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APPLICATION OF INTERVAL ANALYSIS FOR GIBBS AND HELMHOLTZ FREE ENERGY GLOBAL MINIMIZATION IN PHASE STABILITY ANALYSIS

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Abstract - The tangent plane criterion has become important for a correct solution evaluation phase and chemical of equilibrium problem. This method, applicable to single and multiphase systems, is mainly used for a single equation of state modeling all phases involved. The present work is mainly concerned with the application of interval analysis methods for global energy minimization in high-pressure phase stability problems. Two approaches are applied: (i) the Gibbs free energy global minimization under conditions of constant temperature and pressure and (ii) the Helmholtz free energy density global minimization under conditions of constant temperature and volume. Five case studies, one ternary and four binary systems, are analyzed in connection with the Peng-Robinson equation of state (PREOS) model. Five more case studies, for the CO_2 + *trans*-2-hexen-1-ol system at high pressures, are used to compare different methods of phase equilibrium calculation with the approach using interval analysis. Finally, a complex system, clove oil + CO_2, is analyzed. The results indicate that the interval analysis method is robust and reliable for all the problems studied.

Keywords: Phase stability; Interval analysis; Mathematical modeling, Gibbs free energy; Helmholtz free energy.

INTRODUCTION

Nonreactive Phase Stability

Stability analysis of an admissible state is illustratively described in terms of behavior of the system when submitted to perturbations. Depending on this behavior, the state is usually defined as stable, metastable, or unstable equilibrium. In what follows, the main interest is to verify whether or not an admissible state is stable.

The stable equilibrium criterion for closed systems is a well-established result in thermodynamics and may be presented in several equivalent forms. In nonreactive phase stability analysis, much attention has been given to the criterion in terms of the Gibbs free energy, *G* (Michelsen, 1982a,b; Sun and Seider, 1995; McKinnon, et al., 1996; Wasylkiewicz, et al., 1996; McDonald and Floudas, 1997; Hua, et al., 1997), and in terms of the Helmholtz free energy density, $\tilde{A}$ (Nagarajan and Cullick, 1991; Xu, 2001; Xu et al., 2002).

Phase Stability Analysis Using the Gibbs Free Energy

The equilibrium criterion in terms of the Gibbs free energy can be expressed as follows: the stable equilibrium state of a closed system with given internal constraints at constant $T = T_0$ and $P = P_0$ is characterized by a global minimum of G with regard to all equilibrium states compatible with the fixed

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*To whom correspondence should be addressed values of T_0 and P_0 and the given internal constraints (Callen, 1985; Tester and Modell, 1997).

When applied to a nonreactive single-phase and closed simple system at constant T_0 and P_0, this criterion requires that no admissible two-phase configuration have a value for G value smaller than $G_o = G(T_o, P_o, \vec{n}_o)$, the original value. If $G < G_0$ for any two-phase configuration, then the state under study is not stable.

Suppose that an arbitrarily small perturbation converts the single-phase system into a two-phase system. At constant T_0 and P_0, the following simplified notation will be used: $G(T_o, P_o, \vec{n}) \equiv G(\vec{n})$. Thus, the variation in the Gibbs free energy for the above change of state can be represented by

$$\Delta G = G^{I}(\vec{n}_o - \vec{\varepsilon}) + G^{II}(\vec{\varepsilon}) - G_o \tag{1}$$

A Taylor expansion of G^I in $\vec{\varepsilon}$ becomes

$$\begin{aligned} G^{I}(\vec{n}_o - \vec{\varepsilon}) = G_o - \varepsilon \sum_{i=1}^{N} y_i \mu_i^o + \\ +(\text{higher} - \text{order terms in } \varepsilon) \end{aligned} \tag{2}$$

where μ_i^o is the chemical potential of species ***i*** in the original phase and y_i is the molar fraction of species ***i*** in the new phase. In the above expansion, use was made of

$$\left.\frac{\partial G}{\partial n_i}\right|_{\vec{n}=\vec{n}_o} = \mu_i^o \ ; \quad \varepsilon = \sum_{i=1}^{N} \varepsilon_i \ ; \quad \varepsilon_i = y_i \varepsilon \ ,$$

and

$$G^{II}(\vec{\varepsilon}) = \varepsilon \sum_{i=1}^{N} y_i \mu_i \tag{3}$$

Substituting (2) and (3) into (1) gives

$$\begin{aligned} \Delta G = \varepsilon \sum_{i=1}^{N} y_i(\mu_i - \mu_i^o) + \\ +(\text{higher} - \text{order terms in } \varepsilon) \end{aligned} \tag{4}$$

For sufficiently small ε and taking into account that ε > 0, the sign of ΔG in (4) is given by the sign of

$$D_G(\vec{y}) = \sum_{i=1}^{N} y_i(\mu_i - \mu_i^o) \tag{5}$$

Therefore a necessary and sufficient condition for a phase to be in stable equilibrium is that $D_G(\vec{y}) \geq 0$ for any composition $\vec{y} = (y_1, ..., y_{j-1}, y_{j+1}, ..., y_N)$.

Phase Stability Analysis Using the Helmholtz Free Energy

The equilibrium criterion in terms of the Helmholtz free energy can be expressed as follows: the stable equilibrium state of a closed system with given internal constraints at constant $T = T_0$ and $V = V_0$ is characterized by a global minimum of A with regard to all equilibrium states compatible with the fixed values of T_0 and V_0 and the given internal constraints (Callen, 1985; Tester and Modell, 1997).

This criterion, when applied to a nonreactive single-phase system, requires that no admissible two-phase configuration have a value for A smaller than $A_o = A(T_o, V_o, \vec{n}_o)$, the original value. If $A < A_0$ for any two-phase configuration, then the state studied is not stable.

Suppose that an arbitrarily small perturbation converts the single-phase system into a two-phase system. At constant T_0, the following simplified notation will be used: $A(T_o, V, \vec{n}) \equiv A(V, \vec{n})$. Thus, variation in the Helmholtz free energy for the above change of state can be represented by

$$\Delta A = A^{I}(V_o - V_\varepsilon, \vec{n}_o - \vec{\varepsilon}) + A^{II}(V_\varepsilon, \vec{\varepsilon}) - A_o \tag{6}$$

A Taylor expansion of A^I in $\vec{\varepsilon}$ becomes

$$\begin{aligned} A^{I}(V_o - V_\varepsilon, \vec{n}_o - \vec{\varepsilon}) = A_o - \varepsilon(\sum_{i=1}^{N} y_i \mu_i^o - \\ -P_o \underline{V}) + (\text{higher} - \text{order terms in } \varepsilon) \end{aligned} \tag{7}$$

where μ_i^o is the chemical potential of species ***i*** in the original phase and $\underline{V}$ and y_i are the molar volume and molar fraction of species ***i*** in the new phase. In the above expansion, use was made of

$$\left.\frac{\partial A}{\partial n_i}\right|_{(\vec{n},V)=(\vec{n}_o;V_o)} = \mu_i^o \ ;$$

$$\left.\frac{\partial A}{\partial V}\right|_{(\vec{n},V)=(\vec{n}_o;V_o)} =$$

$$-P(T_o, V_o, \vec{n}_o) = -P(T_o, \underline{V}_o, \vec{y}_o) = -P_o$$

$$V_\varepsilon = \varepsilon \underline{V}\ ; \qquad \varepsilon = \sum_{i=1}^{N} \varepsilon_i\ ; \qquad \varepsilon_i = y_i \varepsilon\ , \qquad \text{and}$$

$$A^{II}(V_\varepsilon,\vec{\varepsilon}) = G^{II}(V_\varepsilon,\vec{\varepsilon}) - PV_\varepsilon = \varepsilon\left(\sum_{i=1}^{N} y_i\mu_i - P\underline{V}\right) \qquad (8)$$

where

$$P = P(T_o, V_\varepsilon, \vec{\varepsilon}) = P(T_o, \underline{V}, \vec{y})\ .$$

Substituting (7) and (8) into (6) gives:

$$\begin{aligned}\Delta A &= \varepsilon\left(\sum_{i=1}^{N} y_i(\mu_i - \mu_i^o) - \underline{V}(P - P_o)\right) + \\ &+ (\text{higher} - \text{order terms in } \varepsilon)\end{aligned} \qquad (9)$$

For sufficiently small ε and taking into account that ε > 0, the sign of ΔA in (9) is given by the sign of

$$D_A(\underline{V},\vec{y}) = \sum_{i=1}^{N} y_i(\mu_i - \mu_i^o) - \underline{V}(P - P_o) \qquad (10)$$

Therefore, a necessary and sufficient condition for a phase to be in stable equilibrium is that $D_A(\underline{V},\vec{y}) \geq 0$ for any molar volume $\underline{V}$ and any composition $\vec{y} = (y_1,\ldots,y_{j-1},y_{j+1},\ldots,y_N)$.

Nagarajan and Cullick (1991) developed an alternative criterion involving the Helmholtz free energy for a unit volume (Helmholtz free energy density, Ã), for a system with constant T and P. Using the following species molar densities

$$\vec{\rho} = (\rho_1,\rho_2,\ldots,\rho_N) \quad ; \quad \rho_i = \frac{n_i}{V} \qquad (11)$$

it can be observed that the Helmholtz free energy density at a given temperature can be represented by a $\vec{\rho}$ function:

$$\frac{A(V,\vec{n})}{V} = A(1,\frac{\vec{n}}{V}) = A(1,\vec{\rho}) \equiv \tilde{A}(\vec{\rho}) \qquad (12)$$

It can be readily shown that μ_i and P can also be expressed as $\vec{\rho}$ functions:

$$\mu_i = \frac{\partial A}{\partial n_i} = \frac{\partial \tilde{A}}{\partial \rho_i} \quad ; \quad -P = \frac{\partial A}{\partial V} = \tilde{A} - \sum_{i=1}^{N} \rho_i \frac{\partial \tilde{A}}{\partial \rho_i} \qquad (13)$$

Combining (10) and (13) allows $D_{\tilde{A}}(\vec{\rho}) \equiv \dfrac{D_A(\underline{V},\vec{y})}{\underline{V}}$ to be expressed as a $\vec{\rho}$ function:

$$\begin{aligned}D_{\tilde{A}}(\vec{\rho}) &= \tilde{A} - \tilde{A}_o - \sum_{i=1}^{N}(\rho_i - \rho_i^o)\left(\frac{\partial \tilde{A}}{\partial \rho_i}\right)^o = \\ &= \tilde{A} - \tilde{A}_o - (\vec{\rho} - \vec{\rho}_o)\cdot(\nabla\tilde{A})^o\end{aligned} \qquad (14)$$

Therefore, a necessary and sufficient condition for a phase to be in stable equilibrium is that $D_{\tilde{A}}(\vec{\rho}) \geq 0$ for any acceptable value of $\vec{\rho} = (\rho_1,\rho_2,\ldots,\rho_N)$.

The advantage of using this last approach is that the function *Ã* versus $\vec{\rho}$ is smooth, while *G* versus $\vec{y}$ is not always a smooth function.

Mathematical Modeling

In order to verify whether $D_G \geq 0$ or $D_{\tilde{A}} \geq 0$ for all admissible variable values, it is sufficient to test these criteria at the stationary points of $D_G(\vec{y})$ or $D_{\tilde{A}}(\vec{\rho})$. For the Helmholtz free energy density approach, the stationary points satisfy the following equation:

$$\nabla D_{\tilde{A}} = \nabla\tilde{A} - (\nabla\tilde{A})^o = 0 \qquad (15)$$

Determination of the stationary point coordinates corresponds to finding all the roots of the nonlinear equation given by (15). A reliable and robust method for this is given by the interval for the Newton/generalized bisection algorithm, based on interval analysis and interval arithmetic (Stadtherr, et al., 1995; Kearfott, 1996). The main advantage of this method is that it finds with certainty all the roots of the nonlinear set of equations, proving that each solution is enclosed within some bounds. The main drawback is that, depending on the nature of the problem a long computational time may be required to achieve this certainty.

In this work, the interval Newton/generalized bisection algorithm was used in connection with the Peng-Robinson equation of state (PREOS) model to solve the stability problems, using the Van der Walls mixing rules. The INTBIS and INTLIB softwares were used for the numerical calculations of the roots (Kearfott and Novoa, 1990; Kearfott et al., 1994).

NUMERICAL RESULTS

Five stability analysis sample problems and their respective computational results using the Helmholtz free energy density formulation are given below. The results for each case include the stationary point coordinates $\vec{\rho}$ and the corresponding $D_{\tilde{A}}(\vec{\rho})$ values. The same problems were studied by Hua et al. (1997, 1998) with the Gibbs free energy approach. The corresponding results will not be reproduced here and can be found in the above - cited references. With respect to the computational time required to solve the problems, it was observed that the approach based on the Helmholtz free energy density required roughly less than half of the time needed by the approach based on the Gibbs free energy, using the same machine and software.

Problem 1. Hydrogen sulfide (1) + Methane (2)

This is a binary mixture of H_2S (1) and CH_4 (2) at 190 K and 40.35 bar. The PREOS model was used with parameters calculated from T_{c1}=373.2 K, P_{c1}=89.4 bar, w_1=0.1, T_{c2}=190.6 K, P_{c2}=46.0 bar, w_2=0.008, and the binary interaction parameter k_{12}=0.08. Six original compositions were considered, with results shown in Table 1.

Problem 2. Methane (1) + Propane (2)

This is a binary mixture of CH_4 (1) and C_3H_8 (2) at 277.6 K and 50 bar. The PREOS model was used with parameters calculated from methane data given above, T_{c2}=369.8 K, P_{c2}=42.5 bar, w_2=0.152, and the binary interaction parameter k_{12}=0.029. Four original compositions were considered, with results shown in Table 2.

Problem 3. Nitrogen (1) + Ethane (2)

This is a binary mixture of N_2 (1) and C_2H_6 (2) at 270 K and 76 bar. The PREOS model was used with parameters calculated from T_{c1}=126.2 K, P_{c1}=33.9 bar, w_1=0.04, T_{c2}=305.4 K, P_{c2}=48.8 bar, w_2=0.098, and the binary interaction parameter k_{12}=0.08. Four original compositions were considered, with results shown in Table 3.

Problem 4. Carbon dioxide (1) + Methane (2)

This is a binary mixture of CO_2 (1) and CH_4 (2) at 220 K and 60.8 bar. The PREOS model was used with parameters calculated from T_{c1}=304.2 K, P_{c1}=73.8 bar, w_1=0.225, the methane parameters given above, and the binary interaction parameter k_{12}=0.095. Four original compositions were considered, with results shown in Table 4.

Problem 5. Nitrogen (1) + Methane (2) and Ethane (3)

This is a ternary mixture of N_2 (1), CH_4 (2) and C_2H_6 (3) at 270 K and 76 bar. The PREOS model was used with T_{c1}=126.2 K, P_{c1}=33.9 bar, w_1=0.04, T_{c2}=190.6 K, P_{c2}=46.0 bar, w_2=0.008, T_{c3}=305.4 K, P_{c3}=48.8 bar, w_3=0.098, and binary interaction parameters k_{12}=0.038, k_{13}=0.08, and k_{23}=0.021. Four original compositions were considered, with results shown in Table 5.

Table 1: Results for Problem 1: H_2S (1) -CH_4 (2) at P_o=40.53 bar and T_o=190K (PREOS).

$\vec{z}$	**Stationary Points** $\vec{\rho}$ **(mol/L)**	$\frac{D_{\tilde{A}}}{RT}$ **(mol/L)**	**Stable**
(0.0115, 0.9885)	(0.5405 x 10^{-4}, 0.004645)	0.0	Yes
(0.0187, 0.9813)	(0.012425, 0.011713)	0.175990 x 10^{-2}	No
	(0.001237, 0.014545)	-0.621029 x 10^{-4}	
	(0.3148 x 10^{-3}, 0.008963)	0.712628 x 10^{-4}	
	(0.9019 x 10^{-4}, 0.004733)	0.0	
(0.0700, 0.93)	(0.013565, 0.010938)	0.236244 x 10^{-2}	Yes
	(0.001071, 0.014230)	0.0	
	(0.3237 x 10^{-3}, 0.009270)	0.917844 x 10^{-4}	
	(0.8451 x 10^{-4}, 0.004681)	0.704566 x 10^{-5}	
(0.5000, 0.5)	(0.012101, 0.012101)	0.0	No
	(0.001824, 0.016023)	-0.138959 x 10^{-2}	
(0.8880, 0.112)	(0.012072, 0.011940)	0.163676 x 10^{-2}	No
	(0.001270, 0.014554)	-0.387744 x 10^{-4}	
	(0.3285 x 10^{-3}, 0.009062)	0.915577 x 10^{-4}	
	(0.8951 x 10^{-4}, 0.004672)	0.116681 x 10^{-4}	
(0.8900, 0.11)	(0.011905, 0.012029)	0.172977 x 10^{-2}	Yes
	(0.001214, 0.014320)	0.879163 x 10^{-4}	
	(0.3824 x 10^{-3}, 0.009618)	0.174003 x 10^{-3}	
	(0.8379 x 10^{-4}, 0.004459)	0.520280 x 10^{-4}	

Table 2: Results for Problem 2: CH_4 (1) and C_3H_8 (2) at P=50 bar and T=277.6K (PREOS).

$\vec{z}$	**Stationary Points** $\vec{\rho}$ **(mol/L)**	$\frac{D_{\tilde{A}}}{RT}$ **(mol/L)**	**Stable**
(0.10, 0.90)	(0.001153, 0.010380)	0.0	
	(0.001569, 0.003751)	0.213158 x 10^{-2}	Yes
	(0.8008 x 10^{-3}, 0.3945 x 10^{-3})	0.115065 x 10^{-2}	
(0.40, 0.60)	(0.004471, 0.006709)	0.0	
	(0.004766, 0.004044)	0.926279 x 10^{-4}	No
	(0.002903, 0.5440 x 10^{-3})	-0.460877 x 10^{-3}	
(0.60, 0.40)	(0.002397, 0.009779)	-0.265121 x 10^{-2}	
	(0.002772, 0.001849)	0.0	No
	(0.002295, 0.9799 x 10^{-3})	-0.213274 x 10^{-4}	
(0.90, 0.10)	(0.002318, 0.2570 x 10^{-3})	0.0	Yes

Table 3: Results for Problem 3: N_2 (1) and C_2H_6 (2) at P=76 bar and T=270K (PREOS).

$\vec{z}$	**Stationary Points** $\vec{\rho}$ **(mol/L)**	$\frac{D_{\tilde{A}}}{RT}$ **(mol/L)**	**Stable**
(0.10, 0.90)	(0.001406, 0.012660)	0.0	
	(0.001905, 0.004485)	0.556489 x 10^{-3}	Yes
	(0.001813, 0.003017)	0.546979 x 10^{-3}	
(0.18, 0.82)	(0.002290, 0.010440)	0.0	
	(0.002658, 0.006677)	0.532488 x 10^{-4}	No
	(0.002513, 0.002663)	-0.495879 x 10^{-4}	
(0.30, 0.70)	(0.002243, 0.010716)	-0.884250 x 10^{-4}	
	(0.002670, 0.006233)	0.0	No
	(0.002525, 0.002784)	-0.713284 x 10^{-4}	
(0.44, 0.56)	(0.002023, 0.011471)	-0.207527 x 10^{-3}	
	(0.002545, 0.005194)	0.202731 x 10^{-4}	No
	(0.002427, 0.003087)	0.0	
(0.60, 0.40)	(0.002633, 0.001755)	0.0	Yes

Table 4: Results for Problem 4: CO_2 (1) and CH_4 (2) at P=60.8 bar and T=220K (PREOS).

Studied State $\vec{z}$	**Stationary Points** $\vec{\rho}$ **(mol/L)**	$\frac{D_{\tilde{A}}}{RT}$ **(mol/L)**	**Stable**
(0.10, 0.90)	(0.000593, 0.005342)	0.0	Yes
	(0.010854, 0.010387)	-0.156346 x 10^{-3}	
(0.20, 0.80)	(0.003096, 0.008572)	0.253332 x 10^{-4}	No
	(0.001488, 0.005955)	0.0	
	(0.006096, 0.010874)	-0.317790 x 10^{-5}	
(0.30, 0.70)	(0.004299, 0.010032)	0.0	No
	(0.001434, 0.006092)	-0.510149 x 10^{-4}	
	(0.008248, 0.010934)	0.0	
(0.43, 0.57)	(0.003763, 0.009436)	0.407501 x 10^{-4}	No
	(0.001403, 0.005893)	-0.950155 x 10^{-5}	
	(0.013733, 0.009155)	0.0	
(0.60, 0.40)	(0.003915, 0.008904)	0.339640 x 10^{-3}	Yes
	(0.001178, 0.004904)	0.211342 x 10^{-3}	

Table 5: Results for Problem 5: N_2 (1), CH_4 (2) and C_2H_6 (3) at P=76 bar and T=270K (PREOS).

Studied State $\vec{z}$	**Stationary Points** $\vec{\rho}$ **(mol/L)**	$\frac{D_{\tilde{A}}}{RT}$ **(mol/L)**	**Stable**
	(0.001697, 0.8812 x 10^{-3}, 0.010648)	-0.193896 x 10^{-3}	
(0.30, 0.10, 0.60)	(0.002046, 0.6821 x 10^{-3}, 0.004092)	0.0	No
	(0.002034, 0.6635 x 10^{-3}, 0.003832)	-0.384496 x 10^{-7}	
(0.15, 0.30, 0.55)	(0.001069, 0.2725 x 10^{-3}, 0.007391)	-0.130813 x 10^{-4}	No
	(0.001134, 0.2296 x 10^{-3}, 0.004294)	0.0	
(0.08, 0.38, 0.54)	(0.6675 x 10^{-3}, 0.003170, 0.004503)	0.0	Yes
(0.05, 0.05, 0.90)	(0.165 x 10^{-6}, 0.165 x 10^{-6}, 0.165 x 10^{-6})	0.003381	Yes

COMPARING DIFFERENT APPROACHES

In order to show the advantages of using the interval analysis method, a number of different methods in the literature were compared, using as example the CO_2 + *trans*-2-Hexen-1-ol system at high pressures, whose phase behave is known to be difficult to model (Stradi et al., 2001a,b). Table 6 shows the results for the molar fractions (x_{CO2} and x_{CO2}) for different methods used to calculate the flash equilibrium. The case studies are the same as those presented in Stradi et al. (2001a,b), where P1, P2, and P3 are the methods used by those authors, and M1 is the approach used in this paper with interval analysis.

In case study 1, the same results were found with conventional methods P1, P2 and P3, but all were incorrect. In case study 2, using P1, P2, and P3 it was incorrectly found that there would be no phase splitting. In these two cases, the pressure was close to the point of the three-phase line, therefore presenting numerical difficulties that caused these methods to fail. These difficulties were avoided with the approach used in this paper, M1, which resulted in consistently reliable results.

For case studies 3, 4, and 5, it can be observed that methods P1, P2, and P3 failed once for the flash calculations. P3 failed in case study 4 by not predicting the phase splitting. P2 failed in case study 5 by not predicting the phase splitting. In case study 3, P1 correctly predicted the phase split, but it resulted in numerical errors and was not able to find the solution. All these difficulties are very common in conventional methods used to model phase equilibrium. Again, the approach used here was able to find the correct solutions in all cases.

EQUILIBRIUM ANALYSIS FOR A COMPLEX SYSTEM

The approach used in this paper was applied to describe the phase equilibrium behavior of the clove oil + CO_2 system, using experimental data from Souza et al. (2004). The main characteristic of this system, formed of an essential oil and carbon dioxide, is the large variety of different types of chemical groups found in the essential oil, which is in fact a complex system.

The calculations were done at two temperatures, 303.15 K and 308.15 K, and the model predicted a three-phase line at pressures of 71.25 and 80.15 bar, respectively. Above these pressures there is a liquid-liquid phase region, and below these pressures there is a liquid-vapor phase region. This can be observed in Figures 1a and 1b. It can be seen that the model was able to fit the experimental data for the clove oil + CO_2 system reasonably well. The values for the fitted parameters (k_{12}, l_{12}) as well as the critical properties and the accentric factors were determined by Souza et al. (2004).

Table 6: Examples comparing different approaches[1]

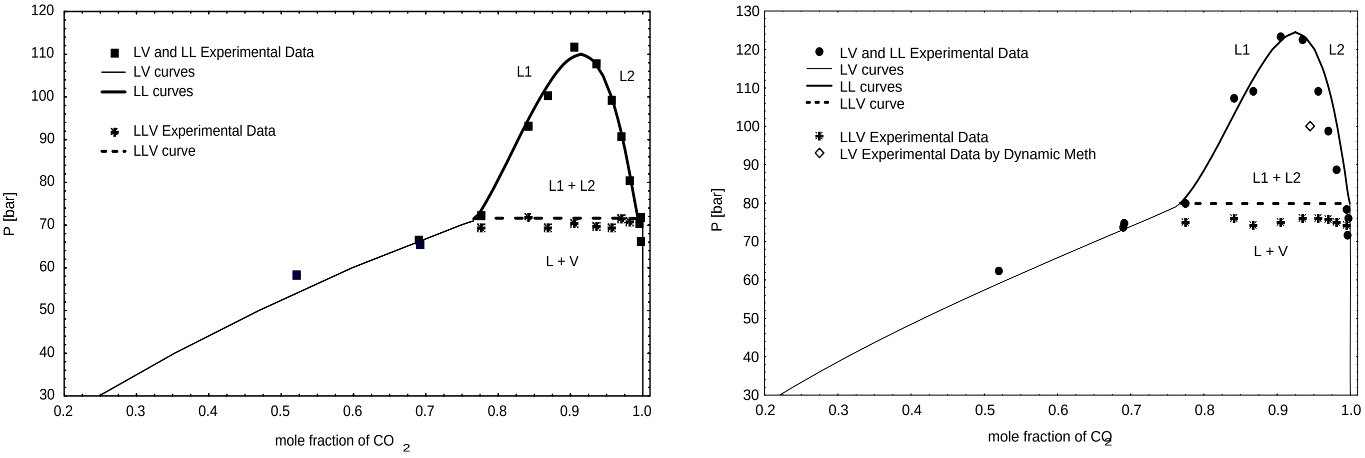
Case	Binary Mixtures			*P1		*P2		*P3		M1	
	Feed z_{CO2}	T (K)	P (bar)	x_{CO2}	y_{CO2}	x_{CO2}	y_{CO2}	x_{CO2}	y_{CO2}	x_{CO2}	y_{CO2}
1	0.800	303.15	71.00725	**0.7315**	**0.9986**	**0.7310**	**0.9987**	**0.7309**	**0.9987**	0.6850	0.9689
2	0.700	303.15	70.09	**NPS**		**NPS**		**NPS**		0.6833	0.9701
3	0.970	323.15	97.75	**NC**		0.6267	0.9948	0.6267	0.9949	0.6283	0.9945
4	0.742	323.15	130	0.7234	0.9554	0.7232	0.9560	**NPS**		07243	0.9560
5[2]	0.742	323.15	135	0.7345	0.9490	**NPS**		0.7347	0.9515	0.7356	0.9488

[1] The molar fractions x_{CO2} and y_{CO2} in each phase are determined. The results in bold indicate an incorrect solution. The notation NPS indicates that no phase splitting was predicted. NC indicates that a phase splitting was predicted, but the method was unable to find the solution due to a numerical problem (the software indicates NaN).

[2] RGIBBS displays an output with an error message.

*Results presented in Stradi et al. (2001a,b).

P1 - LNGFLASH
P2 - FLASH3
P3 - RGIBBS
M1 - Method 1, used in this work.



(a) (b)

Figure 1: P-x-y plot for CO_2-clove oil at 303.2 K (a) and 308.2 K (b).

CONCLUSIONS

The foregoing results show that interval analysis provides a reliable method for solving phase stability problems with the Gibbs or Helmholtz free energy approach. However, higher convergence speeds are obtained with the Helmholtz free energy density formulation than with the Gibbs free energy formulation. This is probably due to the smooth behavior of the Helmholtz energy density function, as pointed out by Nagarajan and Cullick (1991). The method is general purpose and can be applied in connection with other EOS models, such as the SAFT EOS model (Xu et al., 2002).

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NOMENCLATURE

A	Helmholtz free energy
A^I	Helmholtz free energy in phase I
A^{II}	Helmholtz free energy in phase II
$\tilde{A}(\rho)$	Helmholtz energy density surface
D	tangent plane distance
G	Gibbs free energy
G^I	Gibbs free energy in phase I
G^{II}	Gibbs free energy in phase II
k_{ij}	binary interaction parameter of component i in phase j
n	number of moles
N	number of species
P	pressure
P_c	critical pressure
R	gas constant
T	temperature
T_c	critical temperature
V	volume
V_ε	infinitesimal volume of phase formed
$\underline{V}$	molar volume
y_i	mole fraction of species I
Z	molar fraction of the feed
ε	infinitesimal mole number of phase formed
μ_i	chemical potential of species I
ρ_i	molar density of species I
ω	acentric factor
∇	gradient vector
0	used to indicate evaluation of feed composition

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