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Manuscript received February 16, 1983; revision received and accepted July 21, 1983.

High-Pressure Phase Equilibria for the Water/Methane System

A semitheoretical method has been established for superimposing the residual thermodynamic properties of pure methane and of pure water over wide ranges of pressure (0.01 to 1,000 MPa) and temperature (triple point to twice the critical temperature). Using reasonable mixing rules with two binary parameters, this superposition also gives mixture properties, including high-pressure vapor-liquid equilibria.

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SCOPE

Since natural-gas aquifers may become significant sources of energy, there exists a need towards a quantitative description of vapor-liquid equilibria pertinent to aquifers. This work presents a method to correlate, at high densities, thermodynamic properties for mixtures of water and methane, the two most abundant fluids in natural-gas aquifers.

The experimental residual thermodynamic properties for pure methane are superimposed upon those for pure water, using an extended form of corresponding states theory with molecular shape factors. Residual properties are thermodynamic properties of the real fluid minus those that an ideal gas would have at the same temperature, density, and composition.

A semitheoretical equation of state is established to represent the superimposed residual properties. This equation of state is separated into three terms: the first arises from repulsive forces; the second, from attractive contributions to the second virial coefficient; and the third, from attractive contributions to dense-fluid properties. This separation allows different mixing rules for each term in the equation of state.

The equation of state is extended to mixtures with mixing rules that include two adjustable binary parameters that are functions of temperature, but not of density or composition. This extension produces thermodynamic properties for mixtures of water and methane, including vapor-liquid equilibria in the region 300 to 630 K and to 150 MPa.

CONCLUSIONS AND SIGNIFICANCE

The residual thermodynamic properties for pure water and for pure methane are superimposed with good accuracy over wide ranges of temperature and density. Superposition is achieved through extended (Prigogine, 1957) corresponding states, coupled with molecular shape factors (Leach et al., 1968). The resulting equation of state correlates well the PVT behavior and vapor-liquid equilibria for pure water and for pure methane for the pressure range 0.01 to 1,000 MPa and for the temperature range triple point to twice the critical temperature. For methane, all molecular shape parameters are constants. For water, one parameter is a constant, one is a weak function of temperature, and one is a weak function of temperature and density.

For water/methane mixtures, the equation of state gives correct second virial coefficients and good agreement with experimental high-pressure vapor-liquid equilibria and with experimental gas-phase excess enthalpies.

The method presented here may serve as an initial basis for description of vapor-liquid equilibria for natural-gas aquifers.

INTRODUCTION

Natural gas has been a major source of energy for the United States, second only to petroleum. In 1974, 30.4% of the energy in the U.S. came from natural gas (Campbell, 1977). Since our current sources of natural gas are finite, we seek new sources. Natural-gas aquifers (geopressured natural-gas deposits) may offer a new source of natural gas not yet utilized. Aquifers are high-pressure reservoirs containing natural gas (mostly methane) and water (or brine). Estimates of recoverable natural gas from aquifers range from a

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6- to 50-year supply at the current U.S. rate of natural-gas consumption (Kerr, 1980).

Increased interest in natural-gas aquifers has produced a need toward a quantitative description of the high-pressure phase equilibria for the water/methane system. Such a description is required as a first step for efficient recovery of the natural gas and for reliable estimation of how much natural gas can be recovered from a given reservoir. This work presents a molecular-thermodynamic method for correlating the residual properties of pure water and of pure methane over wide ranges of pressure (to 1,000 MPa) and temperature (triple point to twice the critical temperature). Using reasonable mixing rules, the superimposed residual properties of the pure fluids can be used to give also the residual properties of water/methane mixtures. The correlation presented here can serve as an initial basis for representing high-pressure phase equilibria in natural-gas aquifer systems.

THERMODYNAMIC FRAMEWORK

Our objective is to obtain an equation of state for correlation and prediction of water/methane phase equilibria over large ranges of temperature and pressure and over the entire composition range. Attainment of this objective presents two major challenges. First, we describe both pure methane and pure water with the *same* equation of state. Second, having an adequate equation of state for the pure fluids, we need to develop useful mixing rules.

To develop a universal equation of state for pure fluids, we use the theorem of corresponding staes with molecular shape factors (Leach et al., 1968). In addition, we use a particular form for writing the Helmholtz energy to facilitate extension to mixtures.

For a pure fluid, compressibility factor Z is related to molar Helmholtz energy a by

$$Z = \frac{P}{RT\rho} = \rho \left[\frac{\partial \frac{a}{RT}}{\partial \rho} \right]_T \qquad (1)$$

where R is the gas constant, T is the absolute temperature and ρ is the molar density. We desire an expression for the dimensionless quantity a/RT as a function of T and ρ.

We separate a/RT into an ideal-gas part (ig) and a residual part (res)

$$\frac{a}{RT} = \frac{a^{ig}}{RT} + \frac{a^{res}}{RT} \qquad (2)$$

where

$$\frac{a^{ig}}{RT} = \frac{a^o}{RT} - 1 + ln \left[\frac{RT\rho}{P^o} \right] . \qquad (3)$$

In Eq. 3, a^o/RT is a function only of temperature and is not required for the calculations done in this work; P^o is an arbitrary reference-state pressure such as 1 bar. We define a residual thermodynamic property as the property of the real fluid minus that of an ideal gas, all at the same temperature, density, and composition. We assume that the residual Helmholtz energy is given by a function F such that

$$\frac{a^{res}}{RT} = cF(\tilde{T},\tilde{\rho}) \qquad (4)$$

where

$$\tilde{T} = \frac{T}{T^*} \qquad (5)$$

$$\tilde{\rho} = \frac{\rho}{\rho^*} \qquad (6)$$

with

$$T^* = \theta_T T_c \qquad (7)$$

$$\rho^* = \theta_\rho \rho_c . \qquad (8)$$

TABLE 1. PARAMETERS c, T^*, and ρ^* FOR METHANE AND FOR WATER

Methane
c = 1.031 (dimensionless)
T^* = 172.15 K
ρ^* = 67.832 mol/L
Water
c = 1.016 (dimensionless)
T^* = 759.92 − 364.88 exp(−736.37/T) K
$\rho^* = r^{(1)} + r^{(2)}\,\rho$ mol/L
where
$r^{(1)}$ = 39.794 + 134.80 exp(−442.21/T)
$r^{(2)}$ = 1.4741 exp(−T/734.59)

Parameter c (Prigogine, 1957), θ_T and θ_ρ are molecular shape factors. In corresponding states theory for simple fluids, θ_T and θ_ρ are constants, and $c = 1$. For polyatomic fluids, θ_T and θ_ρ may be functions of temperature and/or density, and $c > 1$. T_c and ρ_c are the critical temperature and density, respectively.

To determine the function F (Eq. 4) for pure water and for pure methane, we first superimpose the experimental residual Holmholtz energies of methane and water on that of reference fluid argon (where $c = 1$). Appendix I.A (supplementary material) gives details for calculating experimental residual Helmholtz energies from available data for water, methane, and argon. Superposition of the residual Helmholtz energies for two pure fluids gives only ratios, not absolute values, for c, T^* and ρ^*. These parameters can only be obtained when they have been previously set for the reference fluid. Appendix I.B (supplementary material) explains our procedure for obtaining T^* and ρ^* for argon. These parameters are for convenience only.

For pure water (Haar et al., 1980; Bain, 1964), for pure methane (IUPAC, 1978), and for pure argon (IUPAC, 1971), the experimental data indicate that superposition is not possible unless T^* for water is a weak function of temperature. Further, for successful superposition, it is necessary that ρ^* for water be a weak function of both temperature and density. However, T^* and ρ^* for methane are constants. Table 1 gives parameters c, T^* and ρ^* for methane and water.

Figure 1 shows superposition of the residual Helmholtz energy of pure water and that for pure methane on reduced coordinates

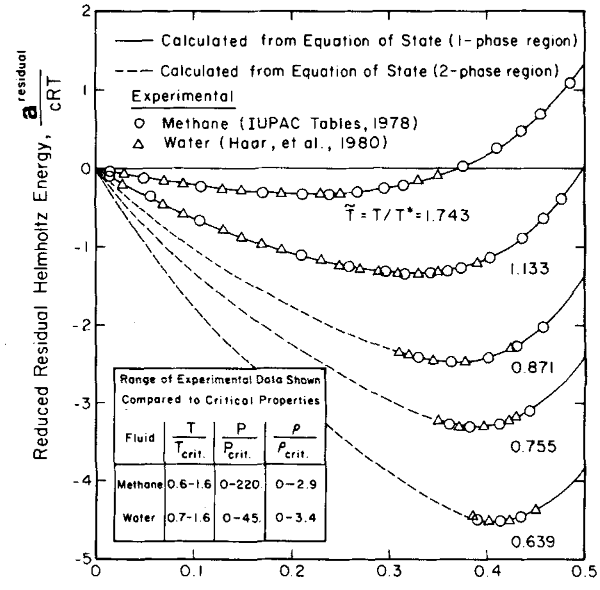

Figure 1. Superposition of reduced residual Helmholtz energy versus reduced density at various reduced temperatures. (T^*, ρ^*, and c determine molecular shape factors; they are not critical properties.)

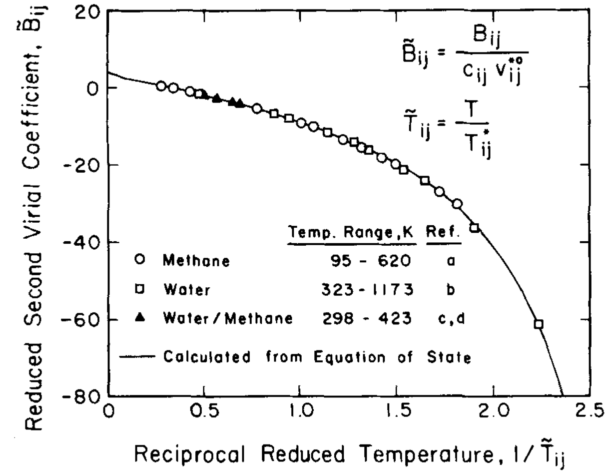

Figure 2. Reduced second virial coefficients: (a) IUPAC (1978); (b) Dymond and Smith (1980); (c) Rigby Prausnitz (1968); (d) Wormald and Colling (1982).

TABLE 2. FORM AND COEFFICIENTS FOR POLYNOMIAL g

$$g = a^{(1)}\tilde{\rho} + a^{(2)}\tilde{\rho}^2 + a^{(3)}\tilde{\rho}^3(1 + a^{(4)}\tilde{\rho} + a^{(5)}\tilde{\rho}^2)$$

$$a^{(1)} = \frac{\alpha^{(1)}}{\tilde{T}^2} + \frac{\alpha^{(2)}}{\tilde{T}^3} + \frac{\alpha^{(3)}}{\tilde{T}^4} + \frac{\alpha^{(4)}}{\tilde{T}^5}$$

$$a^{(2)} = \alpha^{(5)} + \frac{\alpha^{(6)}}{\tilde{T}} + \frac{\alpha^{(7)}}{\tilde{T}^2} + \frac{\alpha^{(8)}}{\tilde{T}^3} + \frac{\alpha^{(9)}}{\tilde{T}^4} + \frac{\alpha^{(10)}}{\tilde{T}^5}$$

$$a^{(3)} = \alpha^{(11)} + \frac{\alpha^{(12)}}{\tilde{T}} + \frac{\alpha^{(13)}}{\tilde{T}^2} + \frac{\alpha^{(14)}}{\tilde{T}^3} + \frac{\alpha^{(15)}}{\tilde{T}^4} + \frac{\alpha^{(16)}}{\tilde{T}^5}$$

$$a^{(4)} = \alpha^{(17)}$$
$$a^{(5)} = \alpha^{(18)}$$

i	$\alpha^{(i)}$	i	$\alpha^{(i)}$
1	−5.057017E + 0	10	7.569813E + 0
2	7.919236E + 0	11	−3.941078E + 0
3	−4.215866E + 0	12	8.553142E + 1
4	8.135902E − 1	13	−1.926637E + 2
5	−2.052461E + 0	14	−4.559255E + 1
6	−1.023550E + 1	15	1.499184E + 2
7	4.263929E + 1	16	−5.174522E + 1
8	−8.274472E + 0	17	−1.894219E + 0
9	−1.777429E + 1	18	1.181016E + 0

A number followed by E + n should be multiplied by 10^n.

for five reduced temperatures. The experimental data for water and for methane superimpose well over the ranges of pressure, temperature and density indicated; these include both subcritical and supercritical regions.

Figure 2 shows superposition in the low-density range where experimental reduced second virial coefficients $\tilde{B}_{ii}$ for pure water (Dymond and Smith, 1980) and for pure methane (IUPAC, 1978) are plotted versus reciprocal reduced temperature. Also shown are several experimental cross second virial coefficients $\tilde{B}_{ij}$ for mixtures of water and methane (Rigby and Prausnitz, 1968; Wormald and Colling, 1982) which we discuss later. The reduced second virial coefficient, for pure fluid i, is given by

$$\tilde{B}_{ii} = \frac{B_{ii}}{c_{ii} v_{ii}^{*o}} \tag{9}$$

where B_{ii} is the second virial coefficient and v_{ii}^{*o} is given by

$$v_{ii}^{*o} = \lim_{\rho \to 0} \frac{1}{\rho_{ii}^{*}} \cdot \tag{10}$$

To obtain an analytic form for function F in Eq. 4, we divide F into three parts: repulsion (rep), second virial (sv), and dense fluid (df). (For a similar development, see Kohler and Haar, 1981.) This novel form is particularly useful for extension to mixtures. Thus,

$$F = F^{\text{rep}} + F^{sv} + F^{df} \cdot \tag{11}$$

For F^{rep}, we use the expression of Carnahan and Starling (1969), giving

$$F^{\text{rep}} = \tilde{\rho} \left[\frac{(4 - 3\tilde{\rho})}{(1 - \tilde{\rho})^2}\right] \cdot \tag{12}$$

For F^{sv} we use

$$F^{sv} = \tilde{B}^{\text{att}}\tilde{\rho} \tag{13}$$

where $\tilde{B}^{\text{att}}$ is the attractive contribution to the reduced second virial coefficient. The repulsive part of the reduced second virial coefficient follows from Eq. 12 giving $\tilde{B}^{\text{rep}} = 4$. Thus,

$$\tilde{B} = \tilde{B}^{\text{rep}} + \tilde{B}^{\text{att}} = 4 + \tilde{B}^{\text{att}} \cdot \tag{14}$$

The reduced quantity $\tilde{B}^{\text{att}}$ is a function only of reduced temperature $\tilde{T}$. By using a weighted least squares regression on experimental second virial coefficients for water (Dymond and Smith, 1980), methane (IUPAC, 1978), and argon (Dymond and Smith, 1980), we obtain

$$\tilde{B}^{\text{att}} = -\frac{17.088}{\tilde{T}} + \frac{27.157}{\tilde{T}^2} - \frac{42.251}{\tilde{T}^3} + \frac{24.959}{\tilde{T}^4} - \frac{5.6396}{\tilde{T}^5} \cdot \tag{15}$$

Equation 15 is shown by the solid line in Figure 2.

The forms for F^{rep} and F^{sv} have a good theoretical foundation. F^{df}, however, must be determined empirically. We have found that a good representation of the dense-fluid contribution to the reduced residual Helmholtz energy is given by

$$F^{df} = -\tilde{B}^{\text{att}}\tilde{\rho} \left[\frac{g}{1 + g}\right] \tag{16}$$

where g is a fifth-order polynomial in reduced density $\tilde{\rho}$ whose coefficients depend on reduced temperature $\tilde{T}$. An important property of g is that

$$g \to 0 \text{ as } \tilde{\rho} \to 0 \cdot \tag{17}$$

Further, to assure that F^{df} does not contribute to the second virial coefficient,

$$g \sim \tilde{\rho} \text{ for small } \tilde{\rho} \cdot \tag{18}$$

Table 2 gives the function g and its coefficients obtained by fitting approximately 400 data points for the residual Helmholtz energy over the entire range of available experimental data for water (Haar et al., 1980; Bain, 1964) and for methane (IUPAC, 1978).

Equation 16 for F^{df} was obtained following observation that F^{df} must compensate for a large F^{sv} effect at high densities. This observation led to the form

$$F^{sv} + F^{df} = \frac{\tilde{B}^{\text{att}}\tilde{\rho}}{1 + g} = \tilde{B}^{\text{att}}\tilde{\rho} - \tilde{B}^{\text{att}}\tilde{\rho}\left[\frac{g}{1 + g}\right] \tag{19}$$

where g is negligible when $\tilde{\rho}$ is small, but g becomes important in the liquid phase where $\tilde{\rho}$ is larger.

For extension to mixtures, we chose to separate the residual Helmholtz energy into contributions from repulsion, attractive second-virial, and attractive dense-fluid intermolecular forces. This choice enables us to write separate mixing rules for each contribution. Equations 4, 11–13, and 16 give for pure fluids

$$\frac{\mathbf{a}^{\text{res}}}{cRT} = \tilde{\rho}\left[\frac{(4 - 3\tilde{\rho})}{(1 - \tilde{\rho})^2}\right] + \tilde{B}^{\text{att}}\tilde{\rho} - \tilde{B}^{\text{att}}\tilde{\rho}\left[\frac{g}{1 + g}\right] \cdot \tag{20}$$

Equation 20 is shown by the solid lines in Figure 1.

Equations 3 and 20 are sufficient to calculate vapor-liquid equilibria and pressure-volume-temperature relations for pure water and for pure methane. Figures 3 and 4 show calculated phase diagrams for pure methane and for pure water, respectively. Agreement between experimental and calculated results is remarkably good when one considers that small errors in the Helmholtz energy can cause large errors in derived properties such as the pressure. Outside the critical region, the largest deviations between calculation and experiment occur for water below about

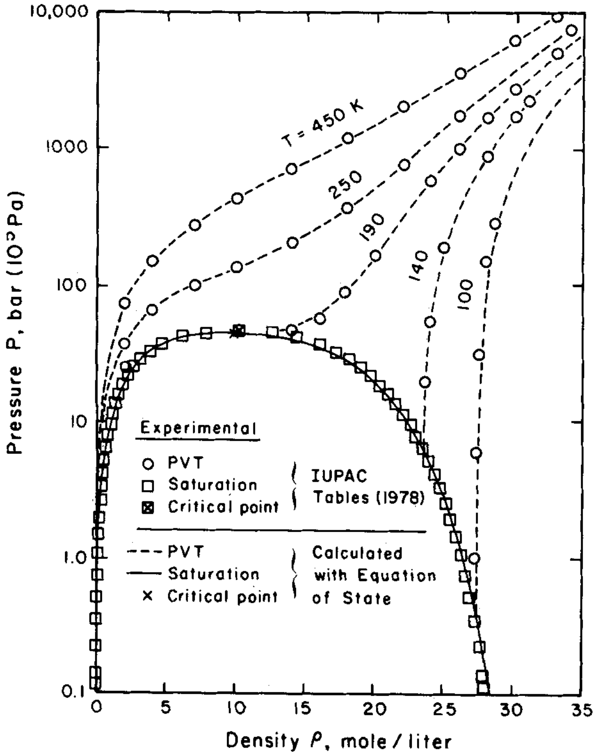

Figure 3. Phase diagram for fluid methane.

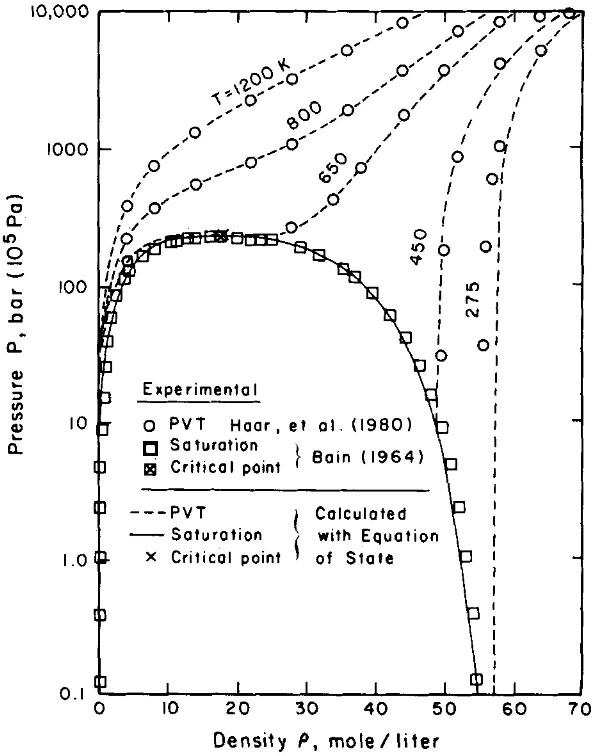

Figure 4. Phase diagram for fluid water.

280 K. Here the maximum errors in liquid density are on the order of about 3 to 4%. Even in the critical region, calculated and experimental results compare surprisingly well as shown in Table 3.

Mixtures

Properties for the water/methane system may be calculated using Eqs. 3 and 20 with a reasonable set of mixing rules. For the mixture M, we write

$$\frac{\mathbf{a}_M}{RT}=\frac{\mathbf{a}_M^{ig}}{RT}+\frac{\mathbf{a}_M^{rep}}{RT}+\frac{\mathbf{a}_M^{sv}}{RT}+\frac{\mathbf{a}_M^{df}}{RT}\,. \tag{21}$$

The mixing rule to use for the ideal gas term (Eq. 3) is

$$\frac{\mathbf{a}_M^{ig}}{RT}=-1+\sum_i x_i\left[\frac{\mathbf{a}_i^o}{RT}\right]+\sum_i x_i\left[\frac{x_iRT\rho}{P^o}\right]\,. \tag{22}$$

The second virial coefficient B_M of a mixture must be a quadratic function of mole fraction x such that

$$B_M=\sum_i\sum_j x_ix_jB_{ij} \tag{23}$$

where B_{ij} is the second virial coefficient reflecting pair interactions between one molecule of type i and one molecule of type j. In the mixing rules that follow, we assure that Eq. 23 is satisfied. For $\mathbf{a}_M^{rep}/RT$ and $\mathbf{a}_M^{sv}/RT$ we use

$$\frac{\mathbf{a}_M^{rep}}{RT}=\langle c\tilde{\rho}\rangle\left[\frac{(4-3\langle\tilde{\rho}\rangle)}{(1-\langle\tilde{\rho}\rangle)^2}\right] \tag{24}$$

$$\frac{\mathbf{a}_M^{sv}}{RT}=\langle c\tilde{B}^{att}\,\tilde{\rho}\rangle \tag{25}$$

where

$$\langle\tilde{\rho}\rangle=\sum_i\sum_j x_ix_j\tilde{\rho}_{ij} \tag{26}$$

$$\langle c\tilde{\rho}\rangle=\sum_i\sum_j x_ix_jc_{ij}\tilde{\rho}_{ij} \tag{27}$$

$$\langle c\tilde{B}^{att}\tilde{\rho}\rangle=\sum_i\sum_j x_ix_jc_{ij}\tilde{B}_{ij}^{att}\tilde{\rho}_{ij}\,. \tag{28}$$

In Eqs. 26–28, we define $\tilde{\rho}_{ij}$ by

$$\tilde{\rho}_{ij}=\frac{\rho_M}{\rho_{ij}^*}\,. \tag{29}$$

$\tilde{B}_{ij}^{att}$, is calculated by replacing $\tilde{T}$ in Eq. 15 with

$$\tilde{T}_{ij}=\frac{T}{T_{ij}^*}\,. \tag{30}$$

When $i\neq j$, we use the following combining rules

$$\rho_{ij}^{*\,-1/3}=\left[\frac{\rho_{ii}^{*\,-1/3}+\rho_{jj}^{*\,-1/3}}{2}\right](1-l_{ij}) \tag{31}$$

$$c_{ij}=\left[\frac{c_{ii}+c_{jj}}{2}\right] \tag{32}$$

$$T_{ij}^*=\frac{(c_{ii}c_{jj})^{1/2}}{c_{ij}}(1-k_{ij})(T_{ij}^{*np}+T_{ij}^{*p}) \tag{33}$$

where the nonpolar (np) and polar (p) parts of T_{ij}^* are

$$T_{ij}^{*np}=[(T_{ii,T=\infty}^*)(T_{jj,T=\infty}^*)]^{1/2} \tag{34}$$

$$T_{ij}^{*p}=[(T_{ii}^*-T_{ii,T=\infty}^*)(T_{jj}^*-T_{jj,T=\infty}^*)]^{1/2}\,. \tag{35}$$

In Eqs. 31 and 33, l_{ij} and k_{ij} are binary parameters which may be determined empirically by fitting binary mixture data. In our extension of corresponding states to mixtures, it is possible for bi-

TABLE 3. EXPERIMENTAL AND CALCULATED CRITICAL PROPERTIES

Critical Property	Methane		Water	
	Exp.[a]	Calc.	Exp.[b]	Calc.
T_c, K	191.	191.	647.	652.
P_c, bar (10^5 Pa)	46.0	45.8	221.	234.
ρ_c, mol/L	10.1	9.75	17.5	17.8
Z_c	0.287	0.296	0.235	0.242

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[a] IUPAC (1978).

[b] Bain (1964).

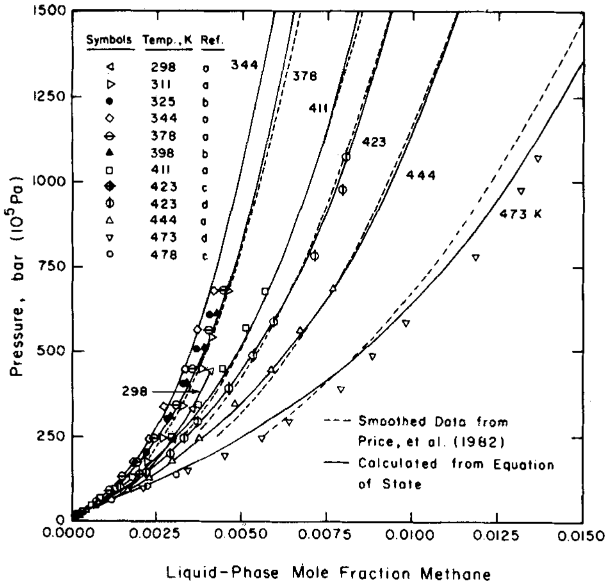

Figure 5. Saturated liquid compositions in water/methane system at high pressures: (a) Culberson and McKetta (1951); (b) O'Sullivan and Smith (1970); (c) Gillespie and Wilson (1982); (d) Sultanov et al. (1972).

nary parameters l_{ij} and k_{ij} to depend on temperature, but they may not depend on density or composition.

Our mixing rule for a^{df}/RT is somewhat arbitrary. For example, we could use a nonrandom mixing rule following the local-composition concept of Wilson (1964). We are free to use what we like because, thanks to the separation shown in Eq. 11, we do not violate the necessary quadratic rule shown in Eq. 23.

For our purposes here, we have chosen a simple mixing rule for a^{df}/RT. We use

$$\frac{\mathrm{a}^{df}}{RT} = \langle c\tilde{B}^{\mathrm{att}}\tilde{\rho}\rangle \left[\frac{\langle g\rangle}{1 + \langle g\rangle}\right] \tag{36}$$

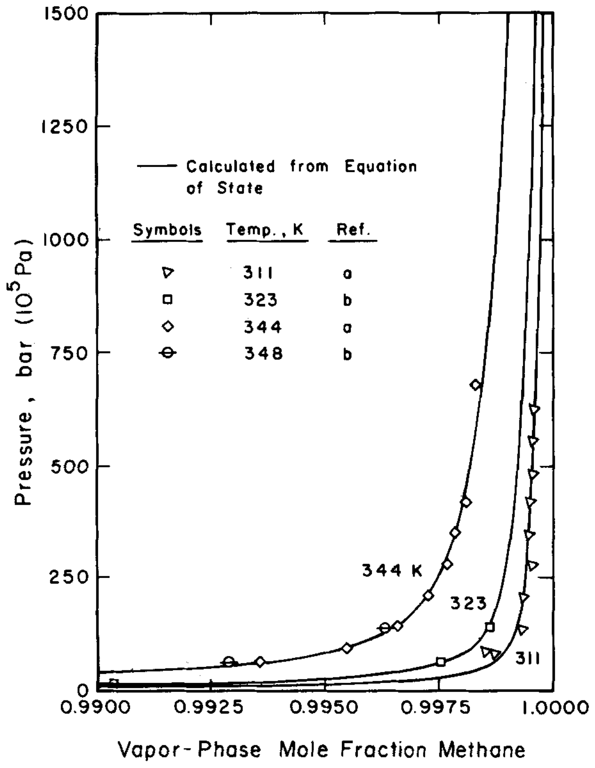

Figure 6. Saturated vapor compositions in water/methane system at high pressures. Highly dilute range at lower temperatures: (a) Olds et al. (1942); (b) Gillespie and Wilson (1982).

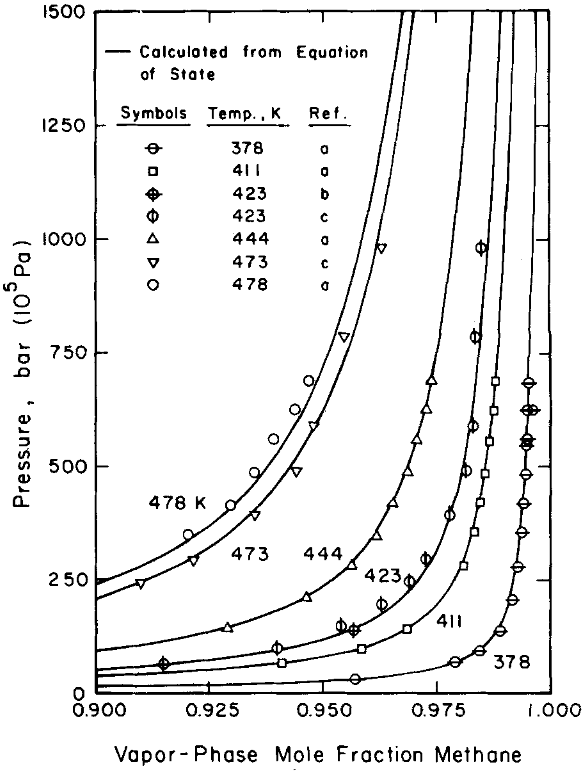

Figure 7. Saturated vapor compositions in water/methane system at high pressures: (a) Olds et al. (1942); (b) Gillespie and Wilson (1982); (c) Sultanov et al. (1971).

where $\langle c\tilde{B}^{\mathrm{att}}\tilde{\rho}\rangle$ is given by Eq. 28 and $\langle g\rangle$ is given by

$$\langle g\rangle = \sum_i \sum_j x_i x_j g_{ij} \cdot \tag{37}$$

To calculate g_{ij}, one replaces $\tilde{\rho}$ and $\tilde{T}$ in Table 2 with $\tilde{\rho}_{ij}$ and $\tilde{T}_{ij}$, respectively, while leaving the α constants unchanged.

RESULTS

Figures 5–8 show experimental and calculated vapor-liquid equilibria for the water/methane system. In all four figures, the pressure range is from 0 to 1,500 bar (1,500 × 10^5 Pa).

Figure 5 gives saturated-liquid compositions for water/methane from 298 to 473 K. Experimental data are from Culberson and

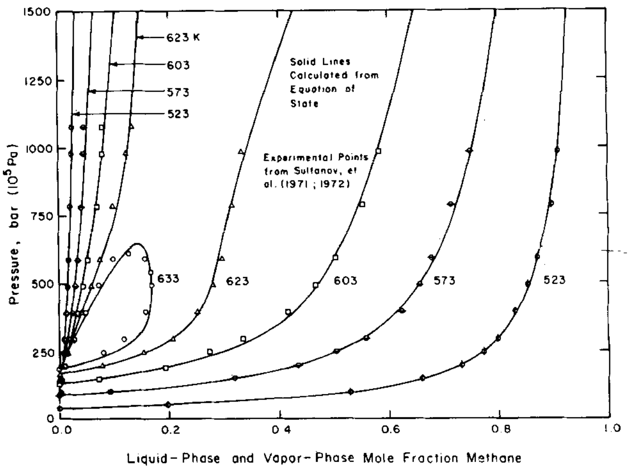

Figure 8. High-pressure vapor-liquid equilibria for the water/methane system.

TABLE 4. RECOMMENDED BINARY PARAMETERS k_{ij} AND L_{ij} FOR WATER/METHANE

T,K	$k_{ij} \times 10^3$	$l_{ij} \times 10^3$
298	205	−27.0
311	200	−19.0
323	196	−13.6
325	195	−12.7
344	190	−5.7
378	181	1.2
411	174	2.5
444	168	0.5
473	163	−1.5
478	163	−1.5
523	150	0.0
573	50	0.0
603	5	−3.0
623	−50	−20.0
633	−55	−30.0

McKetta (1951), O'Sullivan and Smith (1970), Gillespie and Wilson (1982), Price et al. (1982), and Sultanov et al. (1972). The 298 K isotherm ends at about 440 bar where methane/water hydrate forms (Marshall et al., 1964). No hydrate formation occurs for the other isotherms of Figure 5 in the given pressure range. Experimental saturated-liquid compositions are represented well by the equation of state.

The experimental data of Figure 5 indicate that, at fixed pressure, there is a minimum in the methane solubility in water as a function of temperature. This minimum occurs at about 344 K. The equation of state is able to reproduce this behavior.

Figures 6 and 7 give the high-pressure, saturated-vapor compositions for the water/methane system from 311 to 348 K and from 378 to 478 K, respectively. Experimental data are from Olds et al. (1942); Gillespie and Wilson (1982); and Sultanov et al. (1971). The equation of state gives results in good agreement with experiment.

Figure 8 gives experimental and calculated high-pressure vapor-liquid equilibria for water/methane from 523 to 633 K. Experimental data are from Sultanov et al. (1971, 1972). Again, the equation of state gives good results.

The calculated lines in Figures 5–8 were obtained by adjusting binary parameters l_{ij} and k_{ij} in Eqs. 31 and 33 to fit the experimental water/methane data at each temperature. Table 4 gives recommended values for l_{ij} and k_{ij}. These l_{ij} and k_{ij} values are of reasonable magnitude. Their temperature dependence is probably due to the somewhat arbitrary mixing rules used in the a^{df}/RT term (Eq. 36). Although reasonable, these mixing rules could probably be improved.

Using parameters l_{ij} and k_{ij} shown in Table 4, we used the equation of state to calculate the excess enthalpy of gaseous water/methane mixtures at several temperatures and pressures. Figures 9 and 10 compare calculated excess enthalpies with experimental data by Wormald and Colling (1982). Agreement is gratifying when one considers that no experimental excess enthalpies were used to obtain the equation-of-state parameters.

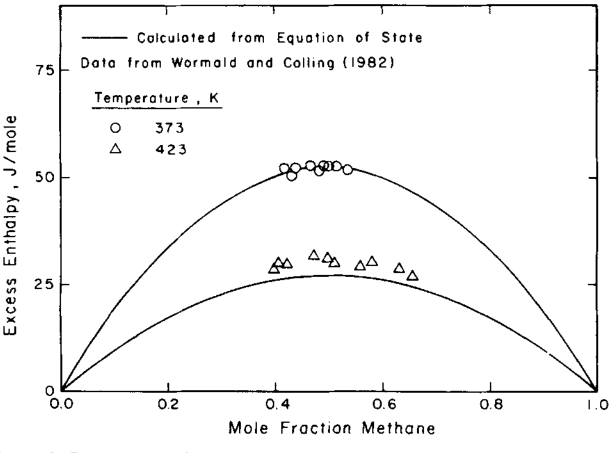

Figure 9. Excess enthalpy for gaseous water/methane at 1.013 bar (1.013 × 10^5 Pa).

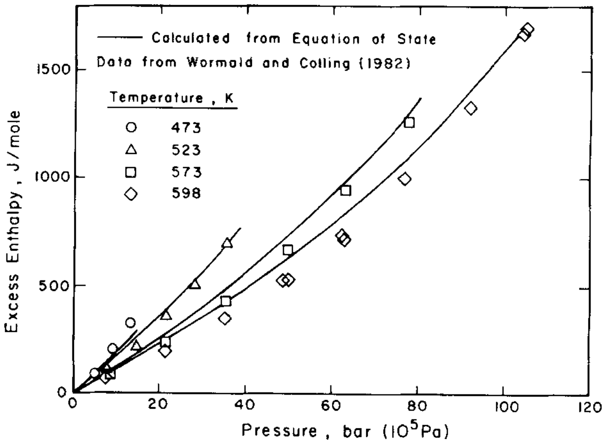

Figure 10. Excess enthalpy for gaseous water/methane at equimolar concentration.

We calculated also excess volumes for gaseous water/methane mixtures using the l_{ij} and k_{ij} parameters in Table 4. Here, calculations are in qualitative agreement with approximate data of Bazaev et al. (1974). Appendix I.C (supplementary material) compares experimental and calculated excess volumes for water/methane.

Finally, Eq. 9 may be used to reduce experimental cross second virial coefficient B_{ij} by replacing subscripts ii with subscripts ij. When this is done for experimental B_{ij}'s of Wormald and Colling (1982) and of Rigby and Prausnitz (1968), the resulting $\tilde{B}_{ij}$'s superimpose well on the pure $\tilde{B}_{ii}$ data shown in Figure 2.

CONCLUSIONS

The residual thermodynamic properties of pure water and of pure methane have been superimposed using the theorem of corresponding states with molecular shape factors. This superposition extends over a wide range of temperature and density. For methane, shape factors c, θ_T and θ_p are constants. For water, c is a constant, θ_T is a weak function of temperature, and θ_p is a weak function of temperature and density.

Using reasonable mixing rules, the superimposed residual thermodynamic properties give properties for the water/methane system. Comparison between calculated and observed properties is good, suggesting that a useful method may now be established for calculating phase equilibria for natural-gas/aquifer systems.

ACKNOWLEDGMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract number DE-AC03-76SF00098.

NOTATION

a = molar Helmholtz energy
$a^{(i)}$ = ith coefficient in polynomial g
B = second virial coefficient
c = ⅓ equivalent external degrees of freedom
F = universal function
g = polynomial defined in Table 2
k_{ij} = binary parameter to correct cross characteristic temperature
l_{ij} = binary parameter to correct cross characteristic size

P = absolute pressure
R = gas constant
T = absolute temperature
v_{ii}^{*o} = characteristic size parameter at zero density for fluid i
x = mole fraction
Z = compressibility factor

Greek Letters

$\alpha^{(i)}$ = constants given in Table 2 for polynomial g
θ_p = density (size) shape factor
θ_T = temperature (energy) shape factor
ρ = molar density (mol/volume)

Operators

$\sim$ = is proportional to
$\sum_i$ = summation over all i
$\langle\ \rangle$ = composition average
$\rightarrow$ = approaches

Subscripts

c = vapor-liquid critical property
i = pure fluid i
ii = pure fluid i
ij = cross between fluid i and fluid j
M = mixture property
T = constant temperature
∞ = infinite temperature

Superscripts

att = attractive contribution
df = attractive dense-fluid contribution
ig = ideal-gas contribution
np = nonpolar
o = arbitrary reference state
p = polar
rep = repulsive contribution
res = residual contribution
sv = attractive second-virial contribution
$*$ = characteristic
$\sim$ = reduced quantity

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Supplementary material has been deposited as Document No. 04197 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 214-13 Jamaica Avenue, Queens Village, N.Y. 11428, and may be obtained for $4.00 for microfiche or $7.75 for photocopies.

Manuscript received January 31, 1983; revision received June 16, and accepted July 1, 1983.