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An equation of state for the CH_4-CO_2-H_2O system: II. Mixtures from 50 to 1000°C and 0 to 1000 bar

ZHENHAO DUAN, NANCY MØLLER, and JOHN H. WEARE
Department of Chemistry, 0340, University of California, San Diego, La Jolla, CA 92093-0340, USA

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Abstract—An equation of state (EOS) for mixtures in the CH_4-CO_2-H_2O system has been developed. The model is based on the highly accurate endmember EOS presented in the previous article and on an empirical mixing rule. The mixing rule is based on an analogy with high order contributions to the virial expansion for mixtures. Comparison with experimental data indicates that the mixed system EOS can predict both phase equilibria and volumetric properties for the binaries with accuracy close to that of the experimental data for a temperature range from 50 to 1000°C and a pressure range from 0 to 1000 bar (or to 3000 bar with less accuracy).

For temperatures below the critical point of water, there is very little PVTX (density) data. However, even for temperatures for which sufficient data exists we found that parameterization from PVTX data alone did not lead to a free energy that would accurately predict liquid-vapor equilibria. On the other hand, using this data alone we obtain a free energy that predicts both liquid-vapor equilibria and the PVTX properties of the binaries with roughly experimental accuracy.

There are very few data inside the ternary. However, the mixing rule contains third order parameters, which require evaluation from ternary mixtures. For the single temperature for which we have data, the adjustment of one parameter gives good prediction of phase equilibrium in the ternary. The resulting EOS predicts that the presence of a small amount of CO_2 can significantly affect the solubility of CH_4. The application of this EOS to the study of fluid inclusions is discussed. The presence of CH_4 in CO_2-rich fluid inclusions can significantly affect the predicted trapping pressure.

I. INTRODUCTION

MANY GEOLOGICAL FLUIDS consist of mixtures, which fall approximately in the system CH_4-CO_2-H_2O-salt (e.g., TOURET, 1976; ROEDDER, 1984; RAMBOZ et al., 1985; THOMAS et al., 1990; LIRA and RIPLEY, 1990). In the previous paper (herein referred to as Part I), equations of state (EOS) for the endmembers H_2O, CO_2, and CH_4 in this system were presented. We demonstrated that these EOS could describe the PVT behavior of the pure subsystems in both vapor and liquid regions nearly within experimental error from 0 to 8000 bar and from 0 to 1000°C. We also discussed mixing and showed that for some high temperatures and low pressures, ideal mixing based on the endmember fugacities can give predictions that are sufficiently accurate for geochemical applications. This is true in spite of the fact that the endmembers are far from ideal in these regions.

However, many applications (e.g., fluid inclusion phase transitions) require the prediction of the mixing behavior at lower temperatures where nonideal mixing effects are very large. For example, for temperatures below the critical temperature of water (374°C) and at water saturation pressures, the volume of a CO_2-H_2O mixture can be twice the sum of the volumes of end-members. The activity can be three or more times larger than that predicted from simple ideal mixing. This can have a great effect on the phase equilibria, mineral assemblages, solubility of gases or minerals, the homogenization of fluid inclusions, etc.

In this paper we describe the extension of the EOS in part I to mixtures in the CH_4-CO_2-H_2O system. In order to interpolate pure system behavior into the binaries and ternaries systems, we introduce a mixing rule in Section II. The binary systems CO_2-H_2O, CH_4-CO_2, and CH_4-H_2O, and the evaluation of binary parameters in the mixing rule are discussed in sections III, IV, and V, respectively. Ternary predictions are discussed in Section VI. Finally, we discuss the application of this EOS to the study of fluid inclusion.

II. THE MIXING RULE

In part I we developed an EOS, which is rewritten as

$$Z = 1 + \frac{BV_c}{V} + \frac{CV_c^2}{V^2} + \frac{DV_c^4}{V^4} + \frac{EV_c^5}{V^5} + \frac{FV_c^2}{V^2}\left(\beta + \frac{\gamma V_c^2}{V^2}\right)\exp\left(-\frac{\gamma V_c^2}{V^2}\right), \quad (1)$$

where B, C, D, E, F are functions of temperature and they are defined in Eqn. (2), V_c is defined by Eqn. (6) of part I. In order to obtain an EOS for mixtures, it is common to extrapolate the single component behavior to mixed system by assuming that the parameters in the EOS at constant temperature and pressures (e.g., B, C, D, etc.) are a function of the composition of the mixture (see the following text). The equations (called mixing rules) chosen must return the parameter values for the end-member systems for pure compositions. Beyond this, however, there is very little guidance as to the form that the mixing equations should take.

For systems at low densities the virial expansion (MASON and SPURLING, 1969) provides a rigorous basis for including nonideal behavior both for mixed and nonmixed systems. This equation takes the form

$$Z = 1 + \frac{B_0}{V} + \frac{C_0}{V^2} + \frac{D_0}{V^3} + \cdots, \qquad (2)$$

where the composition dependence is given by

$$B_0 = \sum_i \sum_j x_i x_j B_{0ij}, \qquad (3a)$$

$$C_0 = \sum_i \sum_j \sum_k x_i x_j x_k C_{0ijk}, \qquad (3b)$$

$$D_0 = \sum_i \sum_j \sum_k \sum_l x_i x_j x_k x_l D_{0ijkl}. \qquad (3c)$$

In order to distinguish the parameters of Eqns. (1) and (2), we use B_0, C_0, and D_0 instead of B, C, and D as Eqn. (1) in the virial expansion. From the form of Eqns. (2) and (3a–c) we identify B_{0ij} as second order in the density and C_{0ijk} as third order, etc. This expansion has a very limited range of application. Nevertheless, since EOS of the form of Eqn. (1) are loosely based on the virial expansion and there are so few guidelines for mixing, the mixing rules that have been suggested for BWR types of EOS (BENEDICT et al., 1942; BISHNOI and ROBINSON, 1972; STARLING and HAN, 1972) are similar to Eqns. (3), qualitatively maintaining consistency with the virial expansion.

The next question is the evaluation of the mixing parameters in the mixed system (as in Eqns. 3a–c). For low density gases in which the virial expansion holds, they are given in terms of integrals over the forces in the system. They may also be evaluated from experimental density data. For phenomenological expansions such as Eqn. (1), a theoretical definition of the coefficients does not exist. They must be evaluated from experimental data as in part I. This approach may be successful for pure systems in which there is often a lot of data. However, for mixtures it is generally not practical to evaluate all the parameters from data. For example, considering Eqn. (1), we see that it would require data for systems up to hexanary to define all the mixing coefficients of the form of those of Eqns. (3a–c). On the other hand, sufficient binary data are not available for many mixtures. Ternary data are almost nonexistent.

Given this situation there have been many considerable efforts to develop methods to estimate mixing parameters from pure system parameters. An early example is the mixing rule proposed by BENEDICT et al. (1942):

$$A = (\sum x_i A_i^{1/m})^m, \qquad (4)$$

with A representing one of the parameter B_0, C_0, D_0, etc. in the EOS and $m = 1, 2$, or 3, depending on the coefficient. If sufficiently accurate, an approach of this sort would be very effective, since only pure system data would be required to predict mixed system behavior. The predictions of the properties of mixtures of hydrocarbons using Eqn. (4) were satisfactory. However, some workers (e.g., CULLEN and KOBE, 1955) reported difficulties in predicting properties of systems containing non-hydrocarbons. Under the influence of PRAUSNITZ and SHIEH (1968), who introduced a binary adjustable interaction parameter for the mixing rule in the REDLICH and KWONG (1949, hereinafter RK) EOS, BISHNOI and ROBINSON (1972) proposed a mixing rule for the BENEDICT, WEBB, and RUBIN (1942; hereinafter BWR) EOS that incorporated a second order adjustable parameter, while evaluating the remaining parameters in the spirit of Eqn. (4). This rule improved the capability of predictions in dissimilar binary mixtures, such as light hydrocarbon-carbon dioxide systems. In order to predict vapor-liquid equilibria of non-hydrocarbons and compounds heavier than hexane, STARLING and HAN (1972) added three more parameters to the original BWR EOS and proposed a new mixing rule, which is similar to that of BISHNOI and ROBINSON (1972). This new modified EOS and mixing rule works for nonpolar mixtures to moderate pressures, but does not work for systems containing very polar components such as water.

More recently ANDERKO and PITZER (1991) introduced an additional third and fourth order adjustable parameters for mixing. The remaining parameters are calculated in the spirit of Eqn. (4) from the corresponding pure system parameters. Their approach satisfactorily describes binary mixing in the CH_4-H_2O system. We have adopted a similar approach and found similar results for the other binaries in this ternary.

In the mixing model, we adopt the highest adjustable parameter that may be evaluated in the ternary. The wide agreement of our EOS with the data seems to indicate that the second and third order adjustable parameters are important in developing an accurate EOS for mixtures. However, higher order parameters appear to play a lesser role, at least for the binaries in which there is enough data to test the accuracy of the mixing equations.

As a brief look at the references cited above shows, the evaluation of the parameters in mixing rules has been rather arbitrary. In our scheme we consider the coefficients as ordered by their density dependence as in the virial expansion. That is, B is a second order parameter, C is a third order parameter, D is a fifth order parameter, and so on. γ is taken to be a third order parameter despite the fact that it appears to all orders through the exponential. We evaluate most of the second order and third order parameters from experimental data. Higher order parameters are evaluated from endmember parameters as Eqn. (3a–c). The explicit equations giving the composition dependence of the coefficients are given in Table 1. For each binary in the ternary there is only one second order B_{ij} parameter, which is evaluated from

Table 1. Mixing Rule of Eq.(1)

$Bv_c = \Sigma\Sigma x_i x_j B_{ij} V_{cij}$	$B_{ij} = (B_i^{1/3} + B_j^{1/3})/2)^3 k_{1,ij}$ $k_{1,ij} = 1 \quad (\text{if } i=j)$ $V_{cij} = ((V_i^{1/3} + V_j^{1/3})/2)^3$
$CV_c^2 = \sum_{i}\sum_{j}\sum_{k} x_i x_j x_k C_{ijk} V_{c,ijk}^2$	$C_{ijk} = ((C_i^{1/3} + C_j^{1/3} + C_k^{1/3})/3)^3 k_{2,ijk}$ $k_{2,ijk} = 1 \quad (\text{if } i=j=k)$ $k_{2,iij} = k_{2,iji}$ $V_{cijk} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3})/3)^3$
$DV_c^4 = \sum_{i}\sum_{j}\sum_{k}\sum_{l}\sum_{m} x_i x_j x_k x_l x_m D_{ijklm} V_{cijklm}^4$	$D_{ijklm} = ((D_i^{1/3} + D_j^{1/3} + D_k^{1/3} + D_l^{1/3} + D_m^{1/3})/5)^3$ $V_{cijklm} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3} + V_{cl}^{1/3} + V_{cm}^{1/3})/5)^3$
$EV_c^5 = \sum_{i}\sum_{j}\sum_{k}\sum_{l}\sum_{m}\sum_{n} x_i x_j x_k x_l x_m x_n E_{ijklmn} V_{cijklmn}^5$	$E_{ijklmn} = ((E_i^{1/3} + E_j^{1/3} + E_k^{1/3} + E_l^{1/3} + E_m^{1/3} + E_n^{1/3})/6)^3$ $V_{cijklmn} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3} + V_{cl}^{1/3} + V_{cm}^{1/3} + V_{cn}^{1/3})/6)^3$
$FV_c^2 = \sum_{i}\sum_{j} x_i x_j F_{ij} V_{cij}^2$	$F_{ij} = ((F_i^{1/3} + F_j^{1/3})/2)^3$ $V_{cij} = ((V_{ci}^{1/3} + V_{cj}^{1/3})/2)^3$
$\beta = \sum_{i} x_i \beta_i$	
$\gamma V_c^2 = \sum_{i}\sum_{j}\sum_{k} x_i x_j x_k \gamma_{ijk} V_{cijk}^2$	$\gamma_{ijk} = ((\gamma_i^{1/3} + \gamma_j^{1/3} + \gamma_k^{1/3})/3)^3 k_{3,ijk}$ $k_{3,ijk} = 1 \quad (\text{if } i=j=k)$ $k_{3,iij} = k_{3,iji}$ $V_{cijk} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3})/3)^3$

experimental data. For a binary there are two third order parameters corresponding to $x_i^2 x_j$ and $x_j^2 x_i$ products. These terms are scaled by a Lorentze combination (termed by BENEDICT et al., 1942) of the Cs and γs, giving for the $x_i^2 x_j$ term, for example,

$$C_{iij} = ((2C_i^{1/3} + C_j^{1/3})/3)^3 \times k_{2,iij}, \qquad (5)$$

where $k_{2,iij}$ is an adjustable third order binary parameter. A similar term gives C_{jji} as proportional to $k_{2,jji}$. In our work we found it sufficiently accurate to assume

$$k_{2,jji} = k_{2,iij}. \qquad (6)$$

These may be evaluated once and for all from binary data. γ is treated in the same way as C. The evaluation of these parameters for each binary will be discussed in the following sections. There are two additional third order terms in a ternary system

$$C_{ijk} = ((C_i^{1/3} + C_j^{1/3} + C_k^{1/3})/3)^3 \times k_{2,ijk}, \quad \text{when } i \neq j \neq k. \qquad (7a)$$

$$\gamma_{ijk} = ((\gamma_i^{1/3} + \gamma_j^{1/3} + \gamma_k^{1/3})/3)^3 \times k_{2,ijk}, \quad \text{when } i \neq j \neq k. \qquad (7b)$$

These terms represent mixing in the ternary and must be evaluated from data inside the ternary. This will be discussed in Section VI.

A large part of our interest in EOS stems from our desire to calculate phase equilibria. In order to do this we need the partial fugacity coefficients (chemical potentials) for the species in the mixed phases. They can be derived from Eqn. (1) using the relation (WALAS, 1985)

$$RT \ln \phi_i = \int_V^\infty \left(\frac{\partial P}{\partial n_i} - \frac{RT}{nV} \right) d(nV) - RT \ln (Z), \qquad (8)$$

where n is the total number of moles in the mixture. This gives

$$\begin{aligned}
\ln \phi_i = {} & -\ln (Z) + \frac{B'}{V} + \frac{C'}{2V^2} + \frac{D'}{4V^4} + \frac{E'}{5V^5} \\
& + \frac{F'\beta + \beta' F V_c^2}{2\gamma V_c^2} \left(1 - \exp\left(-\frac{\gamma V_c^2}{V^2} \right) \right) \\
& + \frac{F'\gamma V_c^2 + \gamma' F V_c^2 - F V_c^2 \beta(\gamma' - \gamma V_c^2)}{2(\gamma V_c^2)^2} \\
& \times \left(1 - \left(\frac{\gamma V_c^2}{V^2} + 1 \right) \exp\left(-\frac{\gamma V_c^2}{V^2} \right) \right) \\
& - \frac{(\gamma' - \gamma V_c^2) F V_c^2}{2(\gamma V_c)^2} \\
& \times \left(2 - \left(\frac{(\gamma V_c^2)^2}{V^4} + \frac{2\gamma V_c^2}{V^2} + 2 \right) \exp\left(-\frac{\gamma V_c^2}{V^2} \right) \right). \qquad (9)
\end{aligned}$$

FV_c^2, β and γV_c^2 are listed in Table 1, and B', C', D', E', F', β', and γ' are derivatives listed in Table 2.

Table 2. Derivatives in Eq. (9)

$B' = 2\Sigma x_j B_{ij} V_{cij}$	$B_{ij} = (B_i^{1/3} + B_j^{1/3})/2)^3 k_{1,ij}$ $k_{1,ij} = 1$ (if i = j) $V_{cij} = ((V_i^{1/3} + V_j^{1/3})/2)^3$
$C' = 3\sum_j\sum_k x_j x_k C_{ijk} V_{c,ijk}^2$	$C_{ijk} = ((C_i^{1/3} + C_j^{1/3} + C_k^{1/3})/3)^3 k_{2,ijk}$ $k_{2,ijk} = 1$ (if i=j=k) $k_{2,iij} = k_{2,jji}$ $V_{cijk} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3})/3)^3$
$D' = 5\sum_j\sum_k\sum_l\sum_m x_j x_k x_l x_m D_{ijklm} V_{cijklm}^4$	$D_{ijklm} = ((D_i^{1/3} + D_j^{1/3} + D_k^{1/3} + D_l^{1/3} + D_m^{1/3})/5)^3$ $V_{cijklm} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3} + V_{cl}^{1/3} + V_{cm}^{1/3})/5)^3$
$E' = 6\sum_j\sum_k\sum_l\sum_m\sum_n x_j x_k x_l x_m x_n E_{ijklmn} V_{cijklm}^5$	$E_{ijklmn} = ((E_i^{1/3} + E_j^{1/3} + E_k^{1/3} + E_l^{1/3} + E_m^{1/3} + E_n^{1/3})/6)^3$ $V_{cijklmn} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3} + V_{cl}^{1/3} + V_{cm}^{1/3} + V_{cn}^{1/3})/6)^3$
$F' = 2\sum_j x_j F_{ij} V_{cij}^2$	$F_{ij} = ((F_i^{1/3} + F_j^{1/3})/2)^3$ $V_{cij} = ((V_{ci}^{1/3} + V_{cj}^{1/3})/2)^3$
$\beta' = \beta_i$	
$\gamma' = 3\sum_j\sum_k x_j x_k \gamma_{ijk} V_{cijk}^2$	$\gamma_{ijk} = ((\gamma_i^{1/3} + \gamma_j^{1/3} + \gamma_k^{1/3})/3)^3 k_{3,ijk}$ $k_{3,ijk} = 1$ (if i=j=k) $k_{3,iij} = k_{3,jji}$ $V_{cijk} = ((V_{ci}^{1/3} + V_{cj}^{1/3} + V_{ck}^{1/3})/3)^3$

In order to calculate $\ln \phi_i$, we need to calculate V. Substituting the mixing rule of Table 1 into Eqn. (1), V at a given temperature and pressure can be found by trial-and-error or an iterative method as discussed in part I. With molar volume determined, it is possible to calculate free energy of the system. Partial fugacity coefficient, partial fugacity, and chemical potential are defined by

$$\begin{aligned}
\mu_i(T, P, X) &= \mu_i^0(T) + RT \ln f_i(T, P, X) \\
&= \mu_i^0(T) + RT \ln \phi_i(T, P, X) x_i P. \qquad (10)
\end{aligned}$$

The standard chemical potential of species i is the chemical potential at 1 bar fugacity.

Once the chemical potentials of components are defined, the total free energy is calculated by

$$G = \sum_j^m \sum_i^n n_{ij} \mu_{ij}, \qquad (11)$$

where m is the number of phases, n_{ij} is mole number of species i in phase j. Two approaches were used to calculate vapor-liquid equilibria. The minimum condition of the free energy gives the following equation relating the chemical potentials of the species in phase α and β:

$$\phi_i^\alpha x_i^\alpha = \phi_i^\beta x_i^\beta. \qquad (12)$$

Because of the nonlinearity of the problem this method is difficult to implement for ternary and more complicated systems. Therefore, we minimized the free energy directly.

III. CO$_2$-H$_2$O

Fluids in a variety of terranes including medium- and high-grade metamorphic environments, epithermal, and lode-type gold deposits, hydrothermal wolframite deposits and several geothermal systems fall approximately into this binary (ROEDDER, 1984; RAMBOZ et al., 1985). Because of its importance, much experimental work including PVTX (density) measurements and phase equilibrium measurements (solvus) has been reported. This is also a very nonideal system with a critical point in the water endmember well above the temperature of many applications. The data we used in the parameter evaluation are listed in Table 3. Phase coexistence data have been reported by MALININ (1959), TODHEIDE and FRANCK (1963), and TAKENOUCHI and KENNEDY (1964). The most comprehensive work is that by TODHEIDE and FRANCK (1963). All these measurements are in close agree-

Table 3. PTVX and Solvus Data

System	Authors	Temperature (°C)	P(bar)	type of data	# of measurements
$CO_2 + H_2O$	Franck et al.	400-750	300-2000	PVTX	298
	Greenwood	450-800	0-500	PVTX	870
	Gehrig	400-500	100-600	TPVX	198
	Shmulovichi et al.	400-500	1000-5000	PVTX	46
	Zakirov	300-400	50-1800	PVTX	121
	Sterner at al	400-700	2000-6000	PVTX	107
	Malinin	200-330	100-600	solvus	26
	Todheide et al.	50-350	200-3500	solvus	110
	Taketouchi et al.	110-350	100-1500	solvus	116
$CH_4 + CO_2$	Reamer et al.	38-238	0-680	PVTX	700
	Mraw et al.	-54 to -120	5 to 64	solvus	55
	Davis et al.	-25 to -140	0.3 to 48	solvus	37
	Donnelly et al.	-1.7 to -43	12 to 78	solvus	94
	Arai et al.	-20 to 15	24 to 145	solvus and PVTX	181
	Seitz et al.	100	100 to 1000	PVTX	-
$CH_4 + H_2O$	Joffrion-Eubank	125-225	0-110	PVTX	169
	Culberson et al.	25-171	20-680	solubility	71
	Price	154-354	16-1900	solubility	71
	Blount et al.	100-250	100-1560	solubility	642
	Olds et al.	38-238	30-680	dew point	81
	Sultanov et al.	150-360	50-1000	solvus	76
	Welsch	160-425	200-3000	solvus and PVTX	-

ment on the H_2O rich liquid side. However, the reported compositions of the coexisting vapor phase differ by as much as 16 mole%, TAKENOUCHI and KENNEDY (1964) reporting higher H_2O content. The data of MALININ (1959) are in close agreement with that of TODHEIDE and FRANCK (1963) on both H_2O and CO_2 rich sides. The PVTX data reported by FRANCK and TODHEIDE (1959), GREENWOOD (1969), GEHRIG (1980), SHMULOVICH et al. (1980b), ZAKIROV (1984), and STERNER and BODNAR (1991) cover a range of temperature from 300 to 800°C and pressure from 50 to 6000 bar. Most of the reported PVTX data agree within about 5%, except those reported by FRANCK and TODHEIDE (1959) which has a 5–20% higher density than the data of ZAKIROV (1984). There are no density data below 300°C.

Several EOS have been developed to predict the properties of this system in the supercritical regions (HOLLOWAY, 1976; KERRICK and JACOBS (1981, hereinafter KJ); and BOWERS and HELGESON (1983, hereinafter BH). All these equations are modifications of the RK EOS. They used PVT data to establish the endmember EOS and a parameter free mixing rule to generalize to mixtures. These EOS are not sufficiently accurate to treat phase equilibria and density below the critical point of water.

All the data listed in Table 3 were used to evaluate the binary mixing parameters $k_{1,CO_2\text{-}H_2O}$, $k_{2,CO_2\text{-}CO_2\text{-}H_2O}$, and $k_{3,CO_2\text{-}CO_2\text{-}H_2O}$. Our original intention was to use the PVTX data alone to establish the EOS and then to use this equation to predict phase equilibria. An example of the result of this first effort are given by the dashed line in Fig. 1 and was unsatisfactory. Apparently density data alone won't produce a model that accurately predicts two phase equilibria, because small errors in the volume may lead to very large errors in the solvus. This appears to be true even for temperature and pressure ranges in which there are considerable density data close to the solvus pressure. This situation is similar to that which we have encountered in aqueous phase modeling. In that case it was necessary to include solubility data in the data base in order to make reliable predictions of phase coexistence (WEARE, 1987).

As indicated in Table 3, 300°C is the only temperature at which both PVTX and solvus data exist for this subsystem. Below this temperature only solvus data are available. In order to ascertain whether the solvus data alone are sufficient to establish the mixing parameters, we used this data alone in a parameterization at 300°C. The resulting parameters were then used to predict liquid-vapor equilibrium (solid line of Fig. 1) and the volumetric properties (Fig. 2). The results are remarkably good. This suggests that the lack of PVTX data below 300°C may be effectively replaced by solvus data.

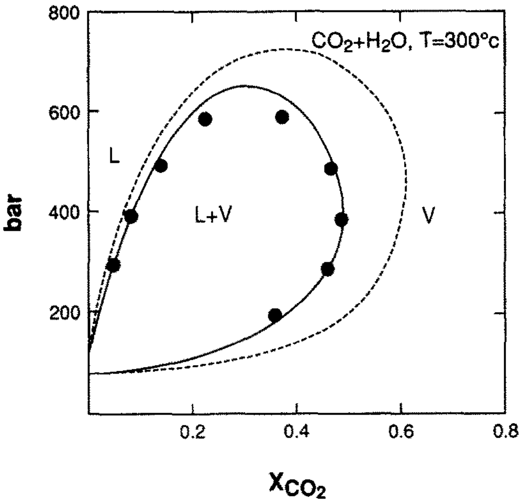

FIG. 1. Two phase coexistence in the CO_2-H_2O system at 300°C. The solid line is obtained by fitting solvus data, while the dashed line was obtained by fitting PVTX data.

In order to use phase equilibrium data, the chemical potentials of the components in both gas phase and liquid phase were calculated from the EOS as described by Eqns. (9) and (10). At a given temperature, parameters $k_{1,CO_2\text{-}H_2O}$, $k_{2,CO_2\text{-}CO_2\text{-}H_2O}$, and $k_{3,CO_2\text{-}CO_2\text{-}H_2O}$ were adjusted until the chemical potential differences of species in the coexisting phases were as small as possible. These parameters were then fitted to temperature dependent formulae shown in Table 4 using a linear least-square method. The phase composition is very sensitive to the parameter values below about 200°C. It is very difficult to fit the parameters to a single formula. There-

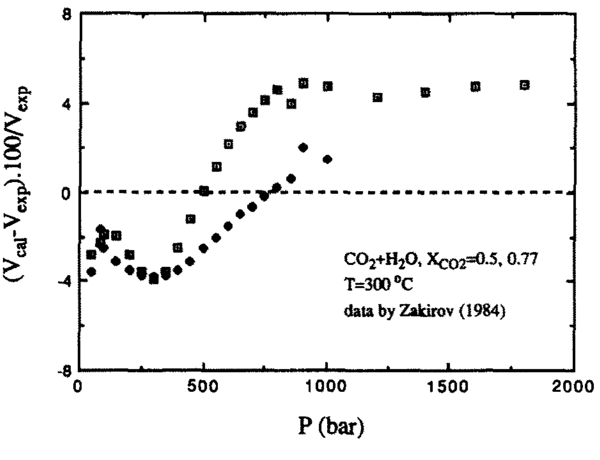

FIG. 2. Comparison of experimental molar volume with the predictions of the EOS of this study at 300°C.

Table 4. The Binary Interaction Parameters of CO_2–H_2O

50-100°C	$k_1 = 0.20611 + 0.0006\,T$ $k_2 = 0.8023278 - 0.0022206\,T + 184.76824/T$ $k_3 = 1.80544 - 0.0032605\,T$
100-222°C	$k_1 = -10084.5042 - 4.27134485\,T + 256477.783/T$ $+ 0.00166997474T^2 + 1816.78 \ln T$ $k_2 = 9.000263 - 0.00623494\,T - 2307.7125/T$ $k_3 = -74.1163 + 0.1800496\,T - 1.40904946\text{e-}04\,T^2 + 10130.5246/T$
222-350°C	$k_1 = -0.3568 + 7.8888\text{e-}04\,T + 333.399/T$ $k_2 = -19.97444 + 0.0192515\,T + 5707.4229/T$ $k_3 = 12.1308 - 0.0099489\,T - 3042.09583/T$
350-1000°C	$k_1 = -4.53122 + 0.0042113\,T + 1619.7/T$ $k_2 = -163.4855 + 0.190552\,T - 7.228514\text{e-}05\,T^2 + 46082.885/T$ $k_3 = 1.7137 - 6.7136\text{e-}04\,T$

fore, we use continuous switching fitting functions across temperatures 100, 222, and 350°C as shown in Table 4.

Figure 3 compares the predictions of our EOS with the experimental phase equilibria data of TODHEIDE and FRANCK (1963). T-X_{CO_2} diagrams, which are useful in interpreting mineral relations in terms of compositions of coexisting fluids (TROMMSDORFF, 1966; GREENWOOD, 1967; and SKIPPEN, 1971, 1974) can be directly obtained from Fig. 3. This will be discussed in more detail in Section VII.

Although the mixing parameters were evaluated solely from phase equilibrium data for temperatures below 374°C, other thermodynamic quantities, for example, molar volume (Fig. 2) and excess volume, are accurately predicted. Figures 4a, b, c, and d show that this EOS can predict the density or molar volume within an error of 7%, which is close or within experimental uncertainty.

It can be seen from Fig. 5 that the excess volume ($V_{ex} = V^M - \sum x_i V_i^{pure}$), a property representing nonideal behavior, becomes increasingly large with decreasing temperature. At 200 and 300°C the excess molar volume of mixing can be as high as 1000 cm^3/mol and 220 cm^3/mol, respectively, more than half of the total volume of the mixture. Above the critical temperature of water (374°C), the excess volumes of mixtures are much smaller. Therefore, the mixing behavior is easier to describe than in the subcritical region, as we have discussed in part I. Below 374°C the maximum excess volume occurs near the saturation pressure of pure water at the corresponding temperature. Our predictions can be compared to data at 300°C (ZAKIROV, 1984). The agreement is remarkable. In most cases excess volume is positive, though a small negative volume may occur below 300°C between 200–400 bar. As an indication of the effect of nonideal mixing, Fig. 6 shows that activity of CO_2 or H_2O at 300°C and 500 bar is poorly predicted by ideal mixing, while at 700°C and the same pressure ideal mixing works well as discussed in Part I.

When the temperature goes below 20°C, clathrates may occur (SEIZE and PASTERIS, 1990). This EOS has not been parameterized to treat such situations and should not be used for temperature below 50°C.

IV. CH_4-CO_2

Geological fluids consisting primarily of CH_4 and CO_2 occur widely in geopressured geothermal systems (CAPUANO, 1990; PRICE, 1981). They have also been found in metamorphic terranes (VAN DEN KERKHOF, 1988a,b). PVTX (density) data were reported by ARAI et al. (1971), SEITZ et al. (1991), and REAMER et al. (1944) from 0 to 238° and from 0 to 1000 bar. Solvus (phase equilibrium) data were reported by DAVIS et al. (1962), ARAI et al. (1971), and MRAW et al. (1978) from −120 to 15°C. There is no PVTX data below 0°C. All the data used for this binary are listed in Table 3. The data above −2°C were used to find mixing parameters. Results are listed in Table 5.

Many EOS for this system have been published (SOAVE, 1972; PENG and ROBINSON (hereinafter PR), 1976; HEYEN, RAMBOZ, and DUBESSY (hereinafter HRD), 1982; JACOB and KERRICK (hereinafter JK), (1981b). HERSKOWITZ (1984) reviewed the EOS by SOAVE (1972), PR, and HRD, comparing their predictions with the data of ARAI et al. (1971) and ANGUS et al. (1976). All three can predict the solubility of CO_2 in CH_4 within 10% of the experimental values in the vapor phase. However, the PR EOS and the HRD EOS give poor predictions of molar volumes in the CH_4-rich phase. The Soave EOS gives poor molar volumes in the CO_2-rich side. We compared the JK EOS with the experimental data of REAMER et al. (1944) and found that although it can predict molar volume properties above 195°C with fairly good accuracy for this binary, it is inapplicable below 195°C. The HRD EOS gives poor results at high pressures because it is only suitable for low pressure data.

Though only solvus data were used in the parameterization below 30°C, volume properties in and around the two phase region (31°C) are predicted close to experimental error (Fig. 7). Above the critical region ($T > 31$°C), where mixing be-

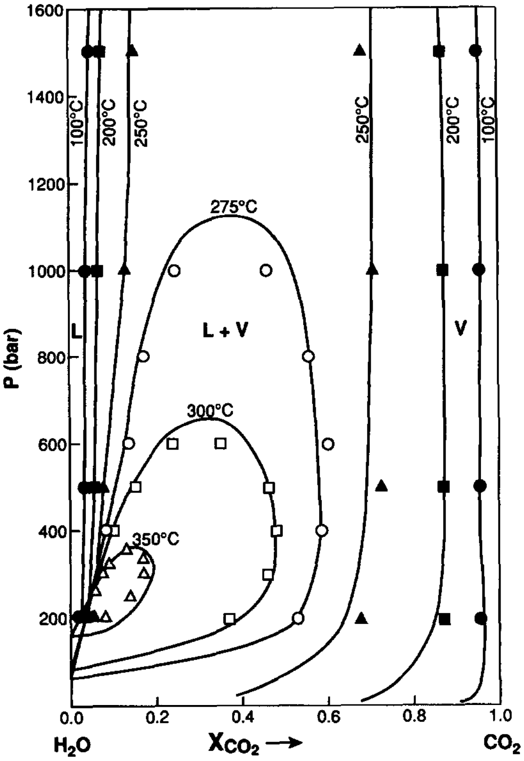

FIG. 3. Phase equilibria for the system CO_2-H_2O. The solid line is the prediction of this EOS, the symbols are experimental data of TODHEIDE and FRANCK (1963) at different temperatures.

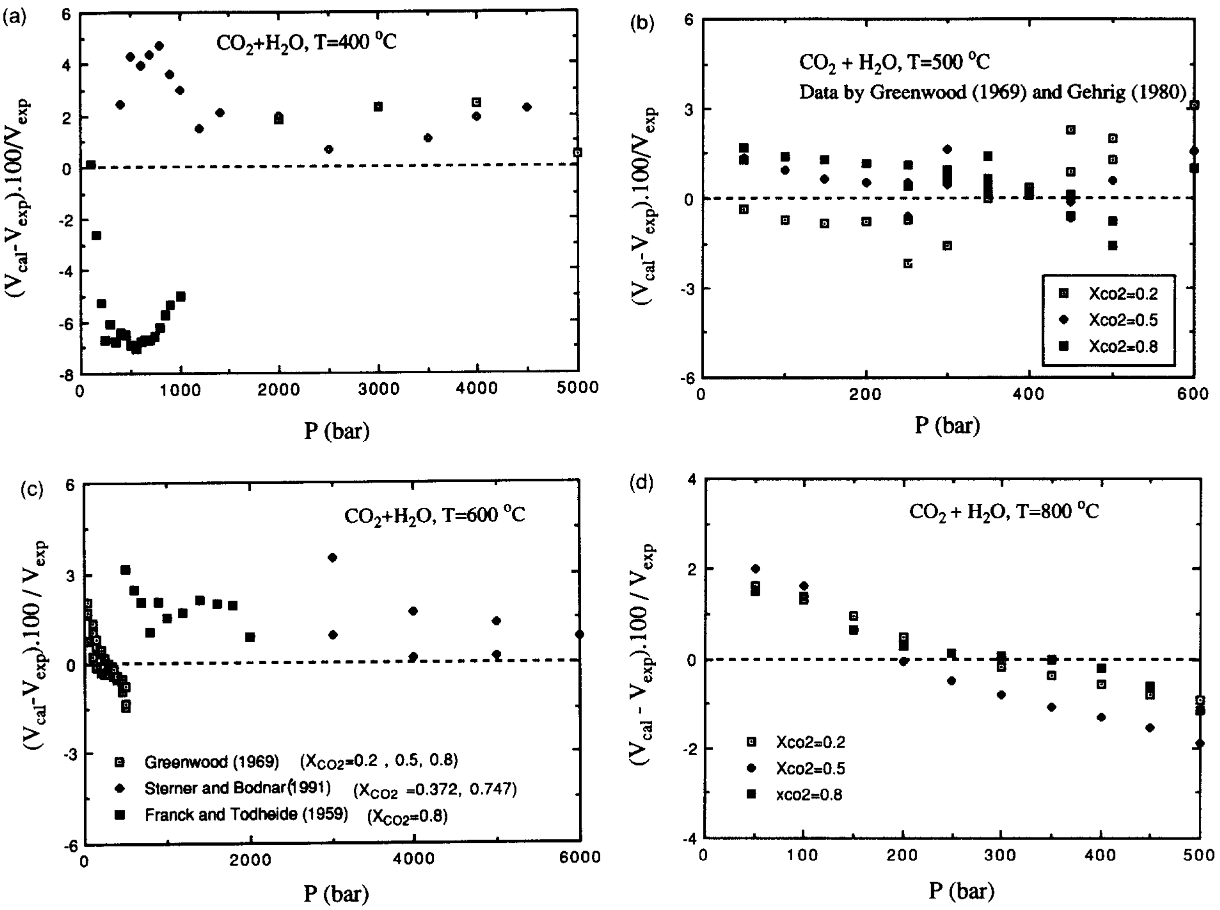

FIG 4. Comparison of experimental molar volume with the predictions of the EOS of this study at 400, 500, 600, and 800°C, respectively. Symbols for (a): □, STERNER and BODNER (1991; X_{CO_2} = 10,496); ◆, FRANCK and TODHEIDE (1959; X_{CO_2} = 0.6); ■, ZAKIROV (1984; X_{CO_2} = 0.6; ◆, SHMULNOVICH et al. (1980a,b; X_{CO_2} = 0.6).

comes more ideal, the volume properties (compressibility factor, density, molar volume) are predicted accurately as demonstrated in Fig. 8. The partial fugacity coefficients of CH_4 and CO_2 in system 90% CH_4 + 10% CO_2 under certain *T-P* conditions are listed in Table 6. The compositions listed in this table are typical of the compositions of the gas phases associated with geothermal fluids. The predictions of phase equilibrium are shown in Fig. 9. It is very difficult to predict phase behavior around the critical region.

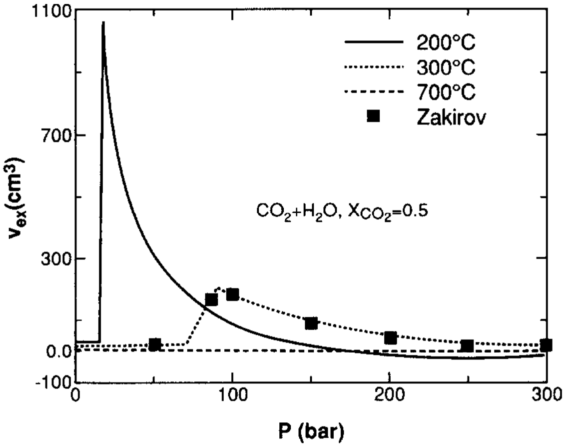

FIG. 5. Excess volume of mixing of the system CO_2-H_2O.

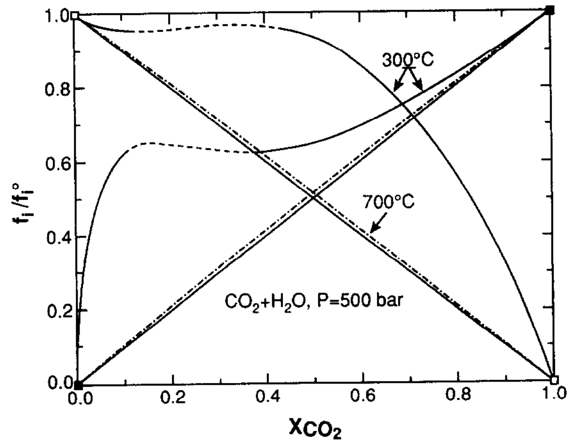

FIG. 6. The activity of CO_2 and H_2O in their mixtures at 300 and 700°C. The dashed-line shows two phase region. The diagonal solid line represents ideal mixing.

Table 5. The Binary Interaction Parameters of CH_4–CO_2

0-31°C	$k_1 = 0.38$ $k_2 = 1.74094 - 0.0058903\,T$ $k_3 = 1.59$
31-225°C	$k_1 = 1.1$ $k_2 = 3.211 - 0.00158\,T - 537.814/T$ $k_3 = -0.7$
225 -1000 °C	$k_1 = 1.0$ $k_2 = 1.0$ $k_3 = 1.0$

The excess molar volume of a mixture of 40.8% CH_4 + 59.2% CO_2 was calculated at 0, 38, and 104°C (Fig. 10). Below 40°C, the excess molar volume can be over 200 cm^3/mol, accounting for almost half of the total molar volume. However, when temperature reaches 100°C, the excess molar volume is only a few cubic centimeters. For temperatures above 100°C mixing should be close to ideal. This is illustrated by Fig. 11, which indicates that for 35°C and 200 bar, the fugacity of CH_4 or CO_2 is larger than that calculated from ideal mixing, while at 200°C and the same pressure ideal mixing works well.

There are very little high temperature data. However, assuming that the binary interaction parameters are equal to 1, the volumes of the mixtures at 238°C are well predicted as shown in Fig. 12. We expect this to remain true at high temperatures, since mixing becomes more ideal. Therefore, we believe that the range of this EOS for this binary system is approximately from 0 to 1000°C and from 0 to 1000 bar or higher, with an accuracy close to that of the experiments. If pressure is above the critical pressure for temperature below 31°C, errors increase to 8%.

V. CH_4-H_2O

CH_4 and H_2O are the major constituents of many geological fluids (e.g., in tectonic melanges, VROLIJK et al., 1988; and in some geothermal systems, OSIF, 1985, and KHARAKA et al., 1985). The question of whether or not sandstone porewaters are saturated with methane is of importance to the exploitation of geopressured resources (PRICE, 1981). Different approaches have been used to calculate density, excess volume, phase equilibria, and the solubility of methane in water. PRICE (1981) and BARTA and BRADLEY (1985) presented empirical and semi-empirical models parameterized from the solubility of methane in water. JACOBS and KERRICK (1981a) developed an EOS using a modified RK EOS. SHMULOVICH et al. (1980a) used the Lennard-Jones molecular interaction potential with some temperature dependent parameters to calculate the excess volume of mixing above 380°C and up to 1000 bar, giving results in good agreement with observed PVT data. None of these models can predict phase equilibria with reasonable accuracy. ANDERKO (1991) developed an EOS incorporating association that can predict phase equilibria of this binary system up to 207 bar. Most recently ANDERKO and PITZER (1991) proposed an EOS which can predict phase equilibrium and volume of this binary close to the experimental accuracy.

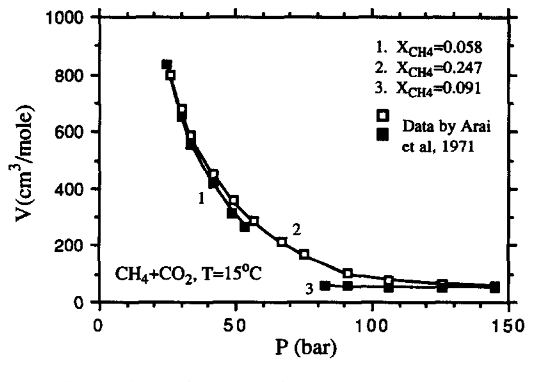

FIG. 7. Comparison of the experimental molar volume with predictions in the system CH_4-CO_2.

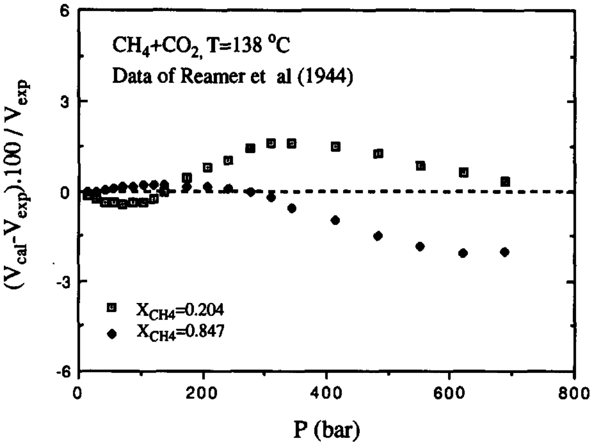

FIG. 8. Comparison of experimental molar volume with predictions in the system CH_4-CO_2.

There are a large number of measurements of the solubility of methane, but few measurements of density. The density data we found are below 130 bar. The solvus data have been reported by OLDS et al. (1942), SULTANOV and SKRIPKA (1971, 1972), and WELSCH (1973). The data set WELSCH (1973) contains phase information from 160 to 360°C and from 0 to 3000 bar. Most of his solvus lines agree with the data of SULTANOV et al. (1971, 1972) within an uncertainty of 4 mol%. At 300°C the deviation is as large as 10 mol%. The data in Table 3 except WELSCH (1973) were used to determine the binary interaction parameters, which are reported in Table 7. We use the data of WELSCH (1973) to check the predictability at high pressures where no data participated in the parameterization. As in the CO_2-H_2O system, phase compositions are very sensitive to the change of parameters. Switching functions are used across 90, 240, and 374°C.

After the mixing parameters are determined, volumetric properties (density, molar volume, compressibility factor),

Table 6 The Partial Fugacity Coefficients of CH_4 and CO_2 in the System 90%CH_4 +10%CO_2

pressure(bar)	CH_4(100°C)	CO_2(100°C)	CH_4(200°C)	CO_2(200°C)
100	0.9444	0.8077	0.9961	0.9420
200	0.9103	0.6832	1.0023	0.9094
300	0.8995	0.6125	1.0188	0.8968
400	0.9089	0.5764	1.0455	0.8988
500	0.9345	0.5609	1.0817	0.9113
600	0.9732	0.5579	1.1267	0.9317
700	1.0232	0.5629	1.1800	0.9582
800	1.0838	0.5733	1.2412	0.9898

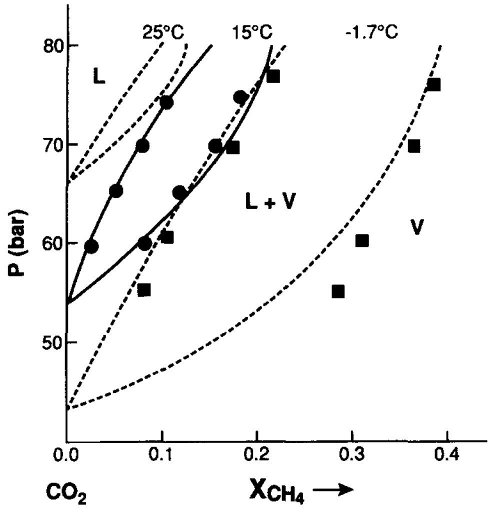

FIG. 9. Prediction of phase equilibria of the system CH_4-CO_2. Solid cycles are the data of DONNELLY and KATZ (1954) and the solid square are the data of ARAI et al. (1971).

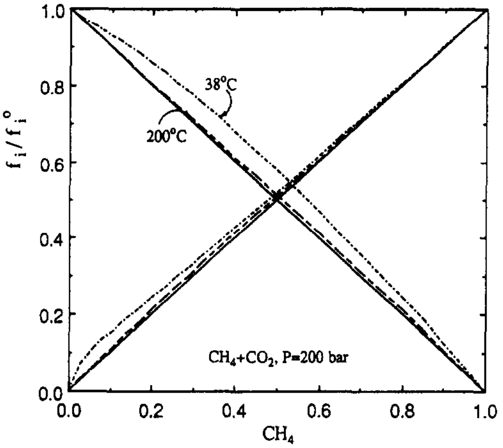

FIG. 11. The activity of CH_4 and CO_2 in their mixtures at 38 and 200°C, at 200 bar. The solid line is ideal mixing prediction.

fugacity coefficients, and phase equilibria can be calculated. The phase composition on the liquid side and vapor side are shown in Fig. 13a,b, respectively. It can be seen that the predictions are within experimental error. It is remarkable that our EOS can predict the phase equilibrium well above 1000 bar (see Fig. 14), where no data were used in the parameterization. Figure 15a,b indicate very good agreement with density observations.

CH_4 hydrates may appear in the low temperature range. According to the calculations of SEITZ and PASTERIS (1990) based on the model by JOHN et al. (1985), the CH_4 clathrate association/dissociation curve goes through 10°C at 60 bar, and 20°C at 200 bar. The volumetric and phase behavior becomes more complicated in the presence of clathrate. This is beyond the capabilities of the present model. Therefore, we don't recommend its use below 38°C. We believe that it can predict volumetric properties throughout the temperature range from 50 to 1000°C with errors less than 5%. This conclusion is supported by comparison with the excess volume data of BAZAYEV et al. (1974) at 380°C (Fig. 16).

VI. CALCULATION INSIDE THE TERNARY SYSTEM

Although many geological fluids consist of two dominant constituents with a third at relatively low concentration (VAN DEN KERKHOF, 1990), it may be necessary to include the minor species in accurate calculations (e.g., to calculate the shift in the homogenization temperature due to the addition of the third constituent). Unfortunately there are very little ternary data to evaluate the ternary third order parameters $k_{2,CH_4-CO_2-H_2O}$ and $k_{3,CH_4-CO_2-H_2O}$. To estimate the sensitivity of the model, we tentatively set $k_{2,CH_4-CO_2-H_2O} = 1$, and $k_{3,CH_4-CO_2-H_2O} = 0$. The predicted ternary phase diagram at 200°C and 500 bar is illustrated in Fig. 17. The results agree qualitatively with the observations. For example, JACOBS and KERRICK (1981a) pointed out that the presence of 20% CH_4 significantly decreases the activity coefficient of CO_2 relative to its value in the binary CO_2-H_2O system, but has little influence on the activity of water. Our EOS agrees with this

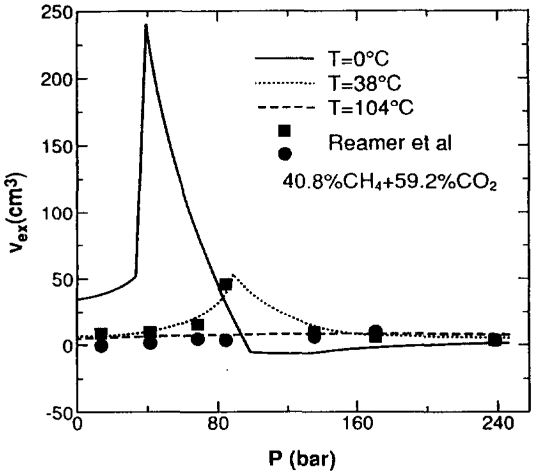

FIG. 10. Excess volume of mixing of the system CH_4-CO_2.

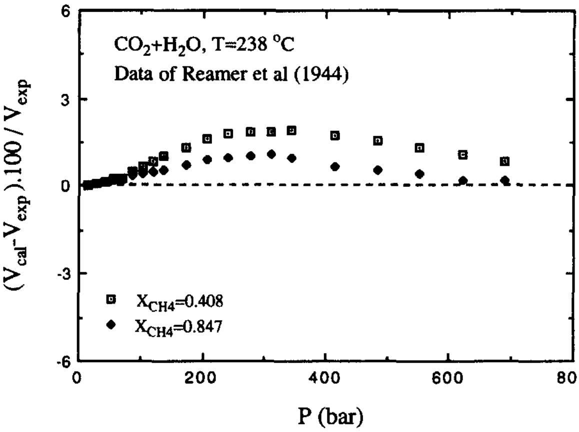

FIG. 12. Comparison of experimental molar volume with predictions of this EOS in the system CH_4-CO_2, assuming $k_{1,CH_4-CH_4-CO_2} = 1$, $k_{2,CH_4-CH_4-CO_2} = 1$, and $k_{3,CH_4-CH_4-CO_2} = 1$.

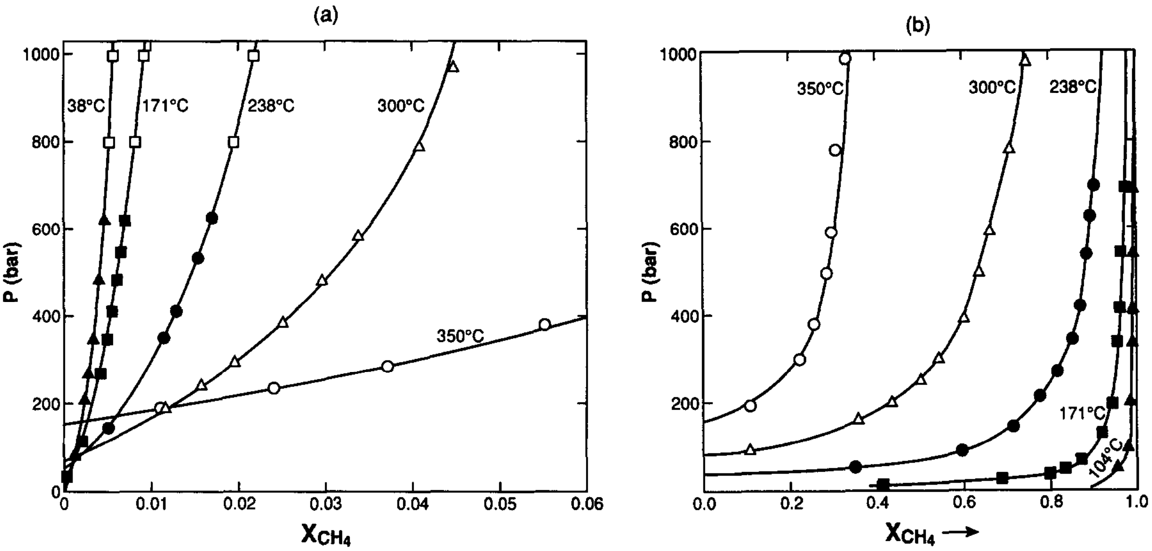

FIG. 13. (a) Prediction of phase equilibrium of the system CH_4-H_2O on the liquid side; the open square marks are from the model of DUAN et al. (1992). The data above 238°C are from SULTANOV and SKRIPKA (1971, 1972), and those at and below 238°C are from CULBERSON and MCKETTA (1952). (b) Prediction of phase equilibria of the system CH_4-H_2O on the vapor side. The data on vapor side are from SULTANOV and SKRIPKA (1971) and OLDS et al. (1942).

phenomenon. This effect becomes more important with increasing water content. The presence of CO_2 also decreases the activity coefficient of CH_4 relative to its value in the CH_4-H_2O system at high temperatures. However, at low temperatures ($< \approx 200°C$), adding a little CO_2 into liquid substantially increases the activity of CH_4 and decreases its solubility. This behavior is illustrated in Fig. 18. PRICE (1981) reported measurements of the solubility of CH_4 and CO_2 in brine containing 5 wt% NaCl at 150°C and 345 bar. The presence 5 wt% NaCl in water decreases the solubility of CH_4 and CO_2 by about 15%. If we assume this to be a linear effect, this shift will be uniform as a function of composition for the fixed NaCl concentration. Therefore 15% was deducted from our calculated result. They are compared to Price's solubilities as the dashed line in Fig. 18. Even though no ternary data were used in establishing the model, this EOS is able to predict ternary properties qualitatively. If we adjust $k_{2,CH_4\text{-}CO_2\text{-}H_2O}$ to a value of 4.2, the solubility can be precisely predicted as indicated by the solid line of Fig. 18. It can be seen that CO_2 can dramatically decrease the solubility of CH_4. In order to completely define the mixing rule and obtain accurate quantitative prediction of ternary phase equilibrium, ternary mixture data is necessary.

Table 7. The Binary Interaction Parameters of CH_4–H_2O

38-90°C	$k_1 = -0.108948 + 0.00035\ T$ $k_2 = 72992.5023 + 41.0912234\ T - 2.0488391e\text{-}02\ T^2 - 1532639.28/T - 13739.4496\ \ln(T)$ $k_3 = 16.6726 - 0.0215979\ T - 2845.934/T$
90-240°C	$k_1 = -0.108948 + 0.00035\ T$ $k_2 = -36.3512 + 0.08256278\ T - 6.175e\text{-}05\ T^2 + 5515.0249/T$ $k_3 = 0.5038515 + 0.00102381\ T$
240-374°C	$k_1 = -288.48617 + 0.293374\ T + 71329.6552/T$ $k_2 = -10.7536 + 0.0135537\ T + 2171.139/T$ $k_3 = -0.0559 + 1.63397258e\text{-}03\ T$
374-1000°C	$k_1 = 42.1575 - 0.05\ T$ $k_2 = 1$ $k_3 = 1$

VII. APPLICATION TO THE STUDY OF FLUID INCLUSIONS

The study of fluid inclusion has contributed to the interpretation of rock evolution in many areas (e.g., RAMBOZ et al., 1985; DUBESSY, 1989; HALL and BODNER, 1990; LIRA and RIPLEY, 1990). Microthermometry, Raman microprobe, and gas chromatography have made it possible to analyze

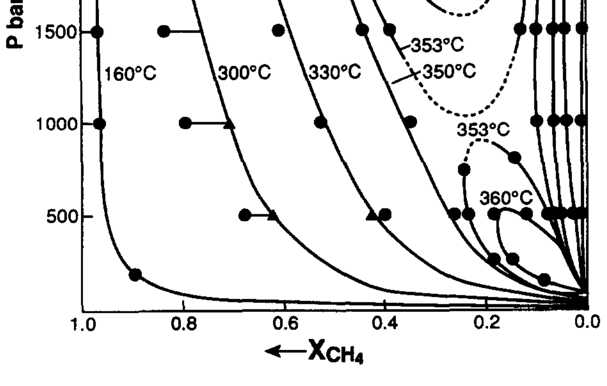

FIG. 14. Phase diagram of the system CH_4-H_2O, the solid line is the prediction of our EOS, the solid cycles are the data from WELSCH (1973) and the solid triangles are the data by SULTANOV and SKRIPKA (1971).

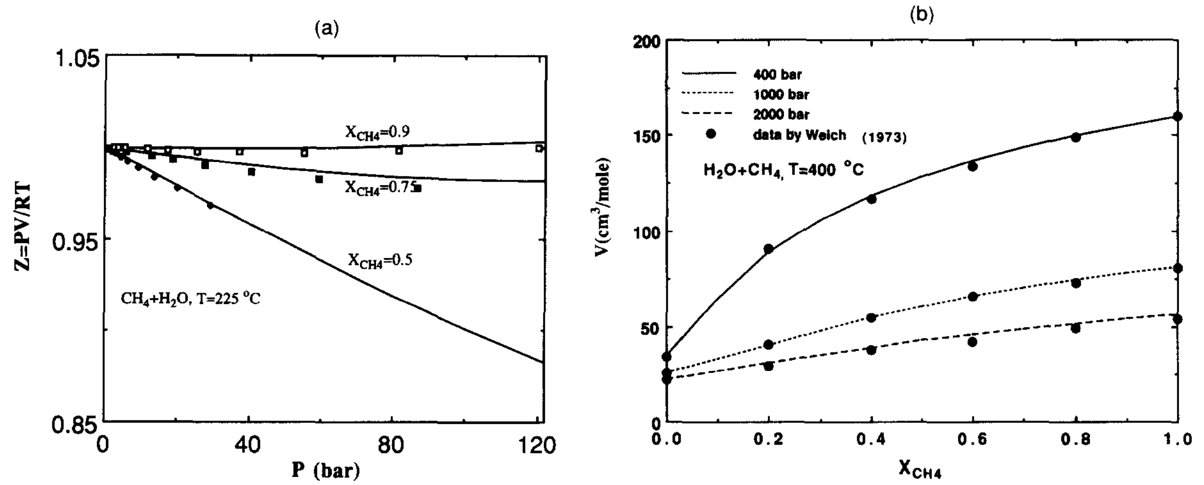

FIG. 15. Comparison of the experimental volumetric properties of the mixture CH_4-H_2O with predictions. (a) Data of JOFFRION and EUBANK (1989) and (b) data of WELSCH (1973).

the homogenization temperature, melting temperature, and composition of the fluids trapped in crystals. The molar volume and trapping pressure are important quantities to be determined and can be calculated from the homogenization temperature and the composition using the proper phase diagrams. Some diagrams for the pure gases CO_2, CH_4, and N_2 and for the binary systems CO_2-CH_4 and CO_2-N_2 are available (SWANEBERG, 1980; HOLLISTER and CRAWFORD, 1981; ROEDDER, 1984; VAN DEN KERKHOF, 1990). However, these diagrams are far from including all the binary compositions over all *T-P* conditions of interest. There are no diagrams for composition inside this ternary. The EOS that we have developed can calculate binary diagrams in the system CH_4-CO_2-H_2O for temperatures above 50°C. Although we don't have enough data to evaluate ternary parameters, we believe this EOS gives qualitative prediction of the ternary system, CH_4-CO_2-H_2O, assuming $k_{2,\mathrm{CH_4\text{-}CO_2\text{-}H_2O}} = 1$ and $k_{3,\mathrm{CH_4\text{-}CO_2\text{-}H_2O}} = 0$ (as in Fig. 17).

Many different kinds of diagrams can be produced, such as *Th-V* (homogenization temperature vs. volume), *Th-X*, *P-T*, and *P-X* diagrams for different temperatures, pressures, and relative proportions of components. Figures 3, 9, and 13 are typical *P-X* diagrams. The *Th-X* diagram can be directly interpreted from the *P-X* diagram. From the *Th-X* diagram, the *Th-V* diagram can be calculated using the EOS. The *P-T* diagram (isochores) can also be calculated from the EOS. Homogenization temperatures (*Th*) and fluid compositions (*X*) are usually measured in the laboratory by microthermometry and Raman microprobe, respectively. Given *Th* and *X*, *P* can be found either in the *P-X* or in the *Th-X* diagram and the volume can be calculated using the EOS.

As an example of this kind of application, consider the evolution of fluids related to a wolframite vein within the low-grade aureole of the Borne granite (French Massif Central). RAMBOZ et al. (1985) studied a series of fluid inclusions, giving homogenization temperature, *Th*, and bulk composition, *X*. Taking sample No. 2 from their analysis, which has a total homogenization (to vapor) temperature of 320°C and a bulk composition of $X_{H_2O} = 67.7\%$, $X_{CO_2} = 31.1\%$, and $X_{CH_4} = 1.2\%$. Because the content of CH_4 is small (less than the experimental error), it is incorporated into CO_2. We have found a constant pressure solvus at 340 bar for the

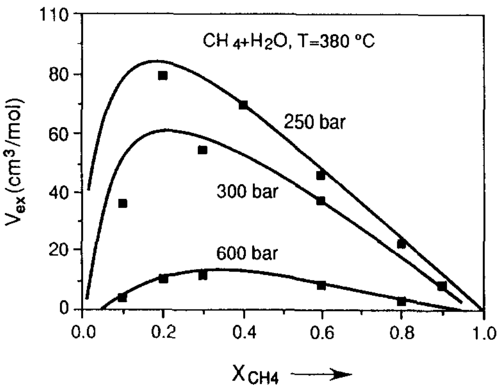

FIG. 16. Excess volumes of mixing in the system CH_4-H_2O. Experimental data by BAZAYEV et al. (1974).

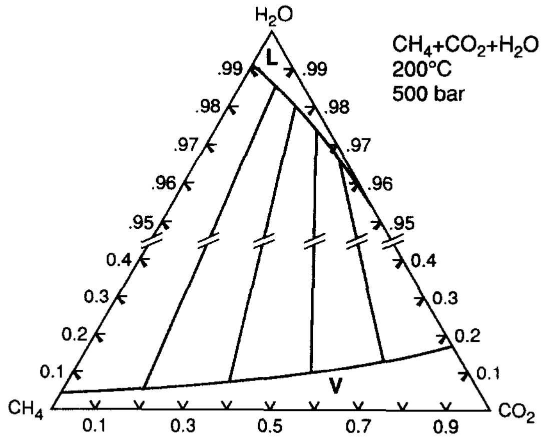

FIG. 17. The calculated phase equilibria of the ternary system CH_4-CO_2-H_2O at 200°C and 500 bar.

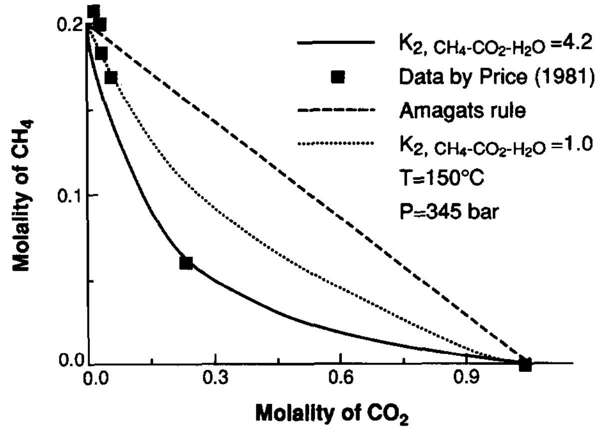

FIG. 18. The solubility of both CH_4 and CO_2 in a 5% NaCl aqueous solution as a function of gas phase composition. Data of PRICE (1981).

composition $X_{H_2O} = 67.7\%$ and $X_{CO_2} = 32.3\%$, at 320°C (see Fig. 19). The pressure of this solvus will be the pressure at which homogenization occurs. With P, Th, and X known, a molar volume of 77.7 cm^3/mol can be calculated from our EOS. RAMBOZ et al. (1985) predicted a trapping temperature of 550°C in the vein which was emplaced soon after the thermal peak of metamorphism (600–650°C) as indicated by the biotite-muscovite-cordierite-andalusite assemblage (WEISBROD, 1968). After trapping the volume of the fluid inclusion can be assumed constant for a small change in temperature. The isochore can be calculated as a function of temperature as in Fig. 20. From this a trapping pressure of 770 bar at 550°C is obtained. This T-P condition is close to the result predicted from other observations, such as the mineral assemblage and from the occurrence of the granite terrane and the results of RAMBOZ et al. (1985).

In aqueous fluid inclusions, CH_4 and CO_2 can both be significant species (HALL and BODNAR, 1990). Adding CH_4 to the CO_2-H_2O system can substantially affect conditions at homogenization. Therefore, in interpreting observed data, neglecting minor species or incorporating a minor to a major species may lead to a sizable error. Suppose, for example, that we have a fluid inclusion which homogenizes to liquid at 300°C and at composition 4% CH_4 + 16% CO_2 + 80% H_2O. If $k_{2,CH_4-CO_2-H_2O} = 1$, and $k_{3,CH_4-CO_2-H_2O} = 0$, the solvus can be calculated as shown by the dashed line of Fig. 21. The homogenization pressure 750 bar can be obtained from this figure. The molar volume of 34.69 cm^3 and its isochore (Fig. 22) can be calculated from the EOS. On the other hand, if we incorporated the 4% CH_4 into CO_2, a lower homogenization pressure of 604 bar will be found from the solid line of Fig. 21, and a molar volume of 36.95 cm^3 and its corresponding isochore can be calculated from the EOS (see Fig. 22). It can be seen from Fig. 22 that the difference of the interpreted trapping pressure is 140–400 bar from 300 to 600°C. Therefore incorporating the 4% CH_4 into CO_2 may cause an error of 15–20%.

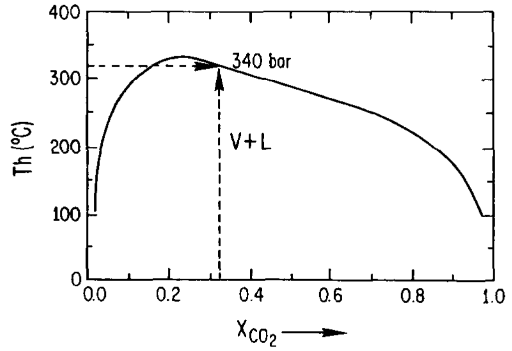

FIG. 19. The Th-X diagram interpreted from Fig. 3.

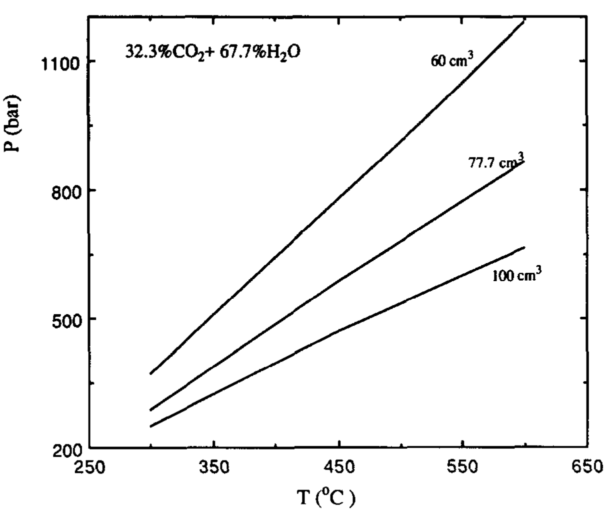

FIG. 20. Calculated isochore curves.

VIII. CONCLUSION

An EOS has been developed for the pure systems and the mixtures in the CH_4-CO_2-H_2O system. The EOS is reliable for the pure endmembers from 0 to 1000°C and from 0 to

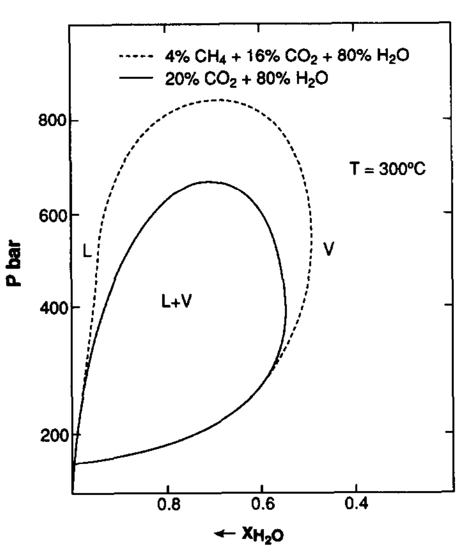

FIG. 21. Solvus as a function of composition in the ternary at 300°C. The solid line is the 20% CO_2 + 80% H_2O system, and the dashed line represents the 4% CH_4 + 16% CO_2 + 80% H_2O system.

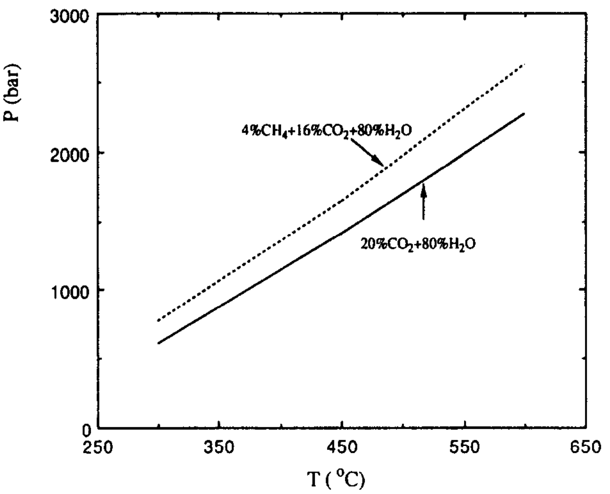

FIG. 22. Comparison of the isochores for the system 20% CO_2-80% H_2O and 4% CH_2 + 16% CO_2 + 80% H_2O. The density is assumed to be the density at their homogenization temperature and pressure for sample 2 of RAMBOZ et al. (1985).

8000 bar and has been discussed in part I. In order to interpolate pure system behavior into the binaries and ternaries systems we introduced a mixing rule based on the virial EOS expansion. We have shown that the resulting EOS can predict both phase equilibrium and volumetric properties with accuracy close to that of experimental data in binary mixtures in a *T-P* range approximately from 50 to 1000°C and 0 to 1000 bars (to 3000 bar with less accuracy). There is very little ternary data. However, dependence on third order behavior is clearly evident in the mixing rule. With the adjustment of the third order parameters, the predictions agree with the limited data available. The resulting EOS predicts that the presence of CO_2 has a great effect on the solubility of CH_4 in water. In order to improve the EOS in the ternary, both density and phase equilibrium data in the ternary are important.

We have also discussed the application of this EOS to the study of fluid inclusion. Homogenization temperatures and pressures are quite sensitive to compositions in the ternary. The water concentration in the vapor phase is substantially larger than that calculated from Raoult's law. Adding CH_4 to the system CO_2-H_2O or adding CO_2 into the system CH_4-H_2O may greatly change the fugacity coefficients of CO_2 or CH_4 and the homogenization temperature or pressure.

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