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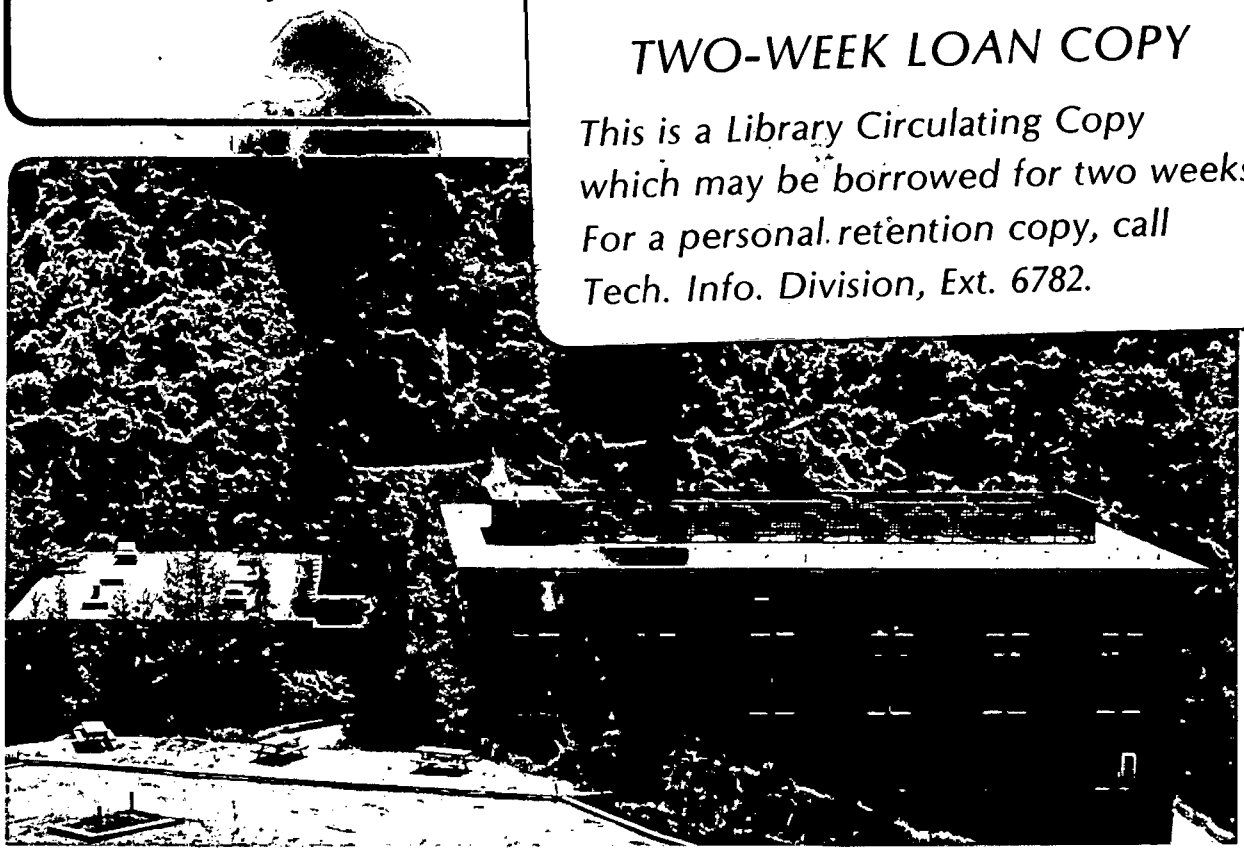

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HIGH-PRESSURE PHASE EQUILIBRIA FOR THE WATER/METHANE SYSTEM[+]

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ABSTRACT

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 1000 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.

[+] For this paper, Appendices I.A, I.B, and I.C are available as supplementary material.

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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 1000 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 equations 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 percent of the energy in the United States 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 6- to 50-year supply at the current US 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 1000 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 seek to 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 states 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

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

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 $\frac{a}{RT}$ as a function of T and ρ.

We separate $\frac{a}{RT}$ into an ideal-gas part (ig) and a residual part (res)

$$\frac{a}{RT} = \frac{a^{ig}}{RT} + \frac{a^{res}}{RT} \tag{2}$$

where

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

In Equation (3), $\frac{a^{o}}{RT}$ 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

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

where

$$\tilde{T} = \frac{T}{T^*} \tag{5}$$

$$\tilde{\rho} = \frac{\rho}{\rho^*} \tag{6}$$

with

$$T^* = \theta_T T_c \tag{7}$$

$$\rho^* = \theta_\rho \rho_c \quad . \tag{8}$$

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 [Equation (4)] for pure water and for pure methane, we first superimpose the experimental residual Helmholtz energies of methane and water on that of reference fluid argon (where c = 1). Appendix I.A gives details for calculating experimental residual Helmholtz energies from available data on 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 explains our procedure for obtaining T^* and ρ^* for argon.

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 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

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

To obtain an analytic form for function F in Equation (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,

$$F = F^{rep} + F^{sv} + F^{df} \quad . \tag{11}$$

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

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

For F^{sv} we use

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

where $\tilde{B}^{att}$ is the attractive contribution to the reduced second virial coefficient. The repulsive part of the reduced second virial coefficient follows from Equation

(12) giving $\tilde{B}^{rep} = 4$. Thus,

$$\tilde{B} = \tilde{B}^{rep} + \tilde{B}^{att} = 4 + \tilde{B}^{att} \quad . \tag{14}$$

The reduced quantity $\tilde{B}^{att}$ 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

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

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

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

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

$$g \rightarrow 0 \text{ as } \tilde{\rho} \rightarrow 0 \quad . \tag{17}$$

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

$$g \propto \tilde{\rho} \quad \text{for small } \tilde{\rho} \quad . \tag{18}$$

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

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

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

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

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 280 K. Here the maximum errors in liquid density are on the order of about 3 to 4 percent. 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 Equations (3) and (20) with a reasonable set of mixing rules. For the mixture M, we write

$$\frac{a_M}{RT} = \frac{a_M^{ig}}{RT} + \frac{a_M^{rep}}{RT} + \frac{a_M^{sv}}{RT} + \frac{a_M^{df}}{RT} \quad . \tag{21}$$

The mixing rule to use for the ideal gas term [Equation (3)] is

$$\frac{a_M^{ig}}{RT} = -1 + \sum_i x_i \left[\frac{a_i^o}{RT}\right] + \sum_i x_i \left[\frac{x_i RT\rho}{p^o}\right] \quad . \tag{22}$$

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

$$B_M = \sum_i\sum_j x_i x_j B_{ij} \tag{23}$$

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 Equation (23) is satisfied. For $\frac{a_M^{rep}}{RT}$ and $\frac{a_M^{sv}}{RT}$ we use

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

$$\frac{a_M^{sv}}{RT} = \langle c\tilde{B}^{att}\tilde{\rho}\rangle \tag{25}$$

where

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

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

$$\langle c\tilde{B}^{att}\tilde{\rho}\rangle = \sum_i\sum_j x_i x_j c_{ij} \tilde{B}_{ij}^{att}\tilde{\rho}_{ij} \quad . \tag{28}$$

In Equations (26)-(28), we define $\tilde{\rho}_{ij}$ by

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

$\tilde{B}_{ij}^{att}$, is calculated by replacing $\tilde{T}$ in Equation (15) with

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

When $i \neq j$, then 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

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

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

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

Our mixing rule for $\frac{a^{df}}{RT}$ 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 Equation (11), we do not violate the necessary

quadratic rule shown in Equation (23).

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

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

where $\langle c\tilde{B}^{att}\tilde{\rho}\rangle$ is given by Equation (28) and $\langle g\rangle$ is given by

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

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 1500 bar (1500×10^5 Pa).

Figure 5 gives saturated-liquid compositions for water/methane from 298 to 473 K. Experimental data are from Culberson and McKetta (1951), O'Sullivan and Smith (1970), Gillespie and Wilson (1982), Price et al. (1982), and Sultanov, et al. (1972). The 298 K isthotherm 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 Equations (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 $\frac{a^{df}}{RT}$ term [Equation (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). The agreement is gratifying when one considers that no experimental excess enthalpies were used to obtain the equation-of-state parameters.

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 compares experimental and calculated excess volumes for water/methane.

Finally, Equation (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_ρ are constants. For water, c is a constant, θ_T is a weak function of temperature, and θ_ρ 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.

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NOTATION

a	=	molar Helmholtz energy
$a^{(i)}$	=	ith coefficient in polynomial g
B	=	second virial coefficient
c	=	$\frac{1}{3}$ 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_ρ	=	density (size) shape factor
θ_T	=	temperature (energy) shape factor
ρ	=	molar density (mole/volume)

Operators

α	=	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

~ = reduced quantity

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TABLE 1.

Parameters c, T^*, and ρ^* for Methane and for Water

Methane

$c = 1.031$ (dimensionless)

$T^* = 172.15$ K

$\rho^* = 67.832$ mole/liter

Water

$c = 1.016$ (dimensionless)

$T^* = 759.92 - 364.88 \exp(-736.37 / T)$ K

$\rho^* = r^{(1)} + r^{(2)} \rho$ mole/liter

where

$r^{(1)} = 39.794 + 134.80 \exp(-442.21 / T)$

$r^{(2)} = 1.4741 \exp(-T / 734.59)$

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

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

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, mole/liter	10.1	9.75	17.5	17.8
Z_c	0.287	0.296	0.235	0.242

[a] IUPAC(1978)

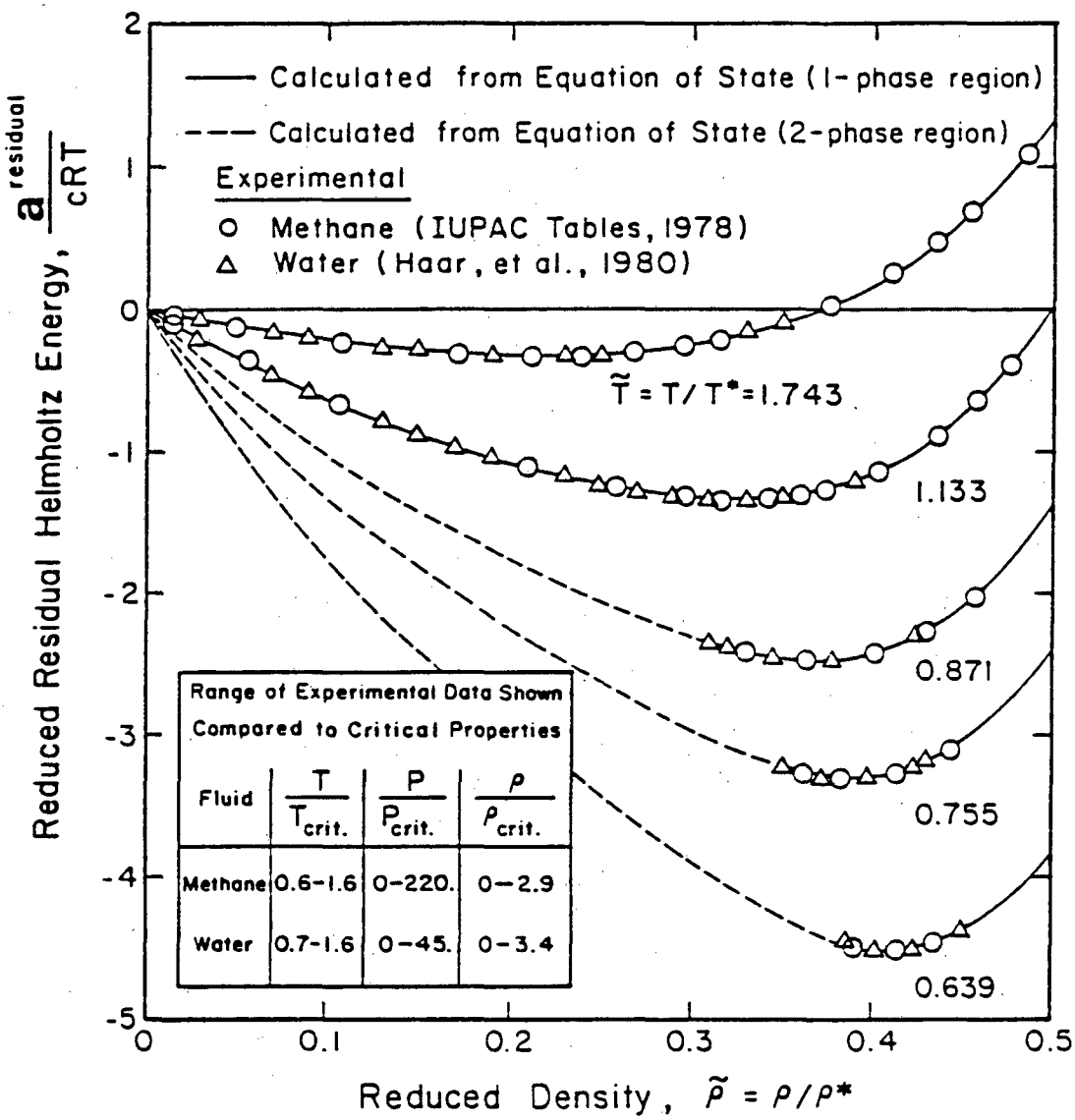
[b] Bain(1964)

TABLE 4.

Recommended Binary Parameters k_{ij} and l_{ij}

for Water/Methane

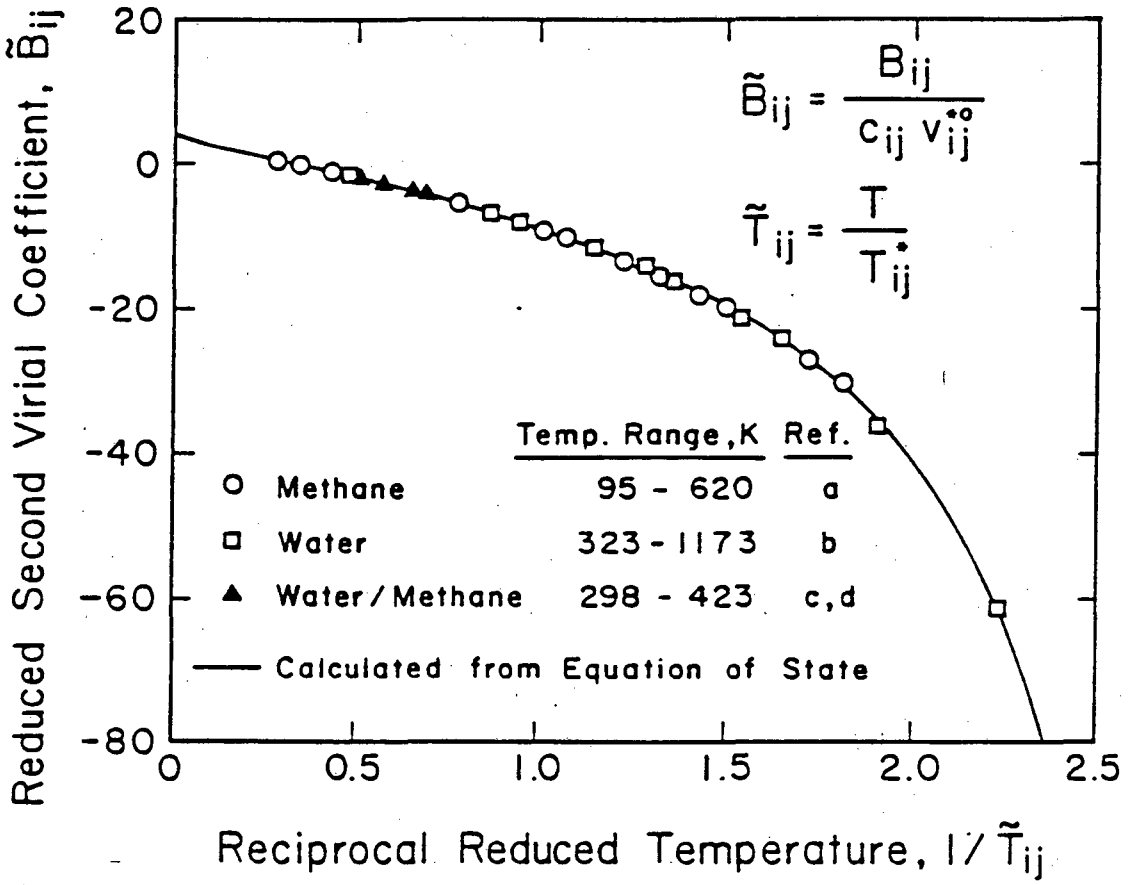
T, K	$k_{ij} x10^3$	$l_{ij} x10^3$
298	205	-27.0
311	200	-19.0
323	196	-13.6
325	195	-12.7
344	190	-5.7
378	181	1.2
411	174	2.5
444	168	0.5
473	163	-1.5
478	163	-1.5
523	150	0.
573	50	0.
603	5	-3.
623	-50	-20.
633	-55	-30.



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.)

XBL 8212-12066

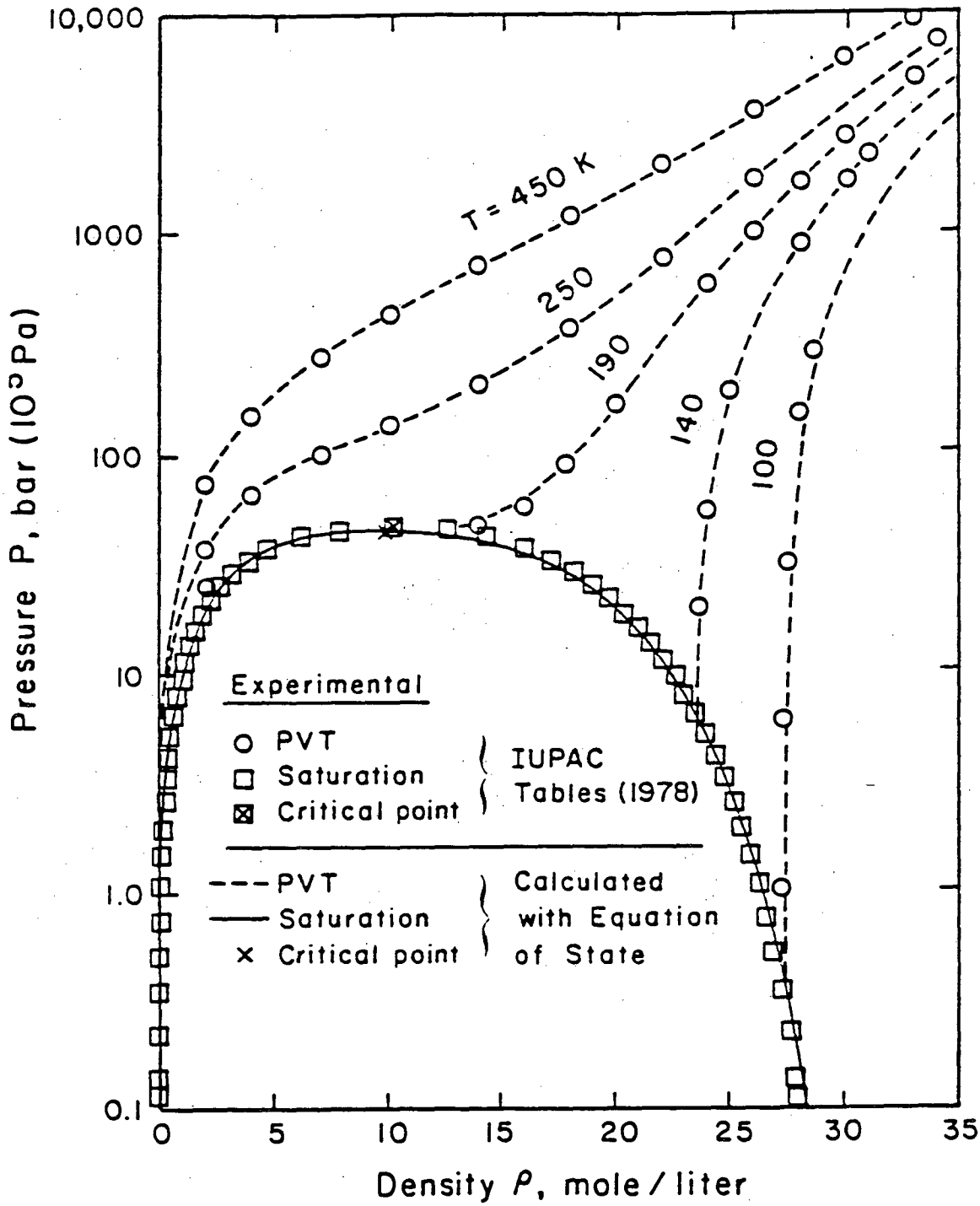
Figure 1



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

XBL 8212-12070

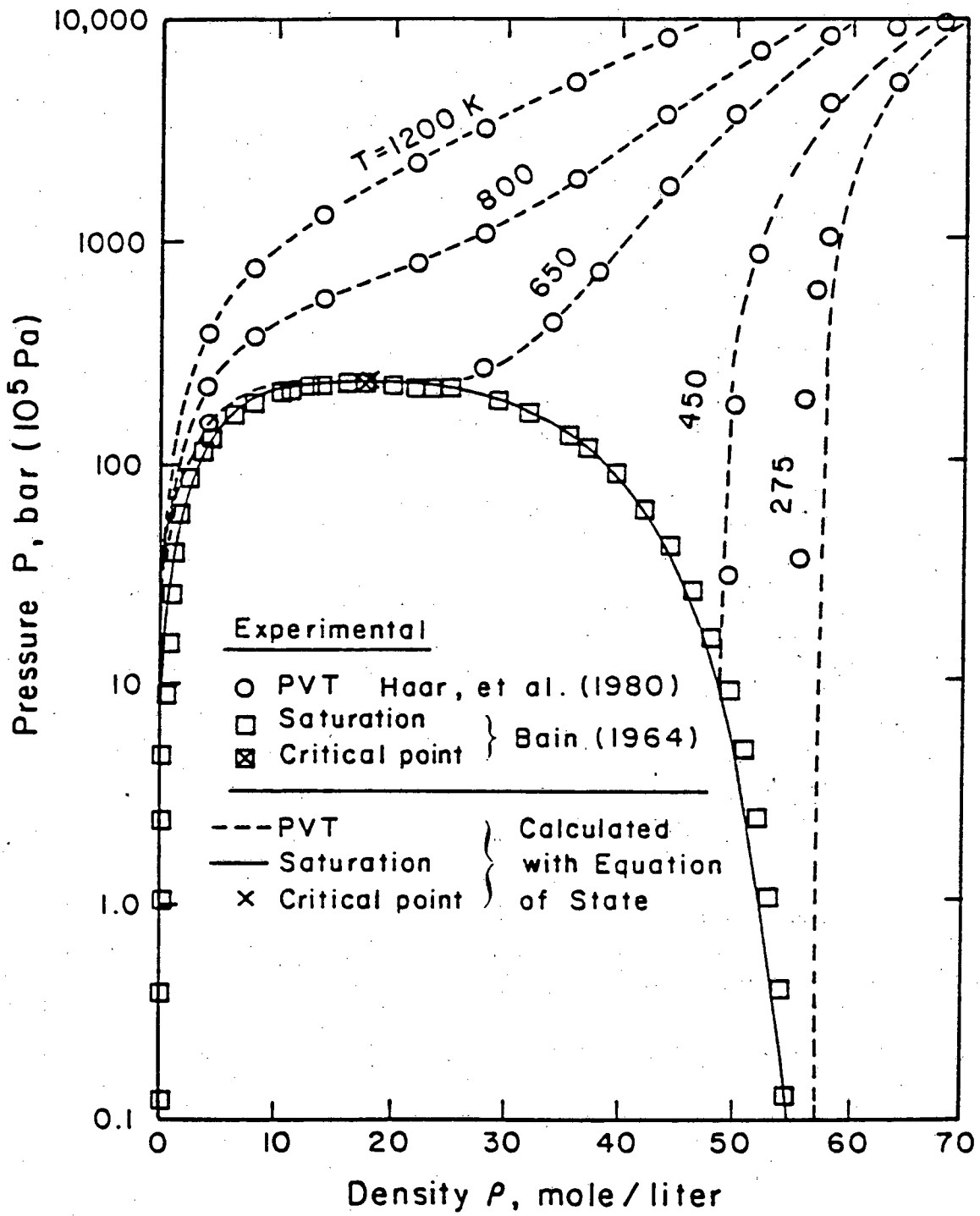
Figure 2



Phase diagram for fluid methane.

XBL 8212-12058

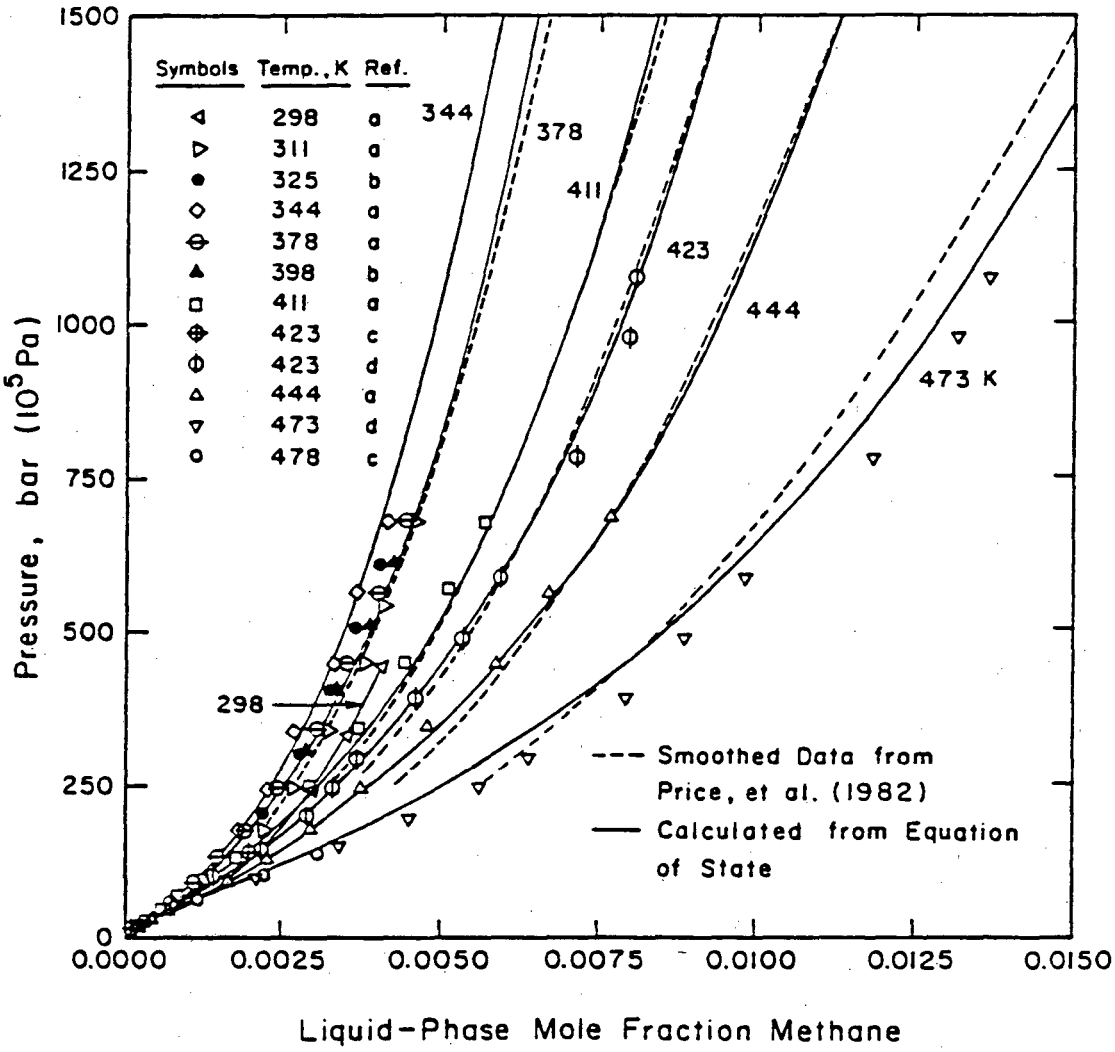
Figure 3



Phase diagram for fluid water.

XBL 8212-12059

Figure 4



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

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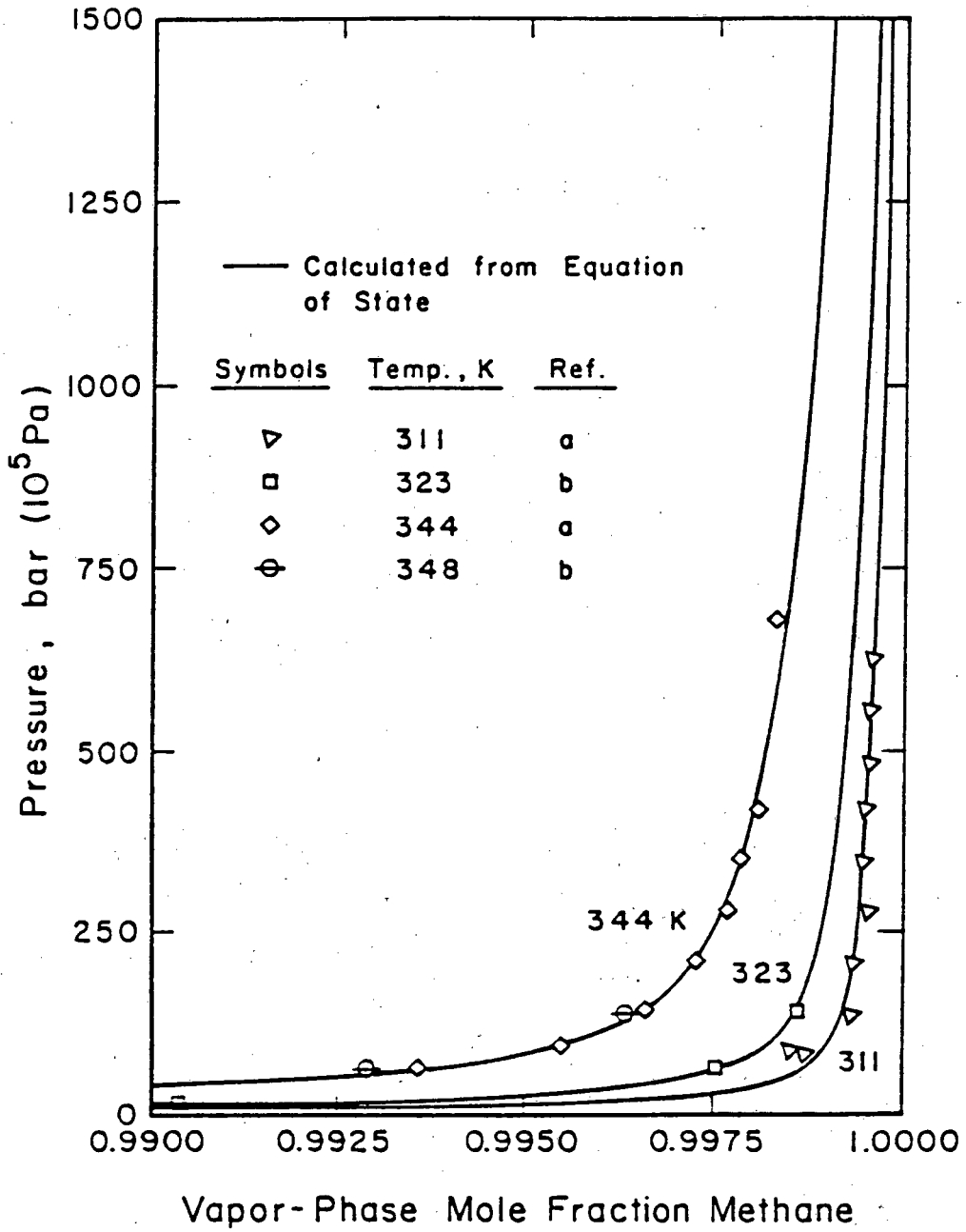
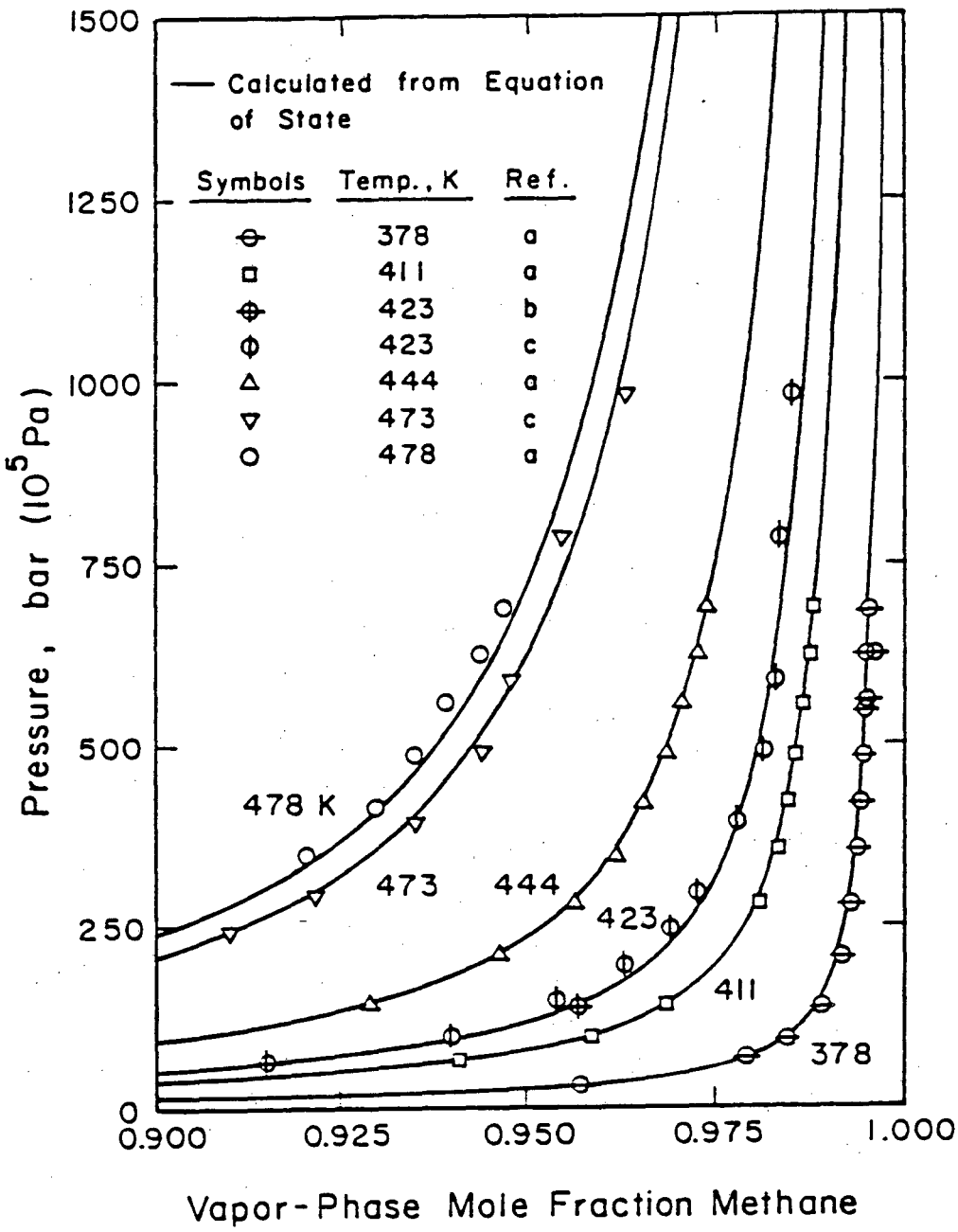
Figure 5



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

Figure 6

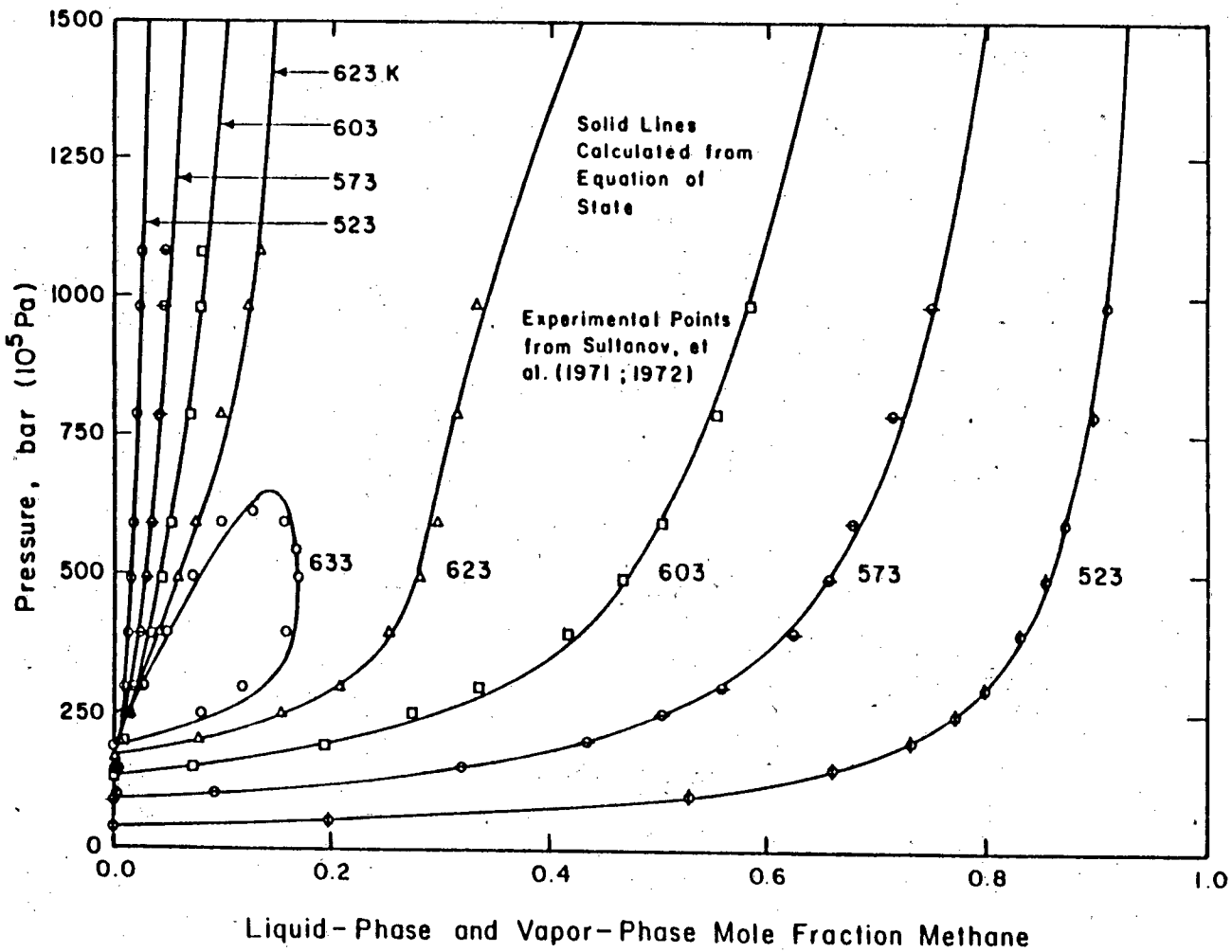
XBL 8212-12061



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

XBL 8212-12068

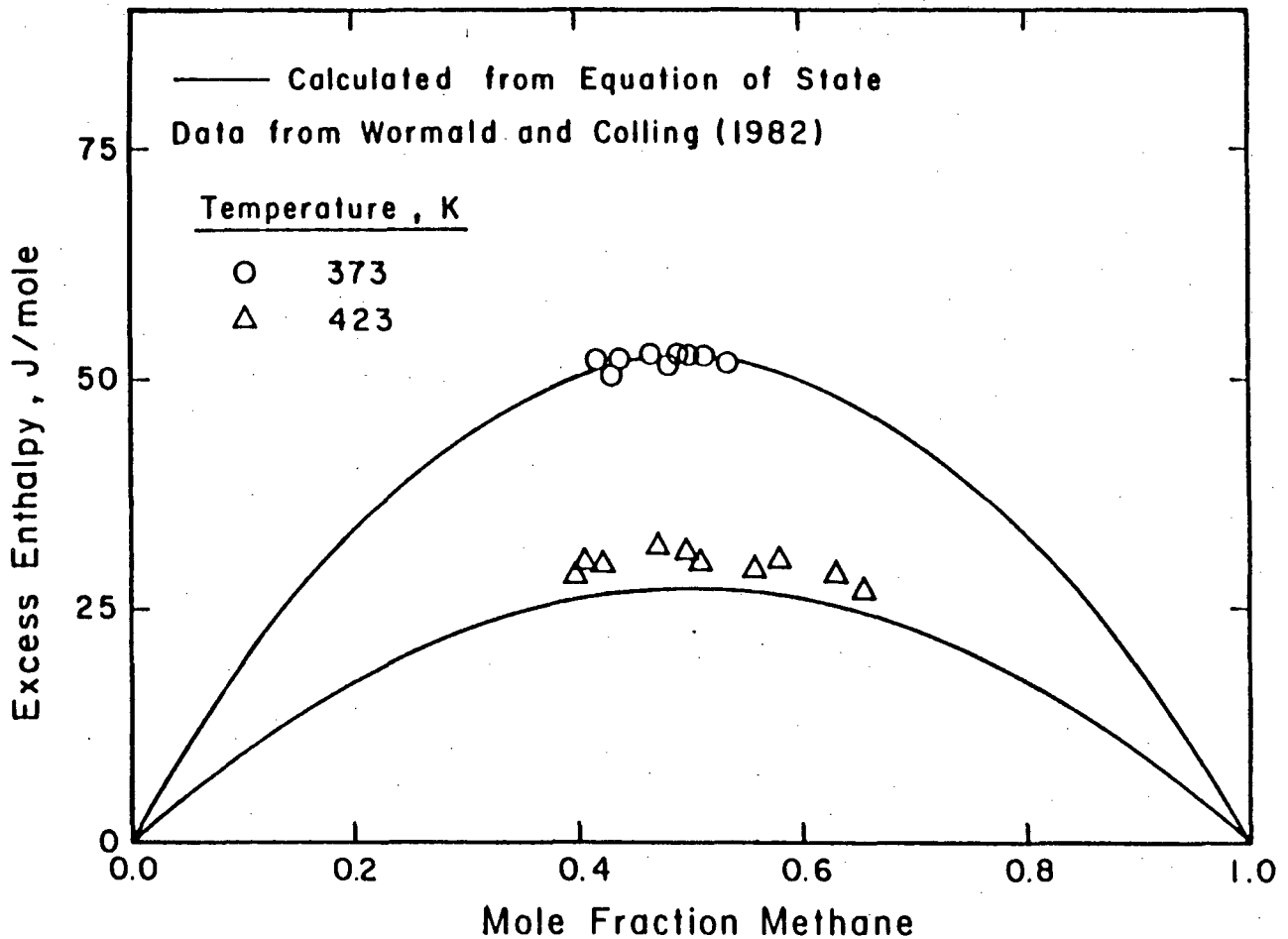
Figure 7



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

XBL 8212-12069

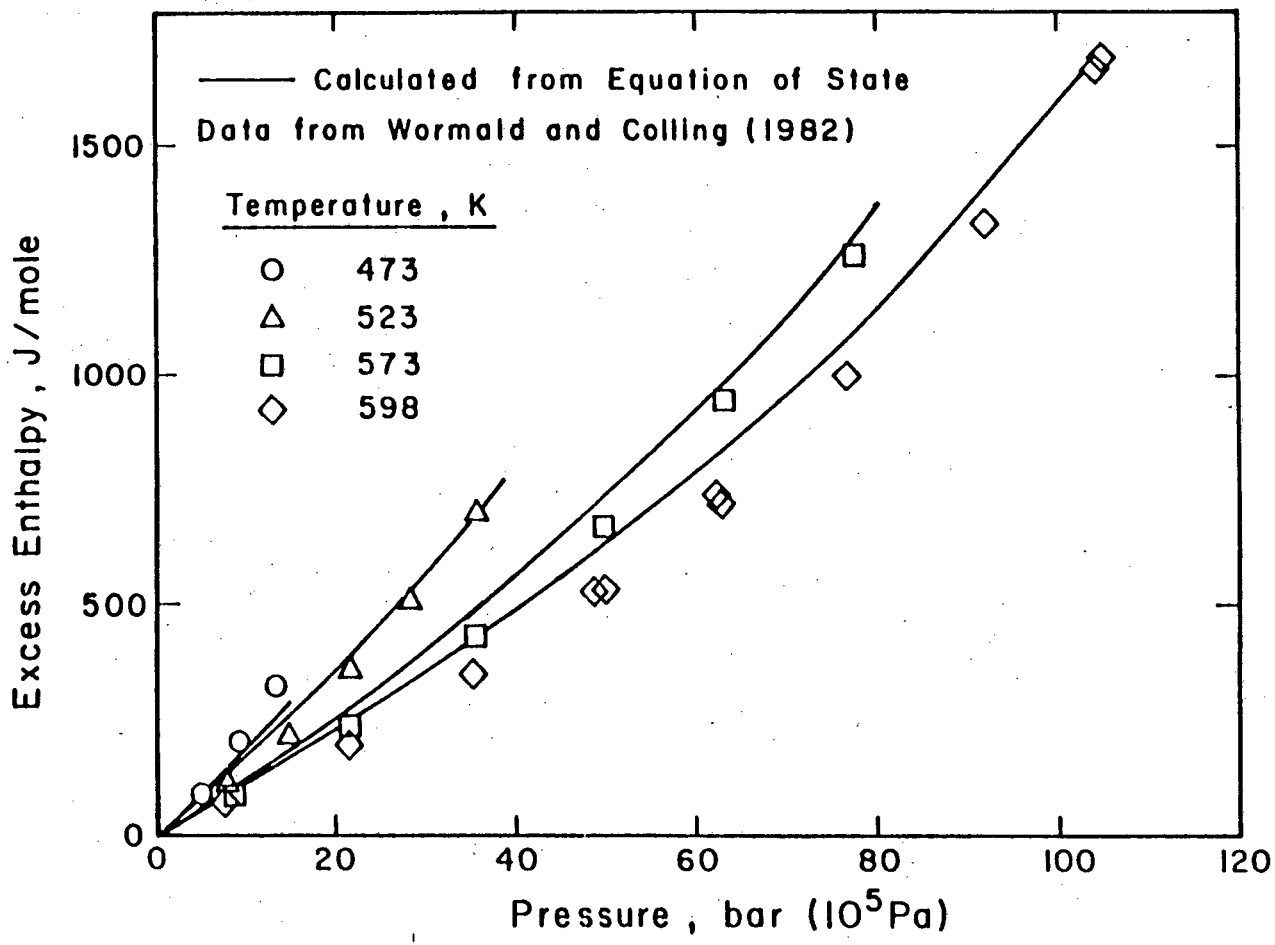
Figure 8



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

XBL 8212-12062

Figure 9



Excess enthalpy for gaseous water/methane at equimolar concentration.

Figure 10

XBL 8212-12063

APPENDIX I

SUPPLEMENTARY MATERIAL FOR:

HIGH-PRESSURE PHASE EQUILIBRIA FOR THE WATER/METHANE SYSTEM

by

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APPENDIX I.A: Calculation of Experimental Residual Helmholtz Energy for Pure Fluids

We define residual Helmholtz energy as the molar Helmholtz energy of a real fluid (vapor or liquid) minus that of an ideal gas at the same temperature T and molar density ρ [See Equation (2)]. Thus,

$$\frac{a^{res}}{RT} = \frac{a}{RT} - \frac{a^{ig}}{RT} \quad . \tag{A1}$$

We introduce, for the real fluid, a reference-state Helmholtz energy $\frac{a^{\delta}}{RT}$, where superscript δ indicates evaluation at the lowest possible gaseous density for which experimental data are available. The behavior of the real fluid and an ideal gas are similar at this very-low-density condition. Introducing this experimental reference state into Equation (A1), we write

$$\frac{a^{res}}{RT} = \frac{a - a^{\delta}}{RT} - \frac{a^{ig} - a^{\delta}}{RT} \quad . \tag{A2}$$

From the definition of Helmholtz energy,

$$\frac{a}{RT} = \frac{h}{RT} - \frac{s}{R} - Z = \frac{u}{RT} - \frac{s}{R} \tag{A3}$$

where h, s, and u are, respectively, the molar enthalpy, entropy, and internal energy. Hence, for the first term to the right of the equal sign in Equation (A2), we can

write for constant temperature

$$\frac{a - a^{\delta}}{RT} = \frac{h - h^{\delta}}{RT} - \frac{s - s^{\delta}}{R} - Z - Z^{\delta} = \frac{u - u^{\delta}}{RT} - \frac{s - s^{\delta}}{RT}. \quad (A4)$$

Many experimental data are available for h, s, Z, u, h^{δ}, s^{δ}, Z^{δ}, and u^{δ} for pure water (Haar, et al., 1980; Bain, 1964), for pure methane (IUPAC, 1978), and for pure argon (IUPAC, 1971) over large ranges of pressure, temperature, and density.

Application of Equation (1) to an ideal gas gives

$$Z^{ig} = \rho \left[\frac{\partial \frac{a^{ig}}{RT}}{\partial \rho} \right]_T = 1 \quad (A5)$$

which implies that at constant temperature

$$d\left(\frac{a^{ig}}{RT}\right) = d \ln \rho \quad . \quad (A6)$$

At reference density ρ^{δ}, the real fluid behaves like an ideal gas. Integration of Equation (A6) from ρ^{δ} to ρ gives the last term in Equation (A2):

$$\frac{a^{ig} - a^{\delta}}{RT} = \ln\left[\frac{\rho}{\rho^{\delta}}\right] \quad . \quad (A7)$$

Combination of Equations (A2), (A4), and (A7) allows calculation of the experimental residual Helmholtz energy.

APPENDIX I.B: Calculation of T^* and ρ^* for Argon

As shown in Figure 1, a plot of experimental resiidual Helmholtz energy versus density produces concave-up isotherms. At temperatures less than the Boyle temperature (where second virial coefficient B = 0), the isotherms go through a minimum with respect to density. Defining ρ_{min} as the density at which $\frac{a^{res}}{RT}$ is a minimum, we find for argon that a plot of experimental ρ_{min} versus temperature T, on Cartesian coordinates, produces a straight line. The T-axis intercept $T_{intercept}$ equals the Boyle temperature. The ρ_{min}-axis intercept $\rho_{intercept}$ (extrapolated) seems to be related to the close-packed density of the molecules at zero temperature. By doing a linear, least-squares regression on such a plot for argon, we obtain: $T_{intercept}$ = 408.73 K and $\rho_{intercept}$ = 46.595 mole/liter. We derive T^* and ρ^* from $T_{intercept}$ and $\rho_{intercept}$ as follows.

T^* and ρ^* may be related to molecular properties (Alder, et al., 1972; Carnahan and Starling, 1969) by

$$T^* = \frac{\varepsilon}{ck} \tag{B1}$$

and

$$\rho^* = \left[\frac{N_A \pi \sigma^3}{6}\right]^{-1} = \left[\frac{\pi v_o V2}{6}\right]^{-1} \tag{B2}$$

where: c = 1 for argon; ε is the maximum depth of the pair-potential energy; σ is the molecular diameter; v_o is the close-packed volume; k is Boltzmann's constant; and, N_A is Avogadro's number. For argon, Dymond and Alder (1969) found $\frac{\varepsilon}{k}$ = 138.2 K and σ = 3.28 A. By arbitrarily defining

$$\rho^* = \frac{\rho_{intercept}}{(\frac{\pi}{6})} \tag{B3}$$

and

$$T^* = \frac{T_{intercept}}{(\frac{2\pi V2}{3})} \tag{B4}$$

we obtain, for argon,

$$T^* = \frac{\varepsilon}{ck} = 138.01 \text{ K} \tag{B5}$$

$$\rho^* = 88.990 \text{ mole/liter} \tag{B6}$$

and from Equation (B2)

$$\sigma = 3.291 \text{ A} \tag{B7}$$

which agree very well with the results of Dymond and Alder. For reference fluid argon, therefore, we choose the ρ^* and T^* given in Equations (B5) and (B6).

From Equations (7), (8), (B5), and (B6), we can obtain shape factors Θ_T and Θ_ρ. For argon (IUPAC, 1971),

T_c = 150.860 K and ρ_c = 13.410 mole/liter giving

$$\theta_{T,Ar} = \frac{T^*}{T_c} = \frac{138.01}{150.86} = 0.91482 \tag{B8}$$

and

$$\rho_{\rho,Ar} = \frac{\rho^*}{\rho_c} = \frac{88.990}{13.410} = 6.6361 \quad . \tag{B9}$$

We now compare θ_T and θ_ρ for pure argon and for pure methane. For methane (See Table 1 and IUPAC, 1978) we get

$$\theta_{T,CH_4} = \frac{T^*}{T_c} = \frac{172.15}{190.56} = 0.9034 \tag{B10}$$

and

$$\theta_{\rho,CH_4} = \frac{\rho^*}{\rho_c} = \frac{67.832}{10.110} = 6.709 \quad . \tag{B11}$$

Thus,

$$\frac{\theta_{T,CH_4}}{\theta_{T,Ar}} = 0.988 \tag{B12}$$

and

$$\frac{\theta_{\rho,CH_4}}{\theta_{\rho,Ar}} = 1.011 \quad . \tag{B13}$$

These ratios are close to unity, as is to be expected for simple fluids.

APPENDIX I.C: Comparison of Calculated and Experimental Excess Volumes for the Water/Methane System

Figures C1-C3 show calculated and experimental excess volumes for the water/methane at 523, 573, and 623 K and at several pressures. The experimental points are from Bazaev, et al. (1974). The solid lines were calculated from our equation of state using the l_{ij} and k_{ij} parameters reported in Table 4. Calcualtion and experiment are in qualitative agreement. In all cases shown, the experimental and calculated excess volumes are positive. Often, however, the magnitude of the calculated excess volume is only half that of the experimental value. The discrepancy could be due to experimental error, or to inability of the equation of state to give correct quantitative behavior, or to both.

The excess volume in Figures C1-C3 is less than 15 percent of the total mixture volume, making difficult the attainment of good experimental accuracy. Skripka (1979) reports experimental cross second virial coefficients B_{ij} for water/methane mixtures. The trend of these B_{ij} values is not in agreement with the experimental B_{ij} values of Wormald and Colling (1982) and Rigby and Prausnitz (1964), whose data superimpose well on the plot of $\tilde{B}_{ij}$ versus $1/\tilde{T}_{ij}$ shown in Figure 2. Skripka's B_{ij} values are too

positive at temperatures greater than about 500 K and are much too negative at temperatures less than 500 K. This trend would give excess volumes too positive above 500 K. If Bazaev, et al., obtained experimental excess volumes for water/methane from the same data that Skripka used to derive experimental cross second virial coefficients, then this could explain the discrepancy between calculation and experiment in Figures C1-C3.

NOTATION

h	=	molar enthalpy
k	=	Boltzmann's constant
N_A	=	Avogadro's number
s	=	molar entropy
u	=	molar internal energy
v_o	=	molecular close-packed volume

Greek Letters

ε	=	maximum depth of pair-potential energy
π	=	pi (3.14159...)
σ	=	molecular diameter

Subscripts

Ar	=	argon
CH_4	=	methane
intercept	=	intersection of straight line with a coordinate axis
min	=	minimum in isothermal residual Helmholtz energy

Superscripts

δ	=	very-low-density reference state

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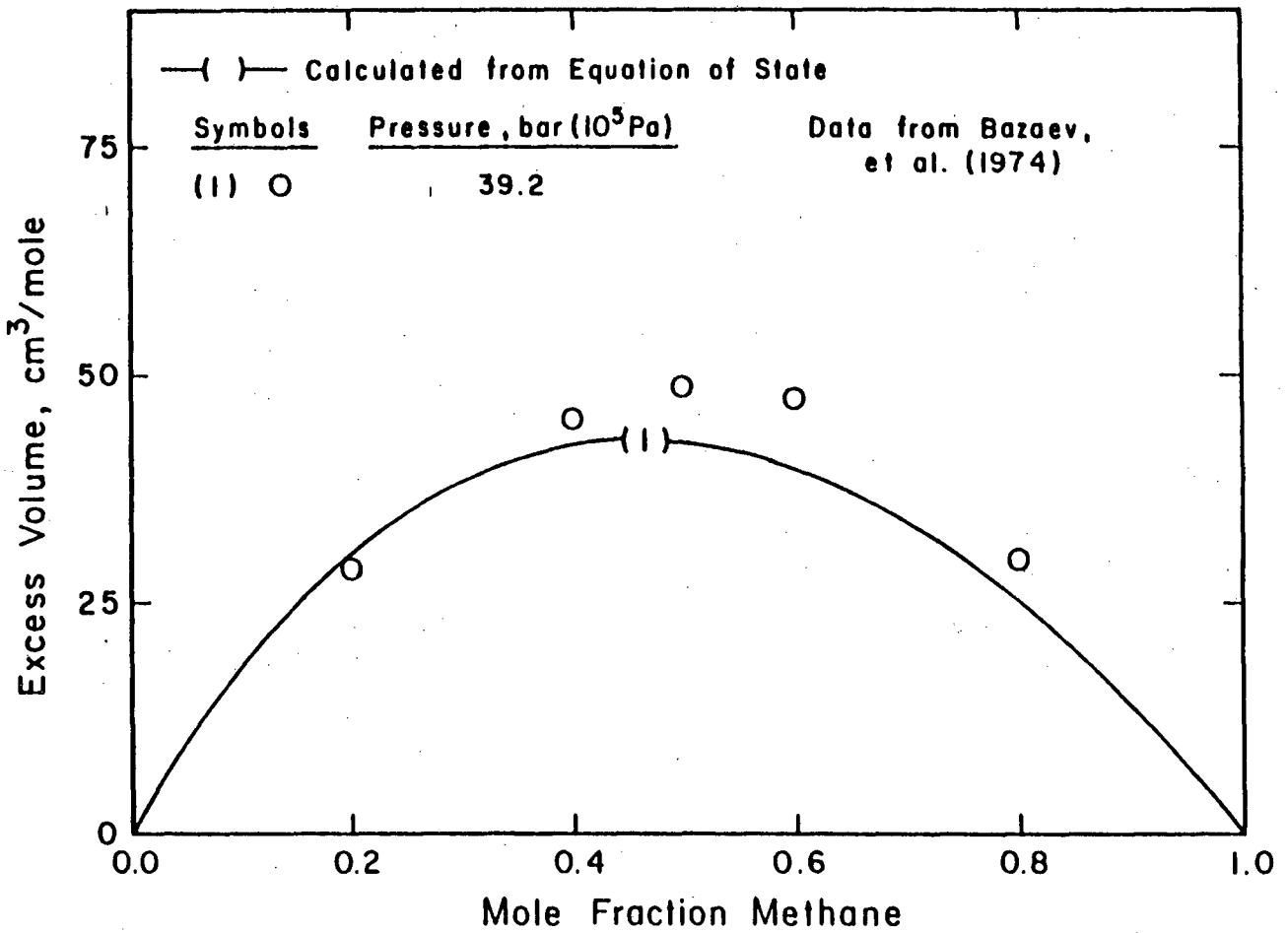
Dymond, J. H., and B. J. Alder, "Pair Potential for Argon," J. Chem. Phys., 51, 309 (1969).

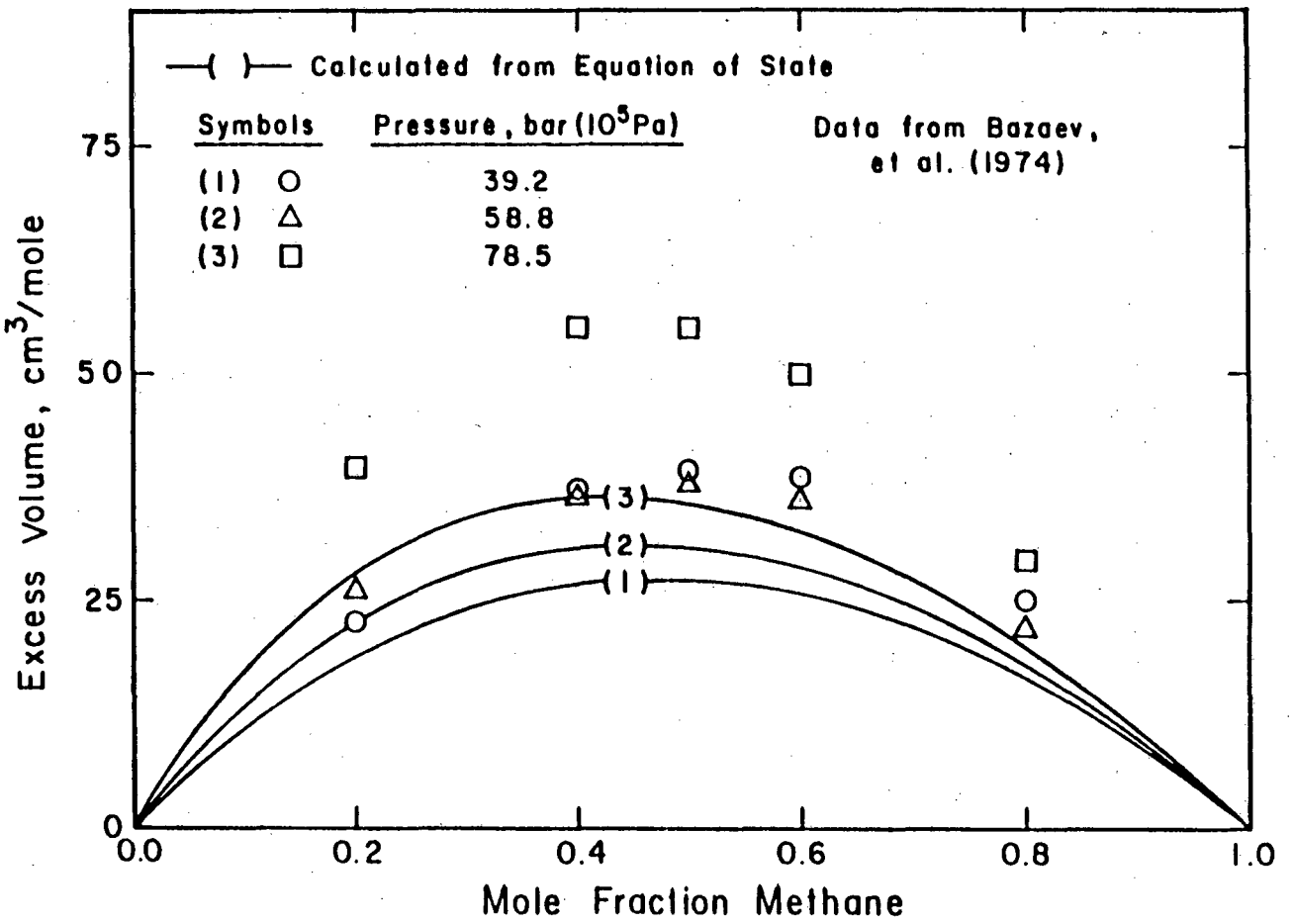
Skripka, V. G., "Volume Behavior of Gaseous Mixtures of a Non-polar Component and Water at High Temperatures," Russ. J. Phys. Chem., 53, 795 (1979).



Excess volumes for water/methane at 523 K.

XBL 8212-12065

Figure C1



Excess volumes for water/methane at 573 K.

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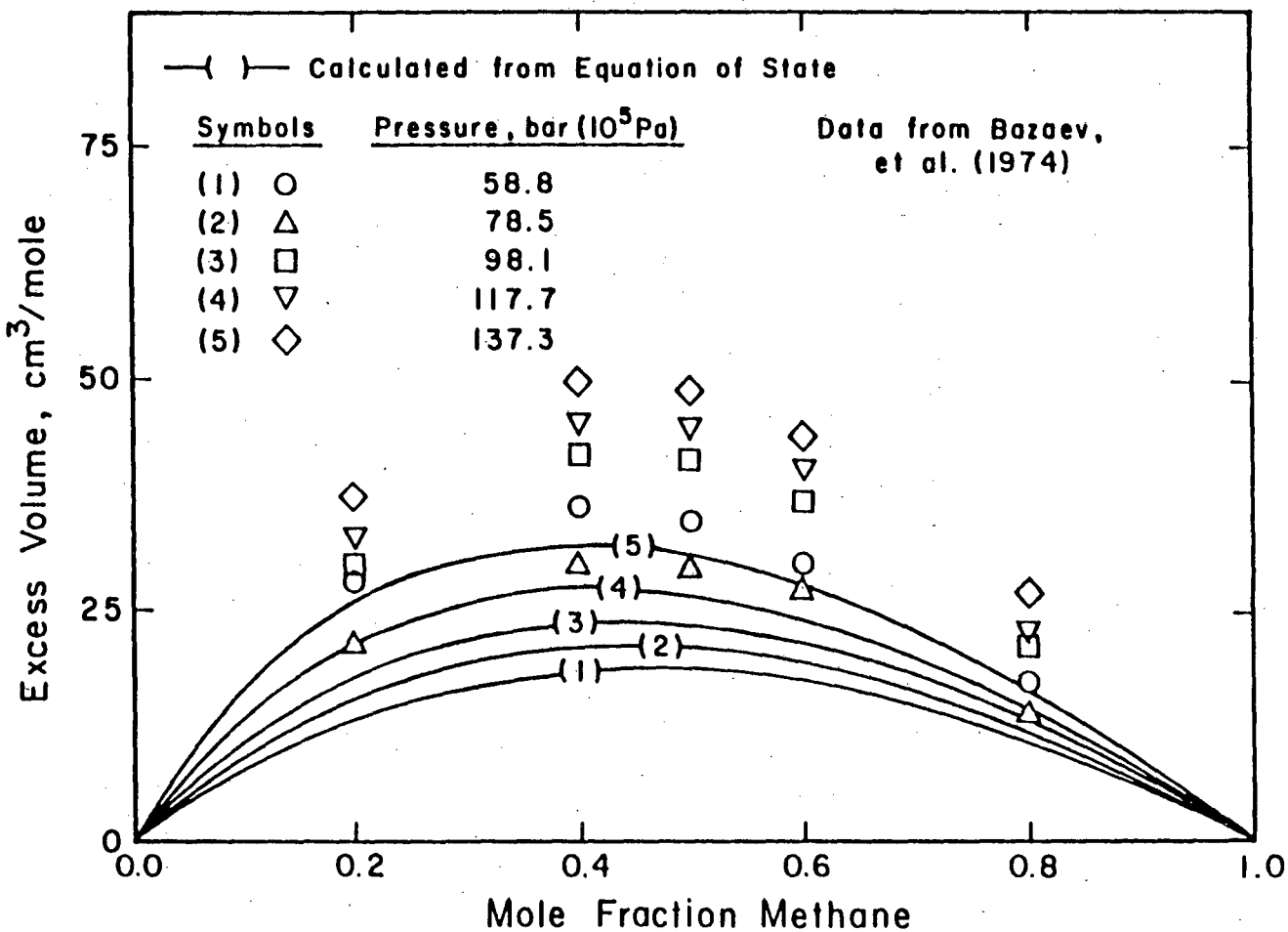
Figure C2



Excess volumes for water/methane at 623 K.

XBL 8212-12060

Figure C3

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