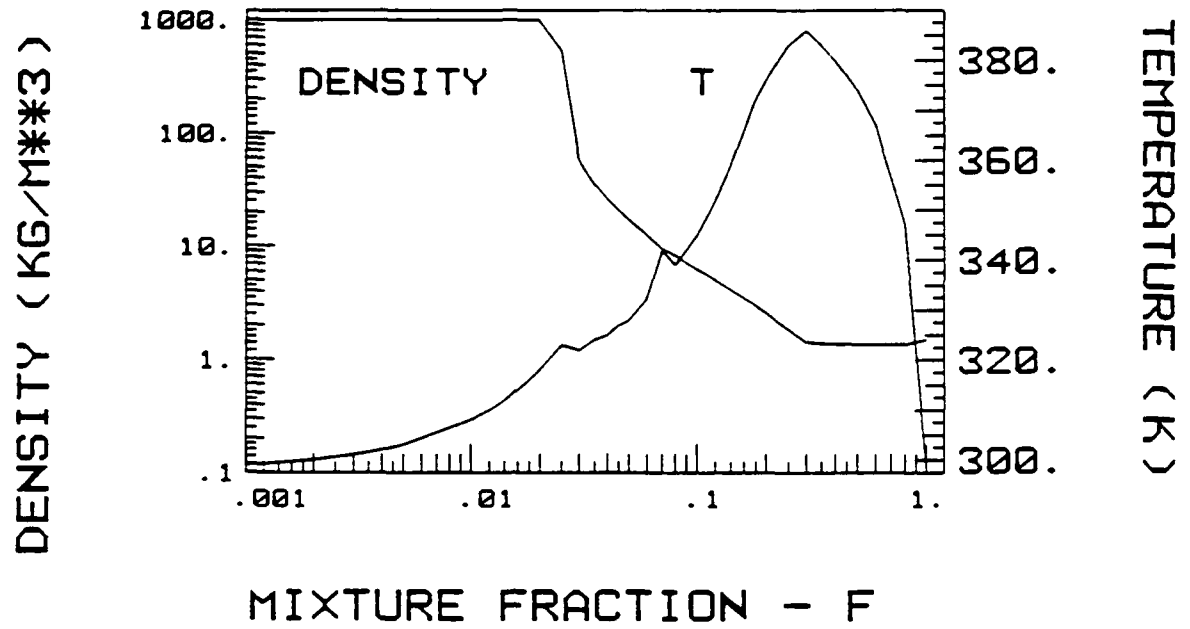


FIGURE 6.14 20% $\text{NH}_3(\text{AQ}) + \text{HCL}(\text{G})$, $T_{\text{INF}} = T_0 = 298\text{K}$, 1 ATU

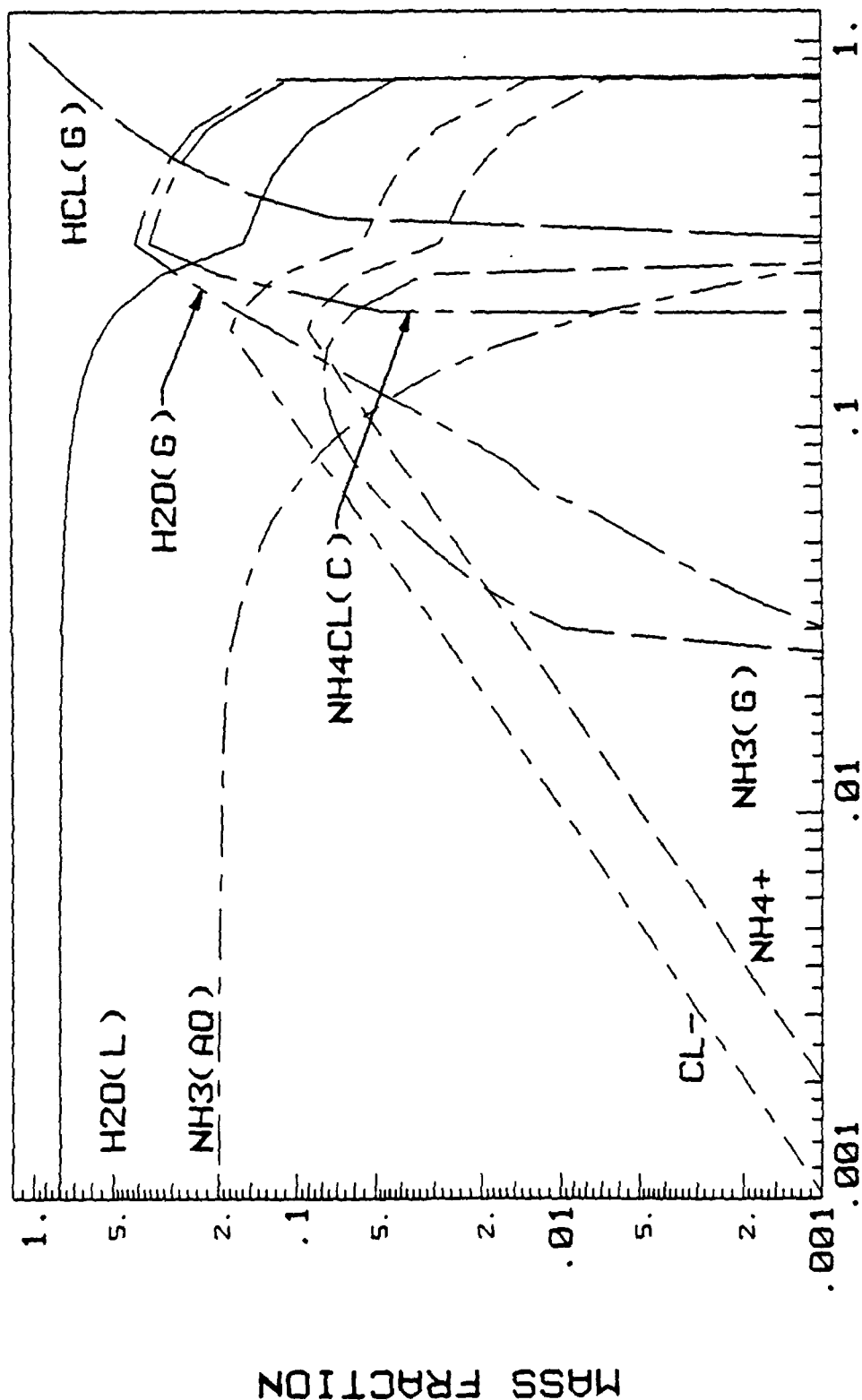


FIGURE 6.15 30/ NH₃(AQ) + HCL(G), T_{INF}=T₀=298K, 1 ATM

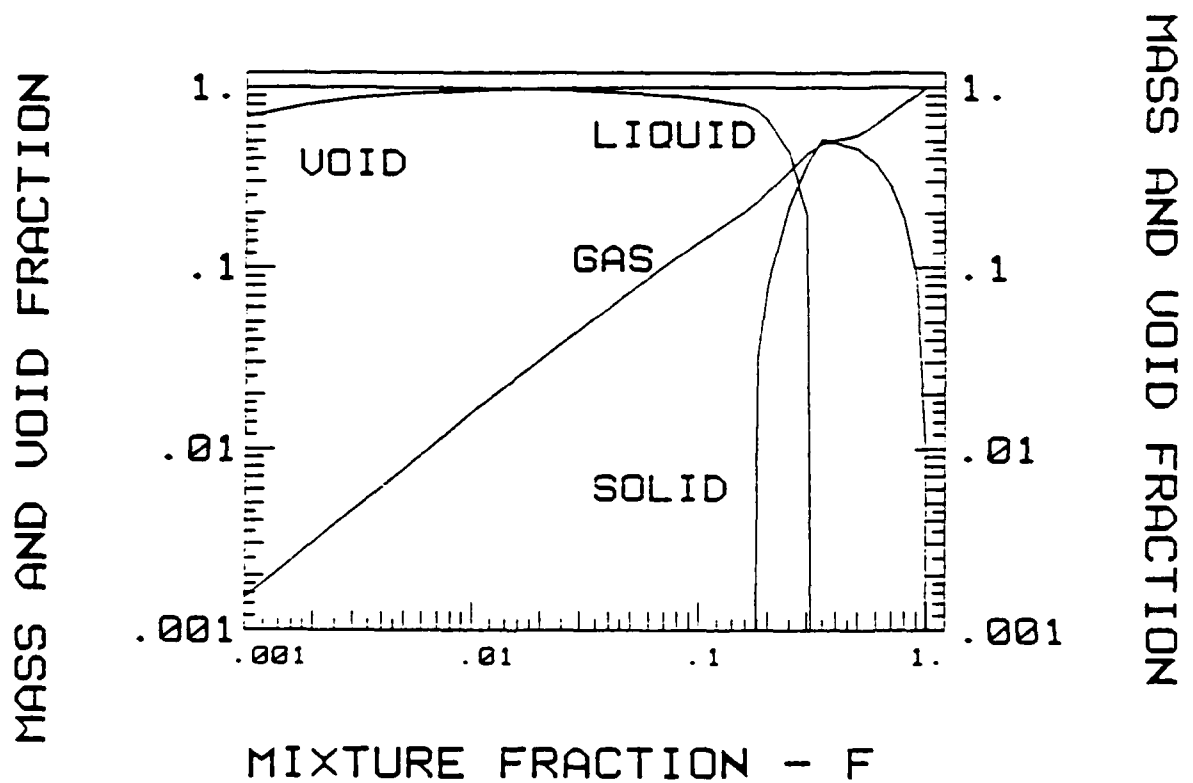
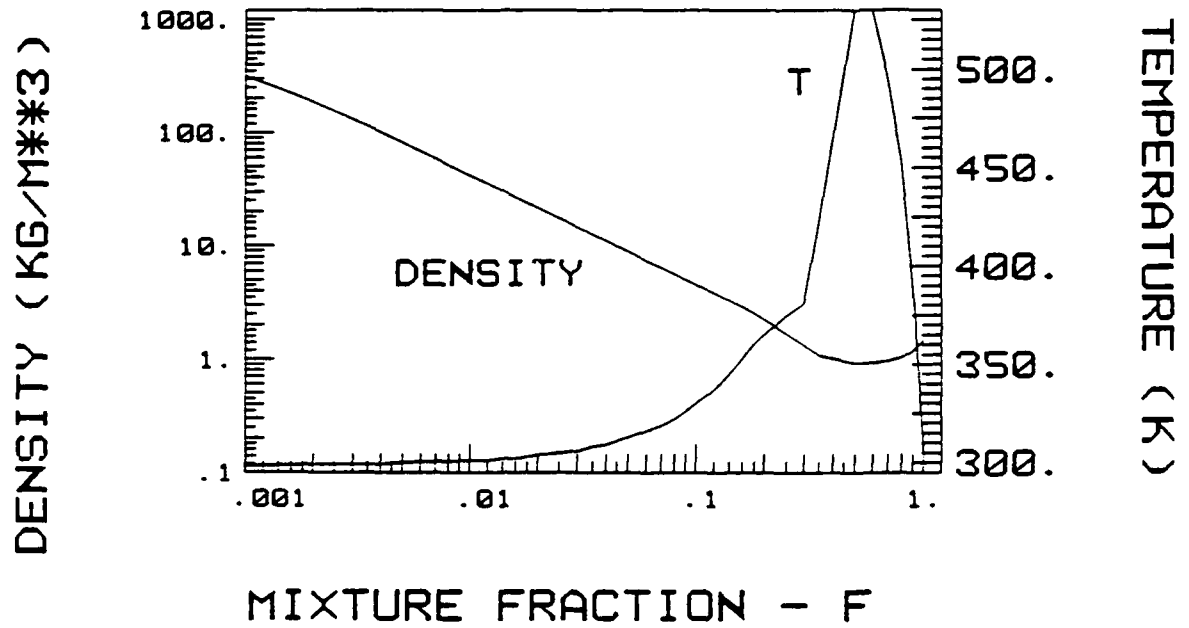
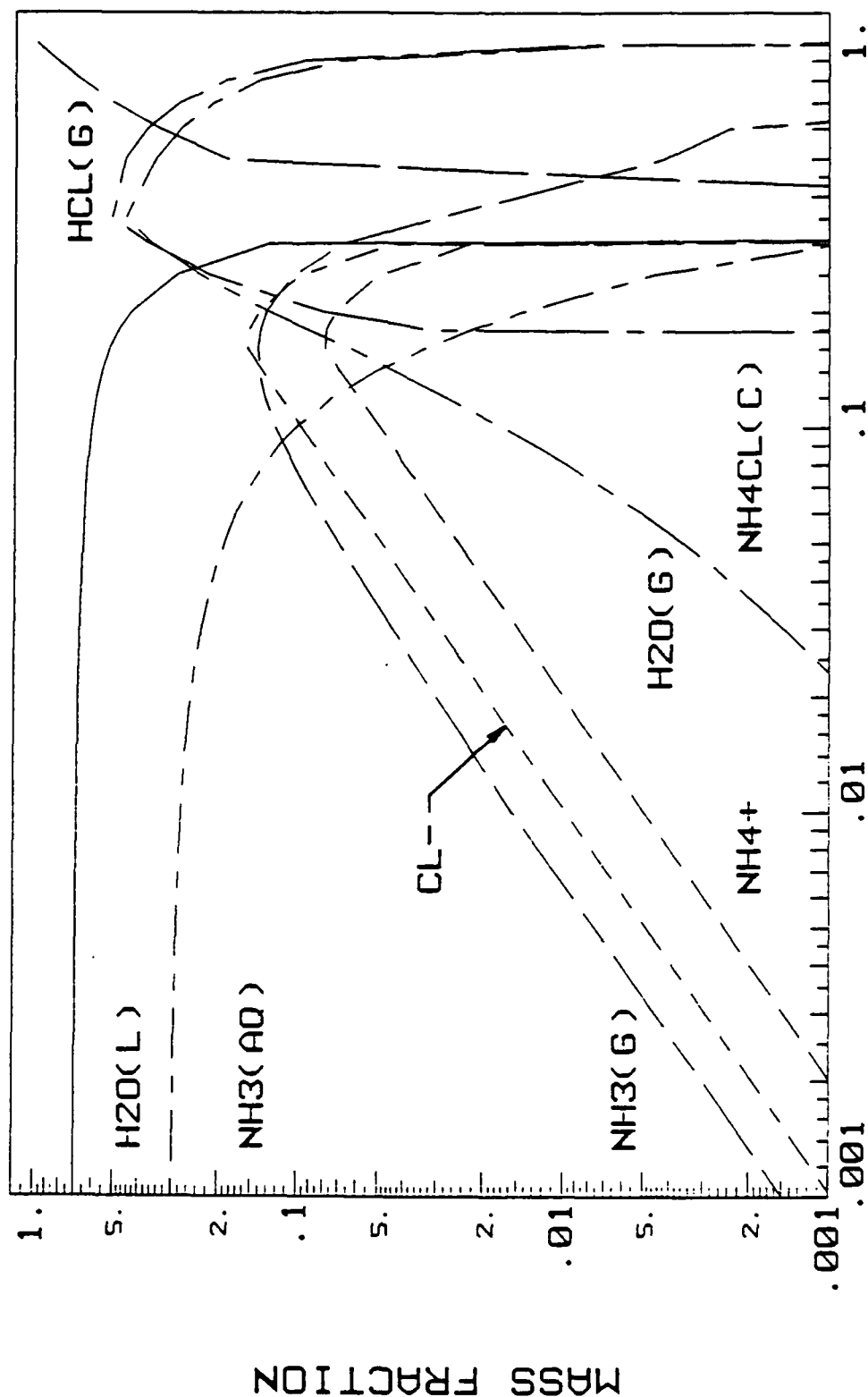


FIGURE 6.16 30% NH₃(AQ) + HCL(G), TINF=T0=298K, 1 ATM



MIXTURE FRACTION - F

7. APPLICATION TO THE SODIUM-CHLORINE SYSTEM

In recent years, several experimental and theoretical studies of the structure of a gaseous chlorine jet discharging into a stagnant bath of liquid sodium have been published (Avery, 1974, Chen and Faeth, 1982, and Cho et al., 1987). Present work by this lab has focused on extending the modeling techniques of Chen and Faeth (1982) to include the effect of radiation and enclosure on the reaction zone (Chan et al., to be published). A necessary input for these calculations is the equilibrium state reached after mixing various amounts of nozzle and bath fluids. In this system the bath fluid (∞) consists of pure liquid sodium, $\text{Na}_{(L)}$. The nozzle fluid (0) is pure chlorine gas, Cl_2 .

7.1 Gas Phase

Following the lead of Avery (1974), the gas phase was assumed to consist of $\text{Cl}_{(g)}$, $\text{Cl}_{2(g)}$, $\text{Na}_{(g)}$, $\text{Na}_{2(g)}$, $\text{NaCl}_{(g)}$, and $\text{Na}_2\text{Cl}_{2(g)}$ in a perfect gas mixture. Thus, the chemical potentials of the gaseous species were described using equation 3.25. Ionization of the gases was neglected, as preliminary calculations revealed extremely low concentrations of ionic species, even at high temperatures.

7.2 Solid Phases

Both the metal, $\text{Na}_{(s)}$, and the salt, $\text{NaCl}_{(s)}$, were considered in single species solid phases. Consequently, equation 3.33 was used to describe the chemical potential of these species. Of course, the solid metal does not appear in the system unless the bath temperature (T^∞) is below the melting point of sodium (371K). The bath temperature in the present calculations is above the melting point of the metal.

7.3 Liquid Phase

The liquid phase consists of the liquid metal, $\text{Na}_{(L)}$, and the molten salt, $\text{NaCl}_{(L)}$. Bredig (1964) has shown that these species may form a two phase, immiscible liquid mixture. The lighter liquid is sodium-rich, containing a small amount of dissolved salt. The heavier liquid is salt-rich, containing a small amount of dissolved sodium. Avery (1974) has used the van Laar model (Lewis and Randall, 1961, pp. 287-288) to accurately predict the mutual solubility of these two species. For a binary solution (denoting species $\text{Na}_{(L)}$ and $\text{NaCl}_{(L)}$ as 1 and 2, respectively), the activity coefficients may be expressed as:

$$\ln \gamma_1 = A_{12} b_1 z_2^2 / RT \quad (7.1)$$

$$\ln \gamma_2 = A_{12} b_2 z_1^2 / RT \quad (7.2)$$

where

$$z_1 \equiv N_1 b_1 / (N_1 b_1 + N_2 b_2) \quad (7.3)$$

$$z_2 \equiv N_2 b_2 / (N_1 b_1 + N_2 b_2) \quad (7.4)$$

The preceding equations contain three empirical parameters which must be fit to experimental solubility data (b_1 , b_2 , and A_{12}). We can reduce this to two parameters by defining $B \equiv b_2/b_1$ and $A'_{12} \equiv b_1 A_{12}$. The equations for the activity coefficients then become:

$$\ln \gamma_1 = A'_{12} [(BN_2)/(N_1 + BN_2)]^2 / RT \quad (7.5)$$

$$\ln \gamma_2 = BA'_{12} [N_1/(N_1 + BN_2)]^2 / RT \quad (7.6)$$

Avery (1974) has fit A'_{12} and B to experimental data. The resulting expressions are

$$B = 0.929 \quad (7.7)$$

$$A'_{12} = 23.36 - 0.01325 T \quad (7.8)$$

where A'_{12} is in units of Kcal/gmole and T in units of K.

7.4 Thermodynamic Data

The necessary thermodynamic data for this system was obtained from data files provided with the CEC-72 computer code (Gordon and McBride, 1971). These files consist of the polynomial constants for curve-fits of the thermochemical data of each species. The original source of the data for most of the species is the JANAF Thermochemical Tables (1971). Each species has a set of 14 coefficients. Seven coefficients apply to the low temperature range (300-1000 K), and seven coefficients apply to the high temperature range (1000-5000 K). The CEC-NMS computer program was modified to read this data file and calculate the specific heat, enthalpy, entropy, and Gibbs energy of the relevant species. For a listing of the computer code, see Appendix B.

7.5 Results

The equilibrium results for $T^\infty = 1130$ K and $T^0 = 298.15$ K are presented in Figures 7.1 and 7.2. These particular conditions were chosen to allow direct comparison with results presented by Chen and Faeth (1982). The sodium-rich liquid is denoted by L-1 and the salt-rich liquid is denoted by L-2. There is essentially no difference in the results calculated by the two different methods.

FIGURE 7.1 $\text{Na(L)}-\text{Cl}_2(\text{G})$ SYSTEM. $T_{\text{INF}}=1130\text{K}$. $T_0=298\text{K}$. 1 ATM

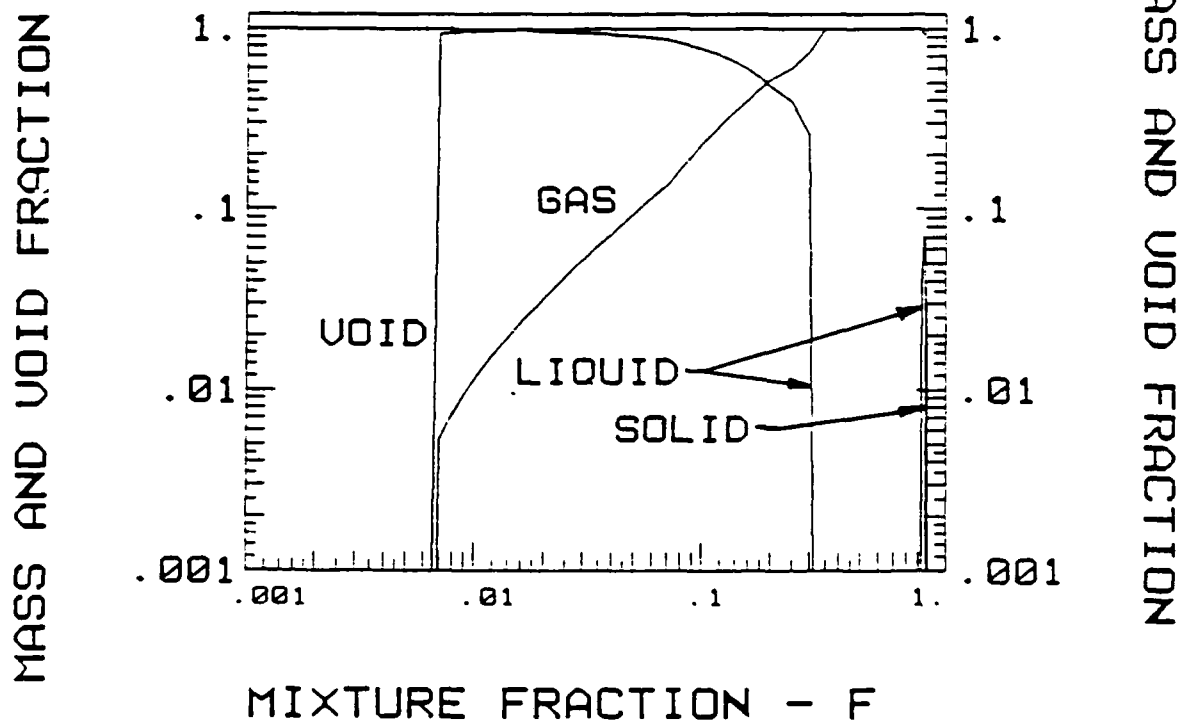
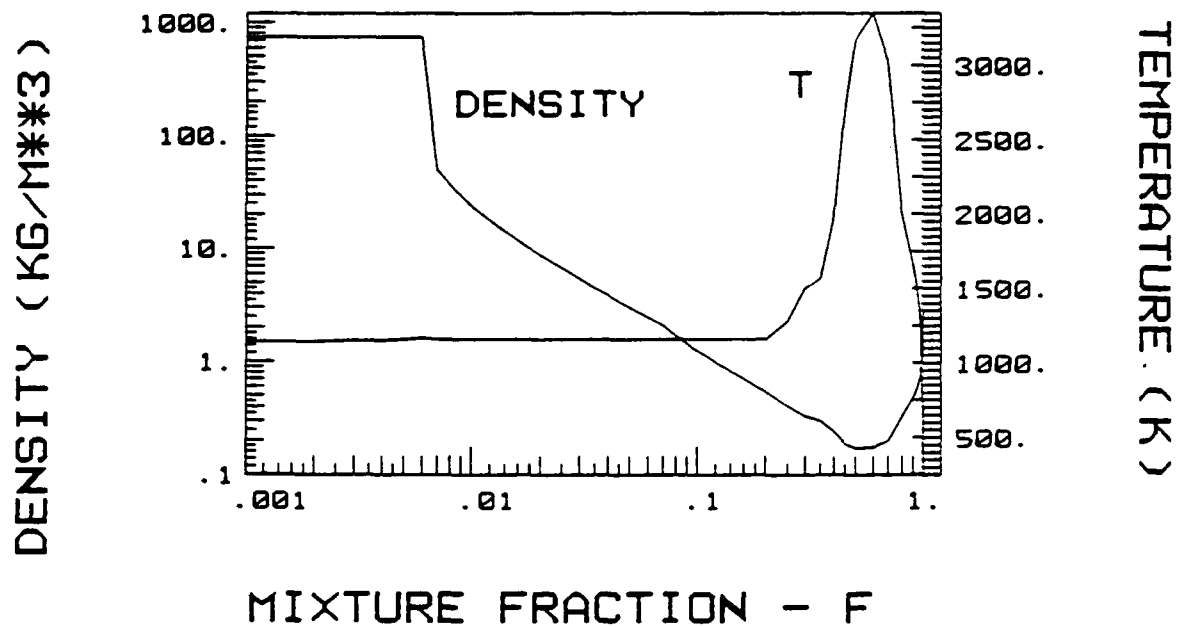


FIGURE 7.2A $\text{Na(L)}-\text{Cl}_2(\text{G})$ SYSTEM, $T_{\text{INF}}=1130\text{K}$, $T_0=298\text{K}$, 1 ATM

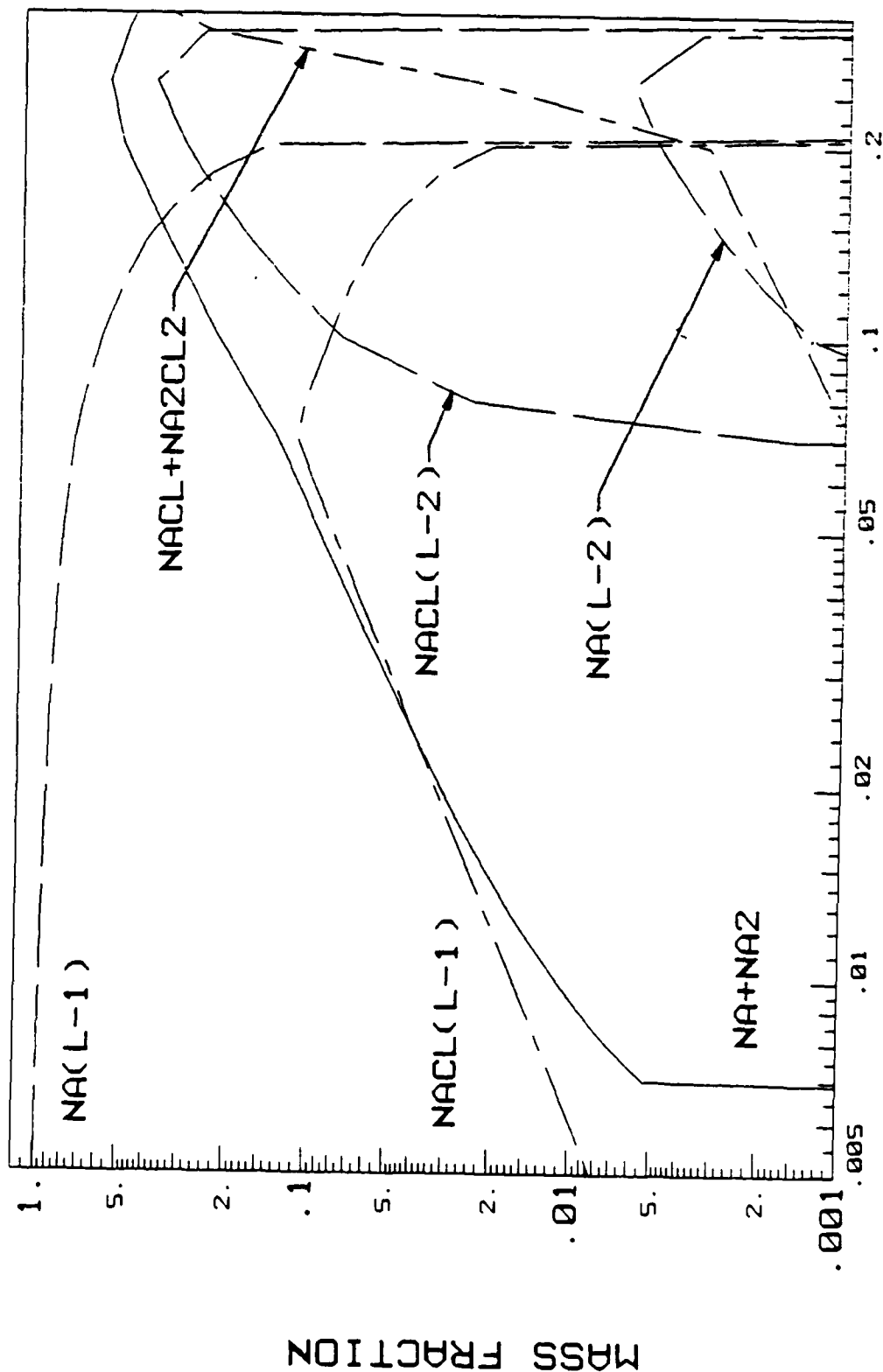
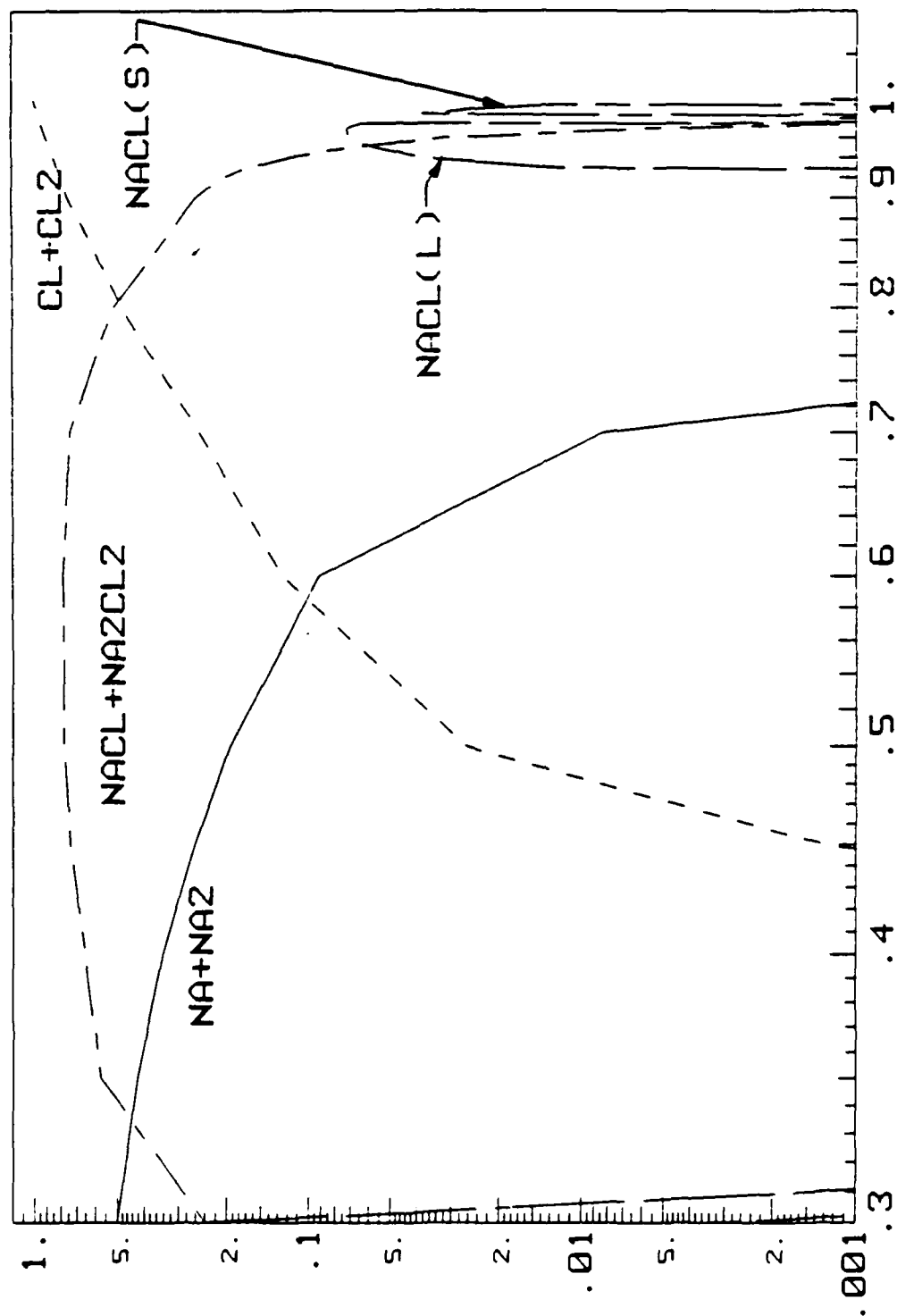


FIGURE 7.28 $\text{NaCl(L)}-\text{Cl}_2(\text{G})$ SYSTEM. $T_{\text{INF}}=1130\text{K}$, $T_0=298\text{K}$, 1 ATM



MIXTURE FRACTION - F

8. APPLICATION TO THE LITHIUM-FLUORINE SYSTEM

A system similar to the sodium-chlorine reactant pair described in the previous section results from the injection of gaseous fluorine, $F_{2(g)}$, into a stagnant liquid lithium ($Li_{(L)}$) bath. Once again, the approach used is based on the thermodynamic work of Avery (1974).

8.1 System

The gaseous phase was assumed to consist of $F_{(g)}$, $F_{2(g)}$, $Li_{(g)}$, $Li_{2(g)}$, $LiF_{(g)}$, $Li_2F_{2(g)}$, and $Li_3F_{3(g)}$ in a perfect gas mixture. Ionization was neglected as preliminary calculations showed that the maximum concentration of ions at the highest temperatures was approximately 1% by mass.

$Li_{(s)}$ and $LiF_{(s)}$, the solid metal and salt, were considered as single species phases. Immiscible liquid phases consisting of $LiF_{(L)}$ dissolved in $Li_{(L)}$ and $Li_{(L)}$ dissolved in $LiF_{(L)}$ were modeled as before, using the van Laar model. The coefficients A'_{12} and B were provided by Avery (1974) as

$$B = 0.725 \quad (8.1)$$

$$A'_{12} = 24.6 - 0.01072 T \quad (8.1)$$

where A'_{12} is in units of Kcal/gmole. Note that $Li_{(L)}$ is designated by 1 and $LiF_{(L)}$ by 2. As in the sodium case, thermodynamic data was read in from the CEC-72 data file.

8.2 Results

The results of the equilibrium calculations for $T^\infty = 1130$ K and $T^0 = 298.15$ K at 1 atmosphere are shown in Figures 8.1 and 8.2. No calculations of this type (based on mixture fraction) for this particular system have been

presented in the literature. Consequently, comparison with other calculation methods is not possible. We can see, however, the similarities of the lithium-fluorine system to the sodium-chlorine system described in Section 7. The primary differences are the higher boiling point of the liquid lithium (1620 K vs 1156 K for sodium), and the higher peak equilibrium temperature (4573 K vs. 3352 K for sodium-chlorine reaction).

For the initial conditions presented here, the liquid phase did not split into two immiscible liquids. For these calculations, the salt-rich liquid does not form until the temperature of the mixture is well above the consolute temperature of 1603 K (Bredig, 1964, p. 373). Note that the consolute temperature is the highest temperature that the two liquids coexist. Had the initial bath temperature been lower, it is likely that the solubility limit of the salt in the metal would have been reached at a lower temperature. Then the salt-rich liquid would begin to form at a temperature below the consolute temperature. In this case an immiscible liquid region would appear as in the sodium system described in the previous chapter.

FIGURE 8.1 LI(L)-F2(G) SYSTEM, $T_{INF}=1130K$, $T_0=298K$, 1 ATM

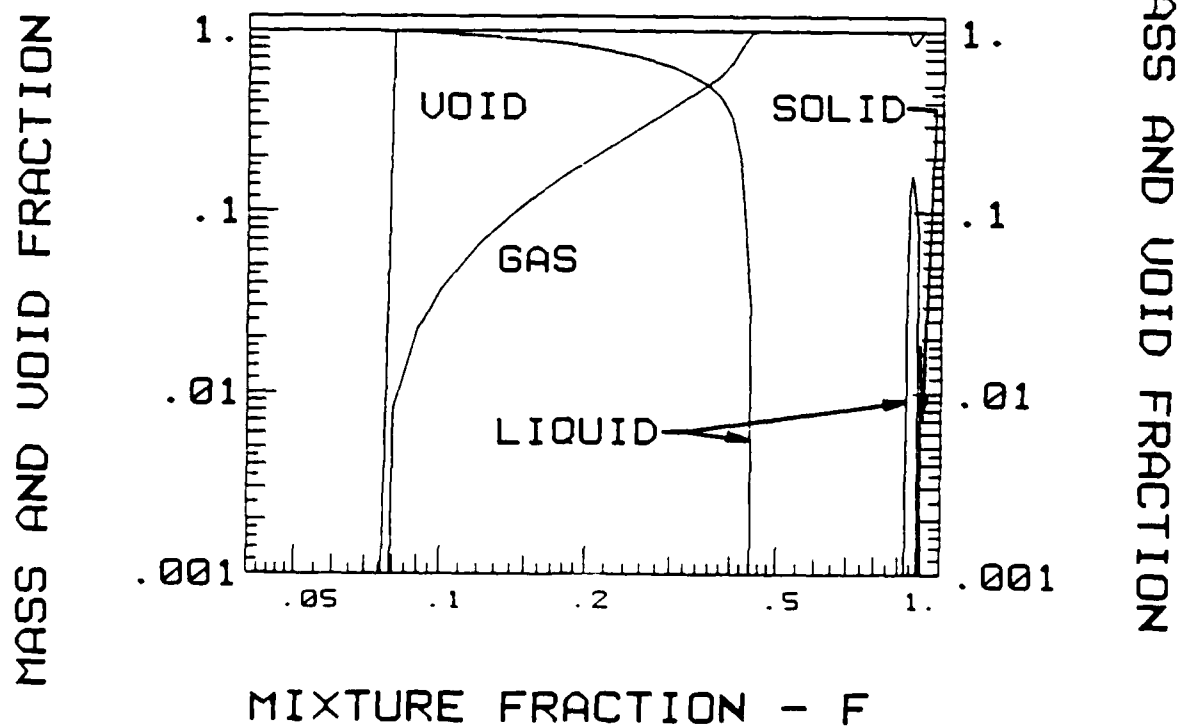
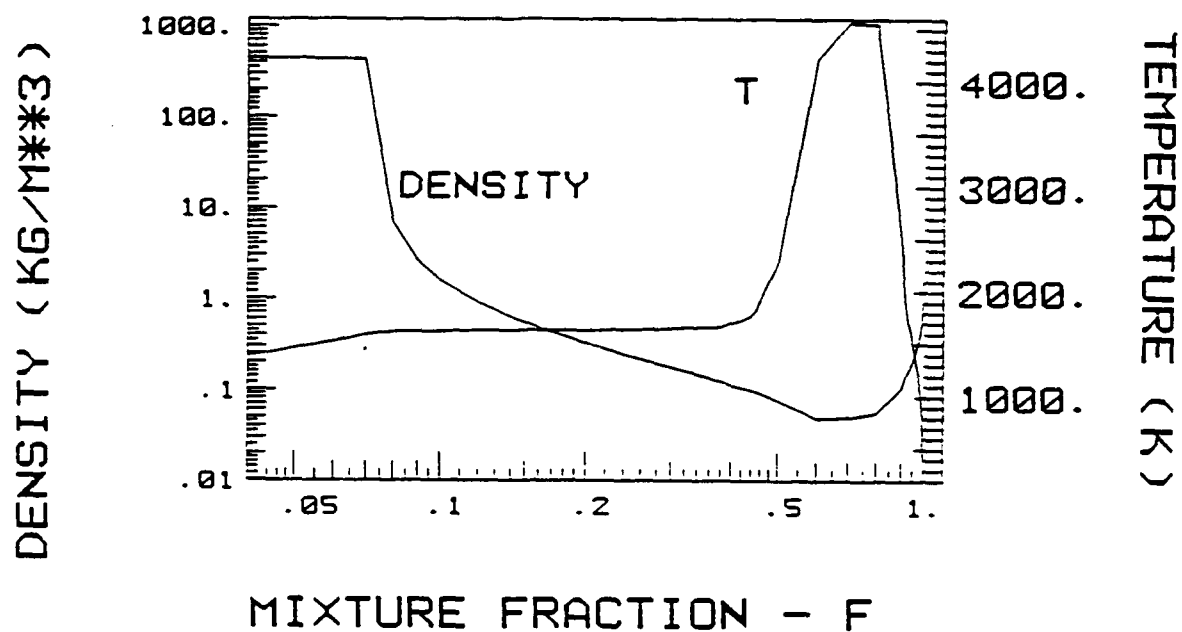
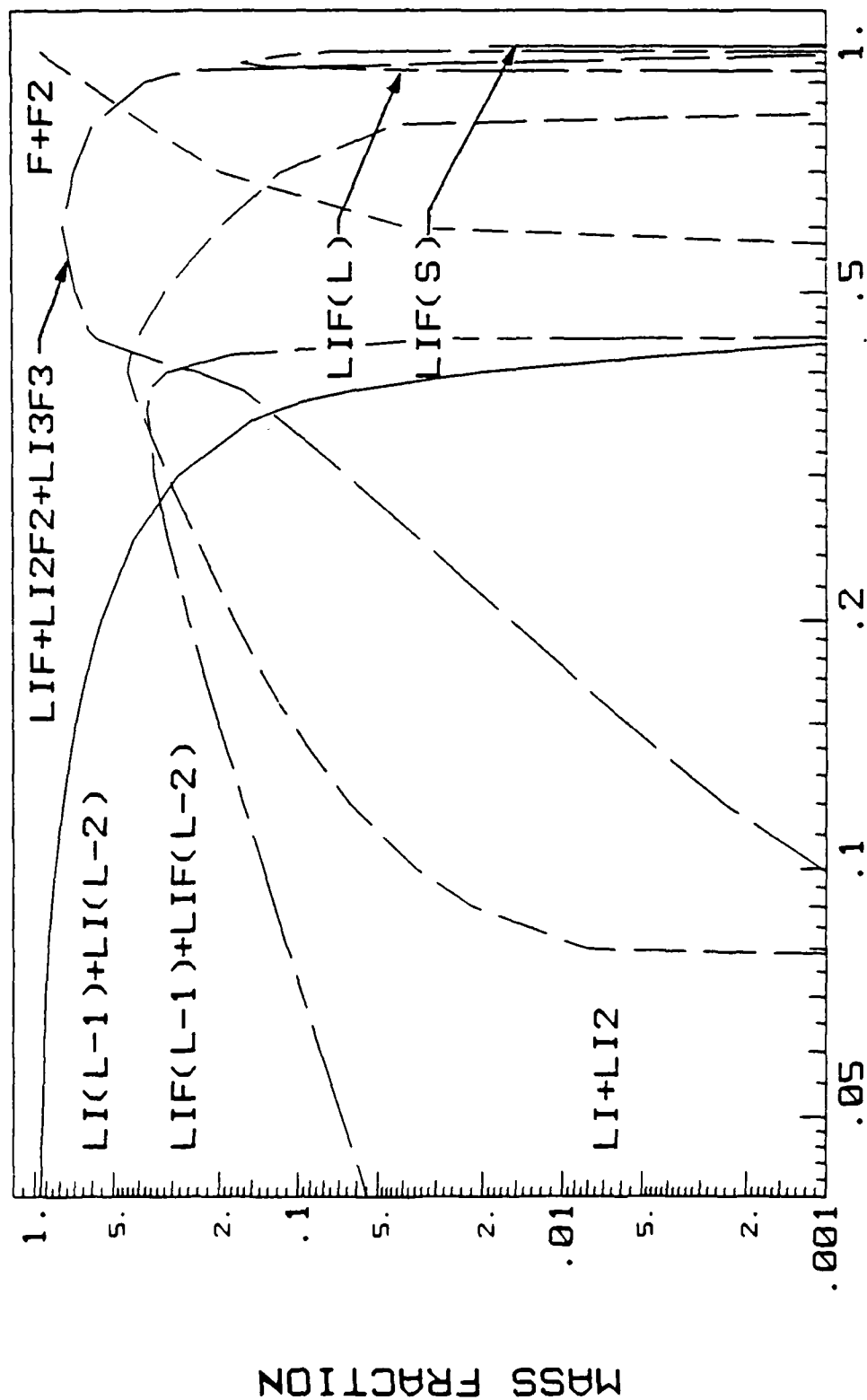


FIGURE 8.2 LI(L)-F2(G) SYSTEM, TINF=1130K, T0=298K, 1 ATM



MIXTURE FRACTION - F

9. APPLICATION TO THE LITHIUM-SULFUR HEXAFLUORIDE SYSTEM

The system resulting from the injection of gaseous sulfur hexafluoride ($\text{SF}_{6(g)}$) into liquid lithium ($\text{Li}_{(L)}$) is discussed in this section. This particular pair of reactants is under consideration as a thermal energy source for underwater applications (Mattavi et al., 1969; van der Sluys, 1975; Biermann, 1975; and Groff and Faeth, 1978A). The thermodynamic model used is based on the work of Groff and Faeth (1976, and 1978B).

9.1 System

The gas phase was assumed to consist of the species $\text{Li}_{(g)}$, $\text{Li}_{2(g)}$, $\text{LiF}_{(g)}$, $\text{Li}_2\text{F}_{2(g)}$, $\text{Li}_3\text{F}_{3(g)}$, $\text{SF}_{6(g)}$, and $\text{Li}_2\text{S}_{(g)}$ in an ideal gas mixture. These preliminary calculations do not include any of the lower sulfur fluorides such as SF_4 , etc. It is likely that they would be present in significant amounts, especially at higher temperatures. The presence of ions in the gas phase was also neglected. Three solid species were considered in separate phases: $\text{Li}_{(s)}$, $\text{LiF}_{(s)}$, and $\text{Li}_2\text{S}_{(s)}$.

As in the previous two sections, the liquid metal, $\text{Li}_{(L)}$, and molten salt, $\text{LiF}_{(L)}$, form two immiscible phases. In the sulfur hexafluoride-lithium system, however, there is an additional component, $\text{Li}_2\text{S}_{(L)}$, dissolved in each phase. The activity coefficients of the immiscible liquid phases are predicted using the van Laar model extended to multicomponent systems (Wohl, 1946). The activity coefficient of the k th species may be given as

$$\ln \gamma_k = \frac{b_k \sum_i \sum_j (A'_{ik} - 0.5A'_{ij}) b_i b_j N_i N_j}{RT (\sum_i N_i b_i)^2} \quad (9.1)$$

where A'_{ij} and b_i are empirical parameters. Note that $A'_{ii} = 0$, and $A'_{ij} = A'_{ji}$. The equation given here differs from that presented by Groff and Faeth (1976, p. 22, and 1978, p. 328). We believe this equation to be the correct one.

For a system with three components, the number of empirical parameters may be reduced by one by defining new parameters A_{ij} and B_i as (Groff and Faeth, 1976, pp. 20-21):

$$A_{ij} = b_i A'_{ij} \quad (9.2)$$

and

$$B_1 = b_1/b_2; \quad B_2 = b_2/b_3; \quad \text{and} \quad B_3 = b_1/b_3 = B_1 B_2 \quad (9.3)$$

The subscripts 1, 2, and 3 refer to $\text{Li}_{(L)}$, $\text{LiF}_{(L)}$, and Li_2S , respectively. Equation 9.1 may then be written as

$$\ln \gamma_k = \frac{\sum_i \sum_j (A_{ik} - 0.5A_{ij}) (b_j/b_k) N_i N_j}{RT [\sum_i N_i (b_i/b_k)]^2} \quad (9.4)$$

Groff and Faeth (1978B) have estimated the empirical parameters from experimental data as a linear function of temperature using the least squares technique. The resulting equations are:

$$A_{12} = 121.53 - 0.05730 T \text{ (kJ/mole)} \quad (9.5)$$

$$A_{13} = 53.287 - 4.00\text{E-}4 T \text{ (kJ/mole)} \quad (9.6)$$

$$A_{23} = 0 \quad (9.7)$$

and

$$B_1 = 2.5846 - 8.132\text{E-}4 T \quad (9.8)$$

$$B_3 = 1.36 \quad (9.9)$$

$$B_2 = B_3/B_1 \quad (9.10)$$

9.2 Thermodynamic Data

Thermodynamic data for all three forms of Li_2S (lithium sulfide) is extremely limited. Groff and Faeth (1976, pp. 131-138) estimated the required spectroscopic data for determining the properties of $\text{Li}_2\text{S}_{(g)}$ using statistical methods. They felt the accuracy of the resulting thermodynamic data for $\text{Li}_2\text{S}_{(g)}$ to be within $\pm 5\%$. Their equations are used in this work to calculate the enthalpy and Gibbs energy of gaseous lithium sulfide. Groff and Faeth estimated thermodynamic data for $\text{Li}_2\text{S}_{(s)}$ and $\text{Li}_2\text{S}_{(L)}$ from Na_2S , Li_2O , and Na_2O using Kopp's rule (Lewis and Randall, 1961, pp. 57-58). Their estimated values were used to calculate the enthalpy and Gibbs energy for solid and liquid lithium sulfide. The thermodynamic data for all other species were taken from the data file provided with the CEC-72 computer program (Gordon and McBride, 1971).

9.3 Results

The equilibrium results for $T^\infty = 1130\text{K}$ and $T^0 = 298\text{K}$ are presented in Figures 9.1 and 9.2. No experimental data is available to compare these results to, nor have any calculations of this type appeared in the literature. As in the lithium-fluorine calculations presented in the previous section, the initial conditions are such that salt-rich and metal-rich liquid phases do not appear simultaneously at any mixture fraction.

FIGURE 9.1 LI(L)-SF6(G) SYSTEM. $T_{INF}=1130K$, $T_0=298K$, 1 ATM

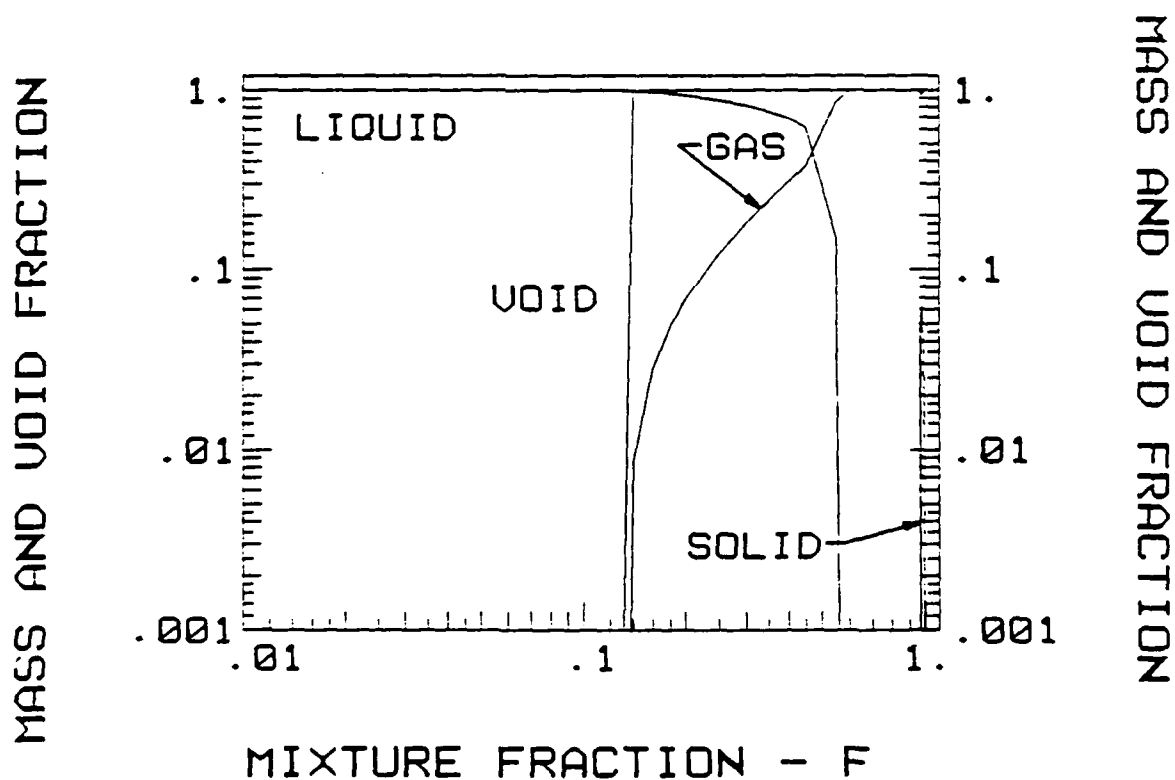
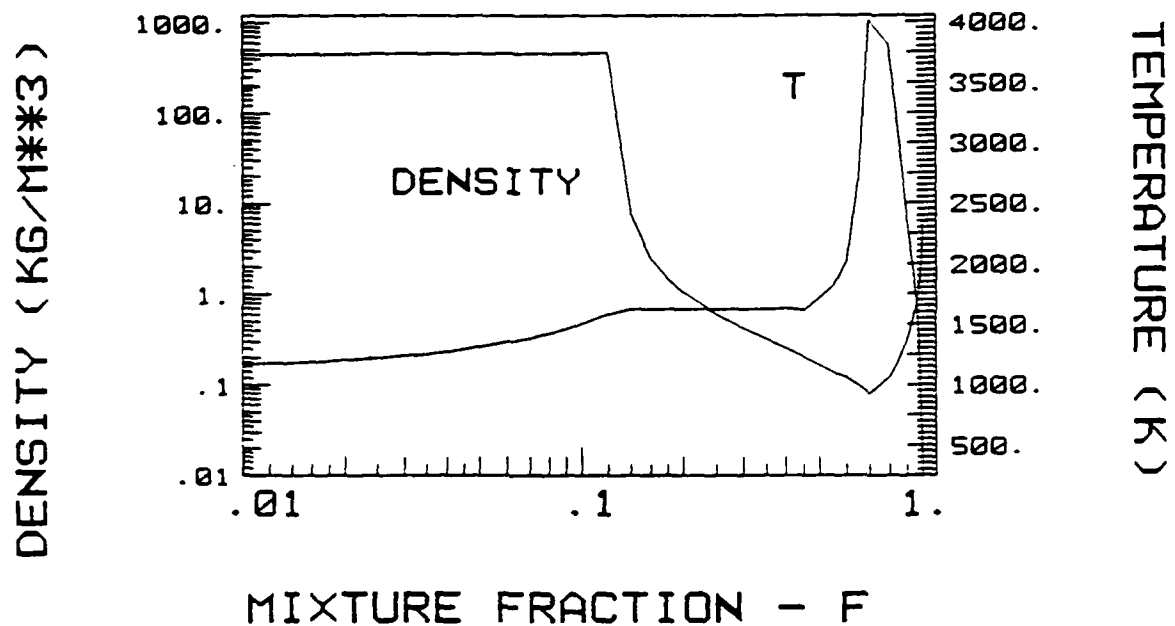
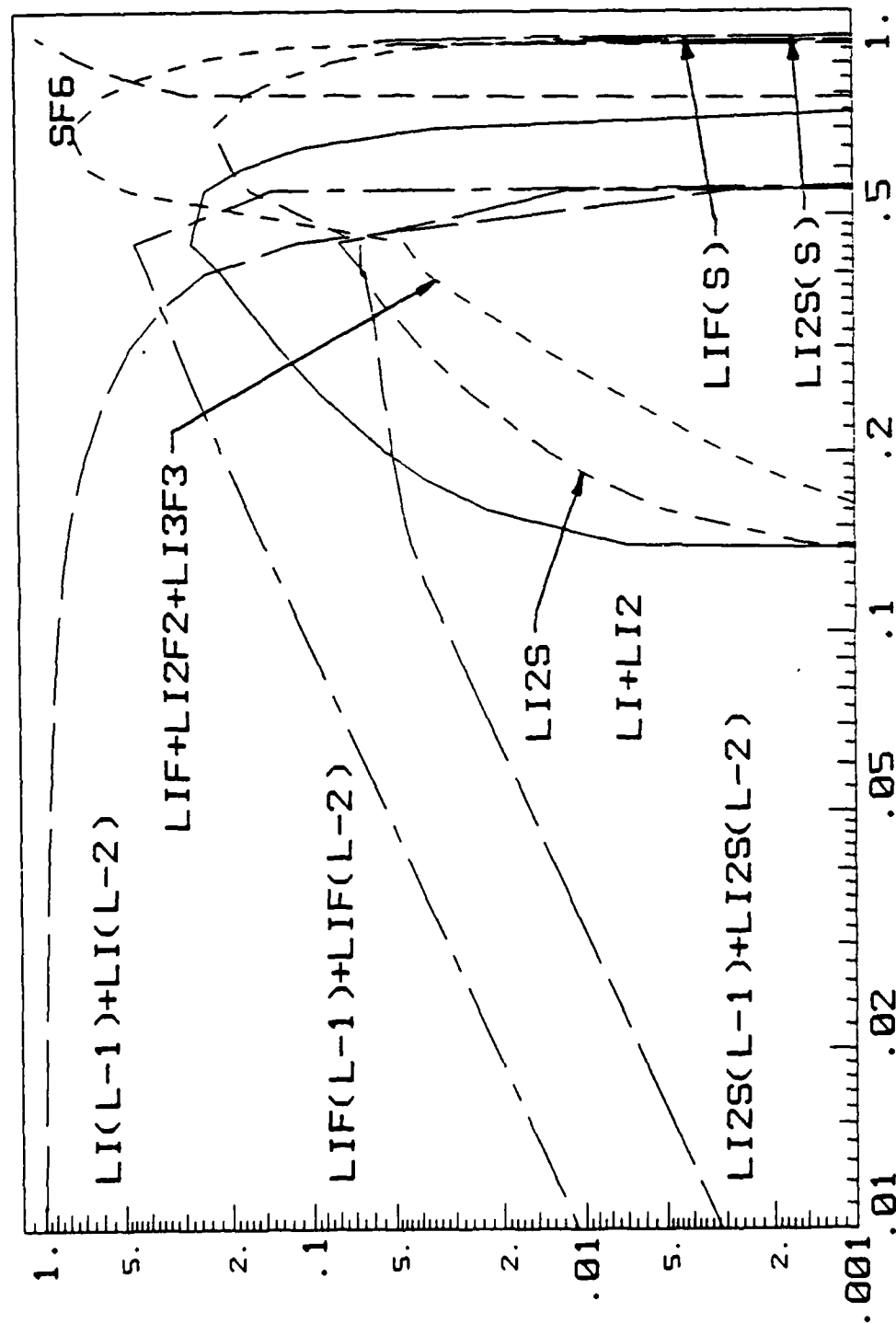


FIGURE 9.2 LI(L)-SF6(G) SYSTEM, TINF=1130K, T0=298K, 1 ATM



MIXTURE FRACTION - F

MASS FRACTION

10. CONCLUSIONS

The computer program CEC-NMS has been found to effectively compute chemical reaction equilibria for a variety of complex systems. Use of the direct minimization technique allows equilibrium to be calculated without regard to the actual reaction equations and allows easier removal of trace species.

For the majority of calculation points, convergence was achieved in under 10 seconds on a Univac 1100 mainframe computer. While not unreasonable, future work might include modifications to the program to reduce this calculation time. This would become more important if the program were to be used on a microcomputer or if extremely complex systems were considered.

While an attempt was made to make the program user-friendly, improvements in this respect are always possible. This might include altering the structure of the program to improve readability and developing more detailed documentation. Another improvement to the program would be adding a routine for automatically checking and modifying the species coefficient matrix if it becomes singular during the course of computation. Finally, while the program has converged with rather arbitrary initial guesses for all attempted systems, there are algorithms available for automatically providing initial estimates based on the Gibbs free energy of the species (Smith and Missen, 1982, pp. 201-204, and van Zeggeren and Storey, 1970, pp. 128-132). The inclusion of such an algorithm may be useful for certain systems.

APPENDIX A-D PROGRAM LISTINGS

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