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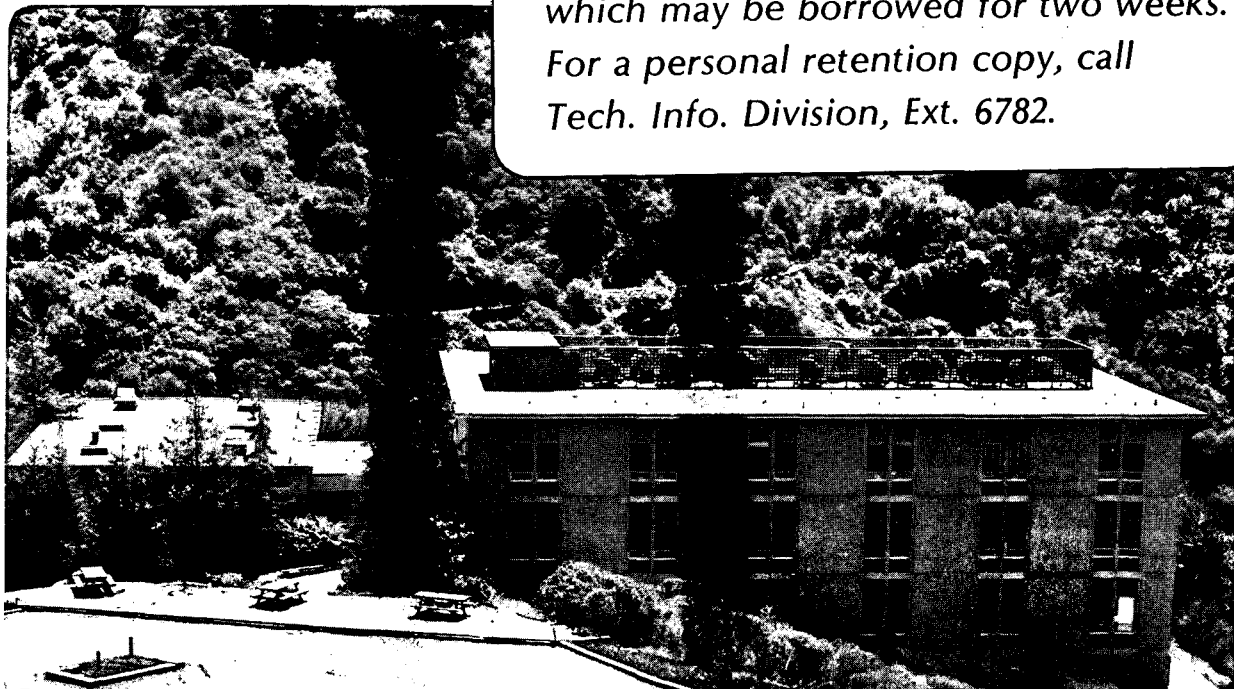## UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

EMPIRICAL CORRECTIONS TO THE VAN DER WAALS
PARTITION FUNCTION FOR DENSE FLUIDS

V. Brandani and J.M. Prausnitz

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EMPIRICAL CORRECTIONS TO THE VAN DER WAALS

PARTITION FUNCTION FOR DENSE FLUIDS

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ABSTRACT

A simple equation of the van der Waals form is used to fit thermodynamic data for methane in the region 100 to 600K and pressures to 600 bar. Only two temperature-dependent constants are used. In determining constants, particular attention is given to vapor-pressure data well below the critical temperature and to superheated volumetric data well above the critical temperature. With these constants, calculated second virial coefficients are in error as is the two-phase boundary in the critical region.

Upon adding simple analytic correction functions to the calculated Helmholtz energy, agreement with experiment is very much improved. For the region 2-12K below the critical temperature, the calculated critical exponent $\beta = 0.38$, in good agreement with experiment ($\beta = 0.36$). These empirical corrections may suggest new techniques for establishing theoretical modifications to improve the van der Waals model.

Much attention has been given to the van der Waals model for fluids; numerous equations of state of the van der Waals form have been proposed.[1,2] Agreement between experimental and calculated thermodynamic properties is generally good only in those regions of temperature and density which are used to determine equation-of-state constants; such good agreement is also restricted to those properties used in data reduction. For example, if constants are determined from saturated-pressure data in the two-phase region, calculated vapor pressures agree well with those observed but calculated saturated liquid densities may differ appreciably from experiment.

In-depth studies of the van der Waals model indicate that the model is best at high temperatures and high densities; it is poor at low temperatures and low densities because one key van der Waals assumption (uniform field of force) is then invalid. Therefore, as has often been observed,[3,4] if equation-of-state constants are fixed from data at high densities, calculated second virial coefficients deviate from those observed, especially at low temperatures.

Further, the van der Waals model is unsuccessful in the critical region. When constants are fixed from data remote from critical conditions, the calculated two-phase region is considerably larger than that observed.

To understand better the deficiencies of the van der Waals model, this work reports empirical modifications needed to overcome the two shortcomings mentioned above: poor second virial coefficients and poor two-phase region near the critical temperature. The modification reported here are those for a flexible form of the popular Redlich-Kwong equation of state, applied to methane, for which reliable experimental data are available. While the details of the modifications are necessarily specific for the equation of state chosen, the general form of these modifications appears to be applicable

to other similar equations, including perturbed-hard-sphere equations using a theoretical (Percus-Yevick) form for the repulsive part.

The modifications discussed here are successful in the sense that they very much improve agreement with experiment. The calculated second virial coefficient is improved without decreasing agreement at higher densities. More important, the two-phase dome near the critical temperature is now dramatically improved.

The modifications are in the form of correction functions added to the Helmholtz energy. These functions are analytic and therefore they do not satisfy the current view that a "true" equation of state at the critical point cannot be analytic. The authors are not disputing that view but they want to show that analytic correction functions can very much improve the performance of a simple equation of state in the region close to the critical point.

Most recent theoretical work on the van der Waals model has been concerned with techniques for expressing the hard-core diameter (cut-off parameter) as a function of temperature and density.[5,6] This approach gives a highly inconvenient result for practical work. We are therefore reporting here our empirical studies using analytic corrections.

1. <u>Partition Function and Equation of State</u>

The canonical partition function Q of a simple fluid at temperature T and volume V is assumed to be given by the generalized van der Waals form

$$(1-1)$$

$$Q = \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N \left(\frac{V_f}{V} \right)^N \left[\exp\left(-\frac{\phi}{2kT} \right) \right]^N \left(q_{int} \right)^N$$

where N is the number of molecules, Λ is the de Broglie wavelength, V_f is the free volume, ϕ is the potential, k is Boltzmann's constant and q_{int} stands for contributions from internal (density-independent) degrees of freedom. The equation of state is then given by the well-known relation

$$P = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N} \qquad (1-2)$$

where P is the pressure.

An empirically successful equation of state is that proposed by Redlich and Kwong. To obtain a generalized form of that equation, we specify[7]

$$(1-3)$$
$$V_f = \left(1 - \tilde{\rho} \right) V$$

$$\phi = - \frac{2a}{N_A b} \ln \left(1 + \tilde{\rho} \right) \qquad (1-4)$$

where $\tilde{\rho}$ is a reduced density ($\tilde{\rho} = Nb/N_A V$); N_A is Avogadro's number and

$$b = (2/3) \pi N_A \sigma^3 \qquad (1-5)$$

with σ = hard-core diameter which may depend on temperature. The quantity a, independent of density, may also depend on temperature. At a characteristic

temperature (e.g. the critical temperature), the quantity a/b represents a characteristic potential energy.

Substitution gives the generalized Redlich-Kwong equation of state

$$(1\text{-}6)$$

$$z = \frac{Pv}{RT} = \frac{1}{1-\tilde{\rho}} - \left(\frac{a}{b}\right)\left(\frac{1}{RT}\right)\left(\frac{\tilde{\rho}}{1+\tilde{\rho}}\right)$$

where z is the compressibility factor and molar volume $v = N_A V/N$.

2.   Data Reduction

For methane, the critical temperature is   190.555 K.
To obtain parameters a and b as functions of temperature, experimental data[8] were used for twelve isotherms (six between 100-150 and six between 240-500K). At temperatures below the critical, particular attention was given to vapor-pressure data and to saturated liquid densities. At temperatures above the critical, particular attention was given to volumetric data in the region 10 to 650 bars. Data reduction was achieved using the principle maximum likelihood, as discussed by Anderson.[9]

The results were fitted to empirical equations

$$a = a^{(o)}\left[1 + a^{(1)} \exp\left(-\frac{a^{(2)}}{T_R}\right)\right] \qquad (2\text{-}1)$$

$$b = b^{(o)}\left[1 + b^{(1)} \exp\left(-\frac{b^{(2)}}{T_R}\right)\right]$$

$$(2\text{-}2)$$

where $T_R = T/T_c$ and T_c is the critical temperature. The six constants of Equations (2-1) and (2-2) are given in Table 1. Plots of these equations are shown in Figure 1.

It is not surprising that "constant" a rises with decreasing temperature. However it is surprising that "constant" b falls with decreasing temperature. Due to the scatter in b , any attempt to interpret this surprise must be viewed with skepticism. A first thought is to ascribe the unexpected behavior to the poor repulsive term in the Redlich-Kwong equation but when similar calculations were carried out using a Carnahan-Starling form for the repulsive

term, a similar trend with temperature was observed. If we regard "constant" b as a characteristic volume proportional to the close-packed volume, it is a little easier to interpret why b may rise with temperature because data reduction is performed over a finite pressure range. The close-packed volume is achieved only at zero kelvin or at infinite pressure. Since the experimental data used here are well above zero kelvin and at pressures well below those where pressure has only a minimal effect on density, we can see that the "experimental" close-packed volume obtained from data reduction rises with temperature in the same sense that the volume of a solid rises with temperature unless very high pressure is imposed.

Figure 2 compares a calculated pressure-density diagram with experimental results for methane. The calculated critical pressure is in good agreement with experiment but the calculated critical temperature and density are not. Calculated saturated-vapor densities are too low, especially in the critical region.

The second and third virial coefficients are given by

$$B = b\left(1 - \frac{a}{bRT}\right) \tag{2-3}$$

$$C = b^2\left(1 + \frac{a}{bRT}\right) \tag{2-4}$$

For methane, these calculated virial coefficients agree reasonably well with experiment[10] as shown by the dashed lines in Figures 3 and 4.

To calculate the two-phase boundaries in Figure 2, it was necessary first to find the residual molar Helmholtz energy a^r from the equation of state, Equation (1-6). This is given by

$$a^r = \int_v^\infty \left[P - \frac{RT}{v}\right] dv \tag{2-5}$$

Here the residual molar Helmholtz energy is the molar Helmholtz energy of the real fluid at T and v minus that of the ideal gas at the same T and v.

3. Empirical Corrections

To improve agreement with experiment, we propose to add two corrections to Equation (2-5):

$$a^r = a^r\left(Eq.\ 2.5\right) + \Delta a^{SV} + \Delta a^{TP} \tag{3-1}$$

where superscript SV stands for second-virial and superscript TP stands for two-phase. The first correction is to improve agreement at low densities,

in particular, the second virial coefficient. The density range of this correction is fixed so as to improve also the third virial coefficient as suggested by El-Twaty[11] and as briefly discussed by Dzialoszynski.[12]

The second correction is to improve agreement with the experimental two-phase boundary, especially in the critical region.

For the first correction term, we propose

$$\frac{\Delta a^{SV}}{RT} = \eta \, \tilde{\rho} \, \exp\left(-\lambda \tilde{\rho}\right) \tag{3-2}$$

where

$$\eta = \frac{B(\text{experimental}) - B(\text{Equation 2-3})}{b} \tag{3-3}$$

and where λ is a temperature-independent parameter to determine the density range of the correction; this range (in reduced terms) is given by $1/\lambda$. For methane we propose $\lambda = 3$, a value close to that found by El-Twaty in his study of argon using perturbed-hard-sphere (Carnahan-Starling) equation of state.

From second-virial-coefficient data for methane, we obtain the empirical equation

$$\eta = \left[0.3707 - 0.08621 \, T_R^{-6}\right]\left[1 - \exp\left(-\frac{1}{T_R}\right)\right] \tag{3-4}$$

This equation has the desireable limit $\eta \to 0$ as $T_R \to \infty$.

For the second correction term, we propose

$$\frac{\Delta a^{TP}}{RT} = \propto \left[(\tilde{\rho}-\delta)^2 - \delta^2\right]^2 \left[\exp\left\{-\tau(\tilde{\rho}-\delta)^2\right\}\right] \tag{3-5}$$

where α and τ are independent of temperature but δ is not.

The compressibility factors is now given by

$$z = z\left(Eq.\ 1.6\right) + \eta\,\tilde{\rho}\left(1-\lambda\tilde{\rho}\right)\exp\left(-\lambda\tilde{\rho}\right) +$$

$$+\ 2\alpha\,\tilde{\rho}^2\left(\tilde{\rho}-\delta\right)\left(\tilde{\rho}-2\delta\right)\left[2-\tau\tilde{\rho}\left(\tilde{\rho}-2\delta\right)\right]\exp\left\{-\tau\left(\tilde{\rho}-\delta\right)^2\right\}$$

(3-6)

Equation (3-5) has no effect on the second virial coefficient but contributes to the third virial coefficient. These corrected virial coefficients are

$$B\left(corrected\right) = B\left(Eq.\ 2.3\right) + b\eta \tag{3-7}$$

$$C\left(corrected\right) = C\left(Eq.\ 2.4\right) - 2\,b^2\left[\lambda\eta - 4\alpha\,\delta^2\exp\left(-\tau\,\delta^2\right)\right] \tag{3-8}$$

To find parameters α, τ and δ (T_c) we use the experimental value of z_c $\left(z_c = \dfrac{P_c v_c}{RT_c}\right)$ which, for methane is 0.290. Further, we use the relations at the critical point

$$\tilde{\rho}\left(\frac{\partial z}{\partial\tilde{\rho}}\right)_c = -\,z_c \tag{3-9}$$

$$\tilde{\rho}^2\left(\frac{\partial^2 z}{\partial\tilde{\rho}^2}\right)_c = 2\,z_c \tag{3-10}$$

which follow from the well-known relations

$$\left(\frac{\partial P}{\partial v}\right)_c = \left(\frac{\partial^2 P}{\partial v^2}\right)_c = 0 \qquad (3-11)$$

We obtain $\gamma = 0.4982$, $\tau = 27.0$ and $\delta(T_c) = 0.4035$.

To fix the effect of temperature on δ, we use saturated-volume data at $T_R < 1$ and the condition that δ should become small as $T_R > 1$. We use the empirical relation

$$\delta = \delta(T_c) + \delta^{(1)}\left[\frac{1}{T_R} - 1\right] + \delta^{(2)}\left[\frac{1}{T_R^2} - 1\right] \qquad (3-12)$$

with $\delta^{(1)} = 0.86$ and $\delta^{(2)} = -0.1494$.

4. Results

Figures 3 and 4 compare calculated and experimental virial coefficients. The calculated second virial coefficient is now in essentially perfect agreement with experiment as required by Equation (3-3). The third virial coefficient is much improved, at least for temperatures above the critical.

Figure 5 compares a calculated pressure-density diagram with experiment. Agreement is now much better than that shown in Figure 2. Figure 6 shows a few isotherms in the critical region to indicate that these isotherms are well behaved, showing no spurious maxima or minima.

Figure 7 shows the two correction functions plotted isothermally against reduced density. At low temperatures, the large maximum in Δa^{TP} probably has no physical significance because it occurs in a physically unattainable region.

At low temperatures, the correction Δa^{SV} is negative.

Finally, Figure 8 shows a logarithmic scaling plot of $|\rho^s - \rho(T_c)|$ versus $T_c - T$ for temperatures below T_c; here ρ^s is the saturated density. This plot was prepared to determine the scaling parameter β given in the equation

$$\left| \rho^s - \rho(T_c) \right| \sim \left(T_c - T \right)^{\beta} \tag{4-1}$$

When the corrected equation of state is used, $\beta \simeq 0.38$ in the range $T_c - T = 2 - 12K$. This calculated result agrees well with the experimental value $(\beta = 0.36)$ but is larger than the theoretical (Ising) result $\beta = 0.325$. Very close to the critical point, our equation of state necessarily gives the mean-field result $\beta = 0.5$.

5. Conclusion

The calculations reported here suggest that two well-known weaknesses in the van der Waals model for fluids can be corrected by adding to the calculated Helmholtz energy analytical correction functions with only a few empirical coefficients. These correction functions improve agreement with experiment for the second and third virial coefficients and for the two-phase region at temperatures near the critical. These empirical corrections may suggest to theorists how a more fundamental correction to the van der Waals model may be constructed without resorting to the currently popular but inconvenient method where the hard-sphere diameter (cut-off parameter) is a function of both temperature and density.

Acknowledgement

Table I

CONSTANTS FOR EQUATIONS (2-1) AND (2-2)

|	
$a^{(0)}$, bars x (liters/mole)^2	3.284
$a^{(1)}$	-8.612×10^{-1}
$a^{(2)}$	1.160
$b^{(0)}$, cm^3/mole	2.935×10^{1}
$b^{(1)}$	7.142×10^{-2}
$b^{(2)}$	1.054

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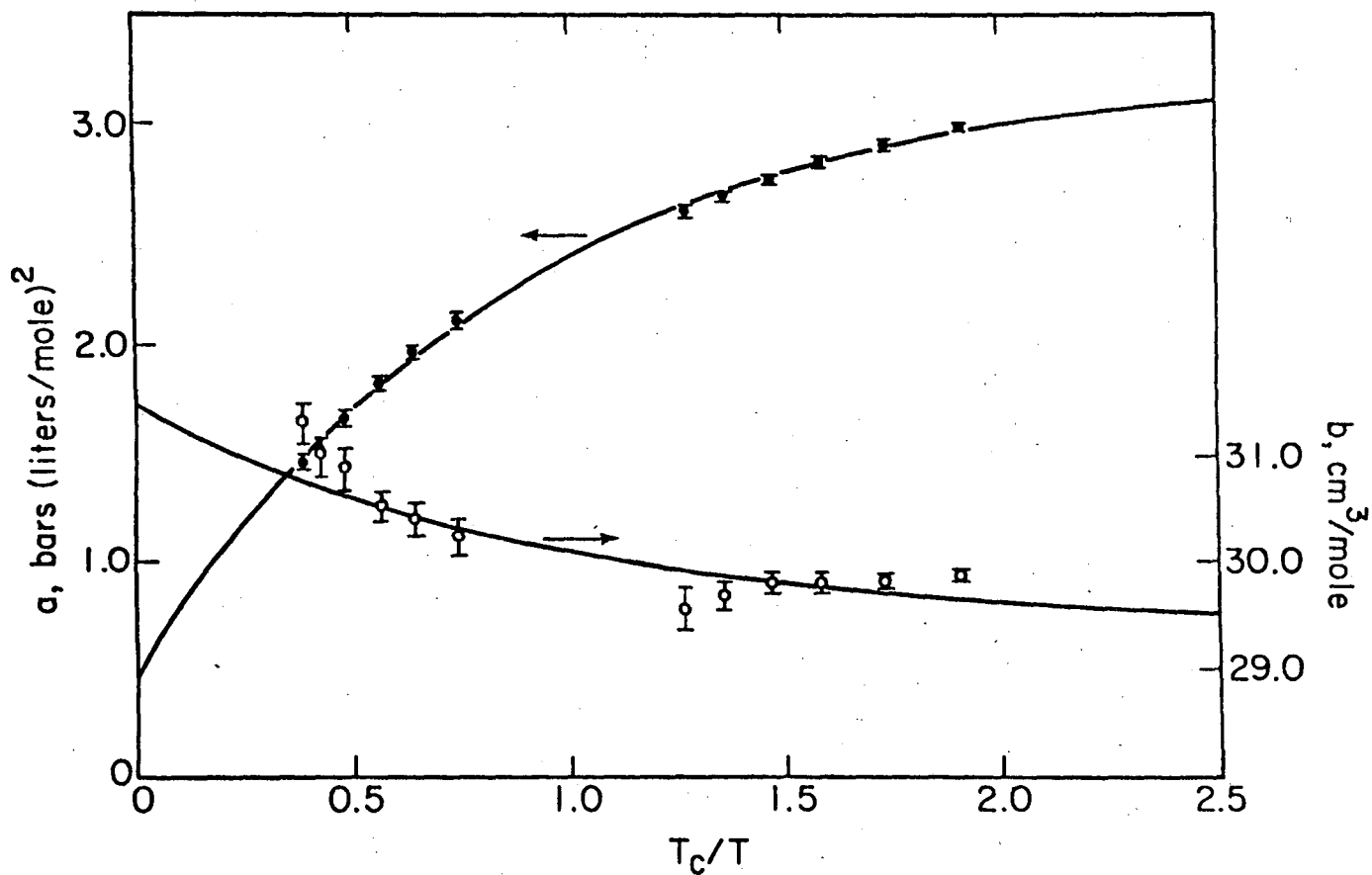
CONSTANTS a AND b AS DETERMINED FROM VAPOR-PRESSURE,
SATURATED-DENSITY AND SUPERHEATED-VOLUMETRIC DATA,
BUT OMITTING DATA IN THE CRITICAL REGION
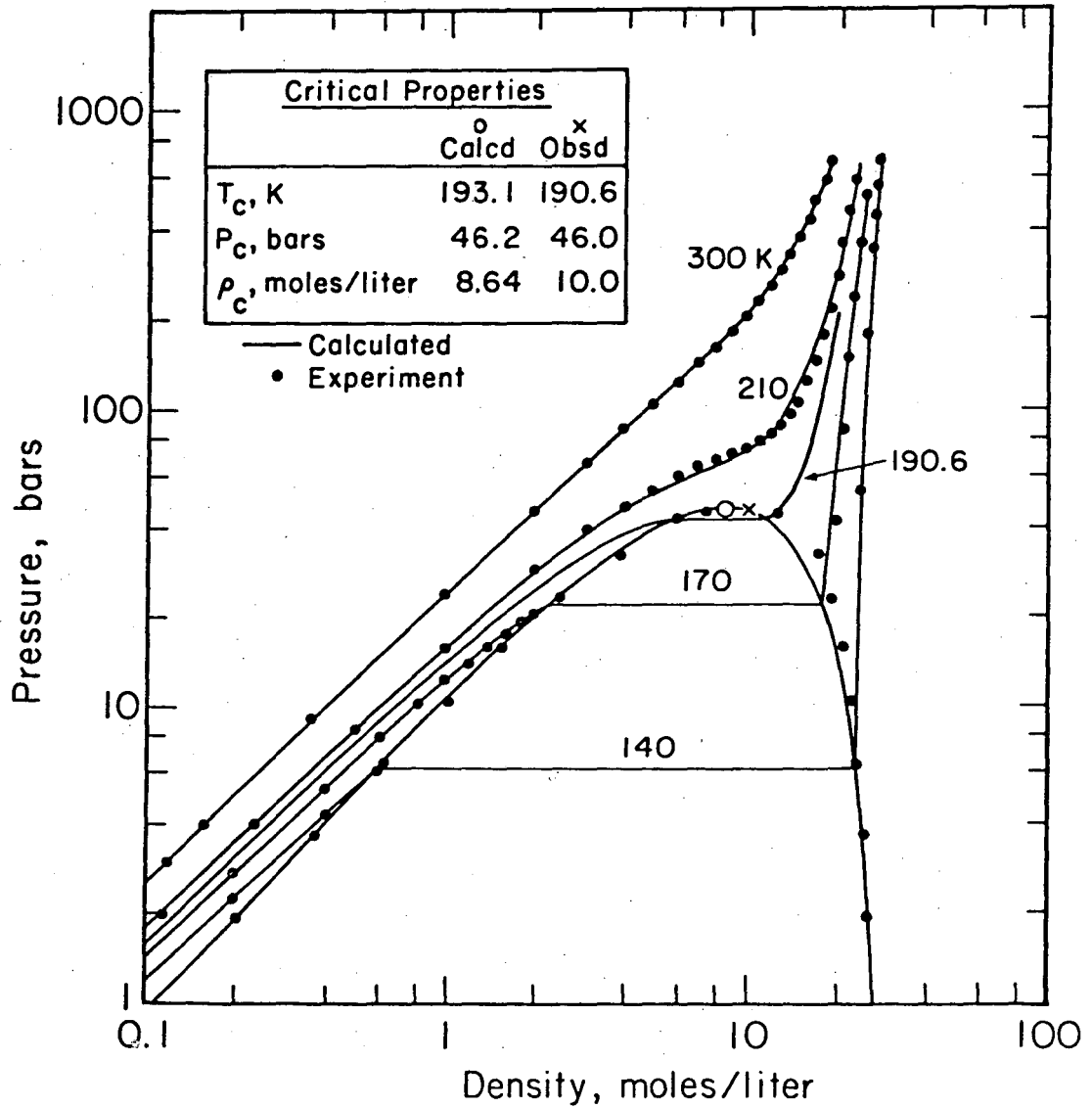
FIGURE 1

PRESSURE–DENSITY DIAGRAM FOR METHANE.
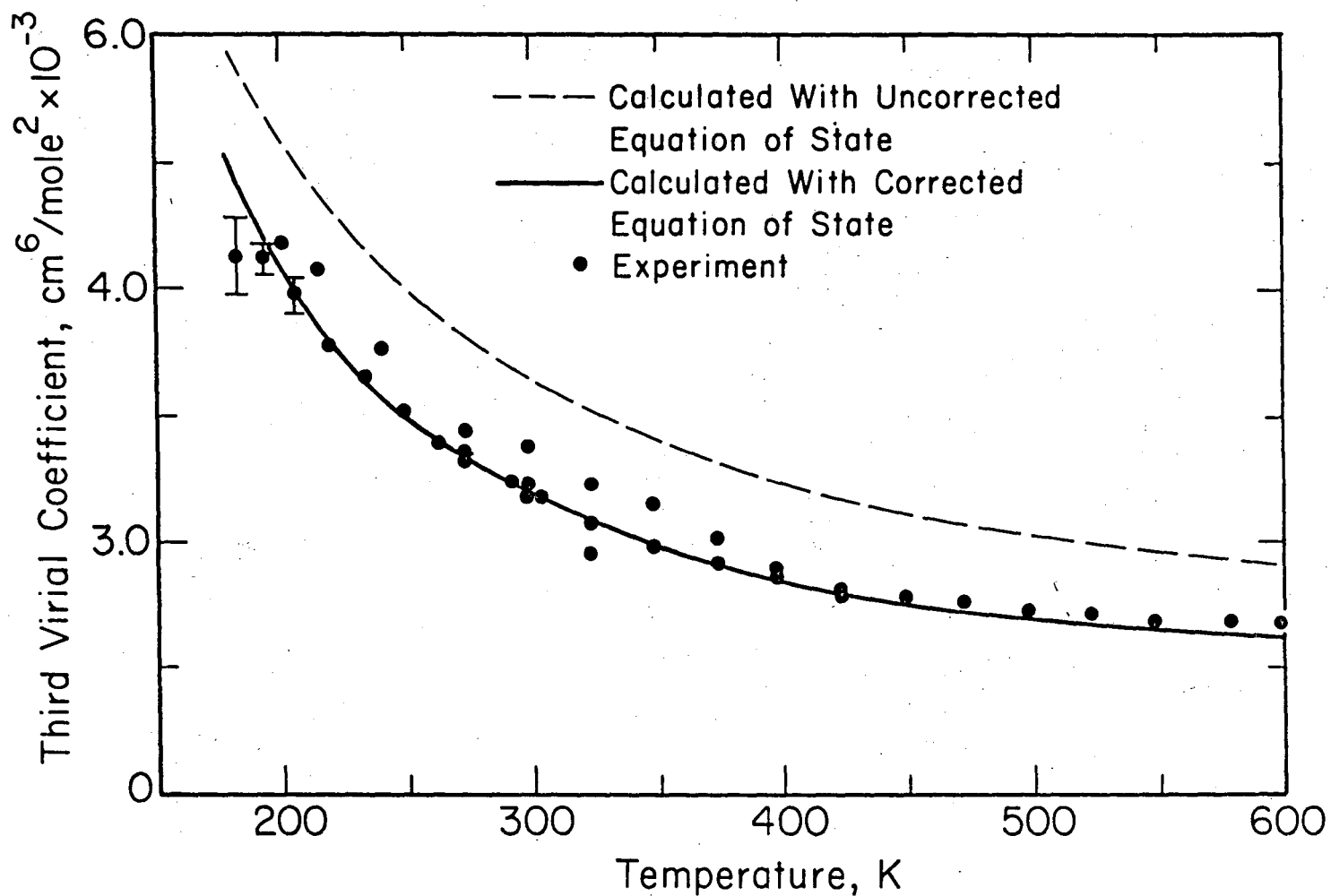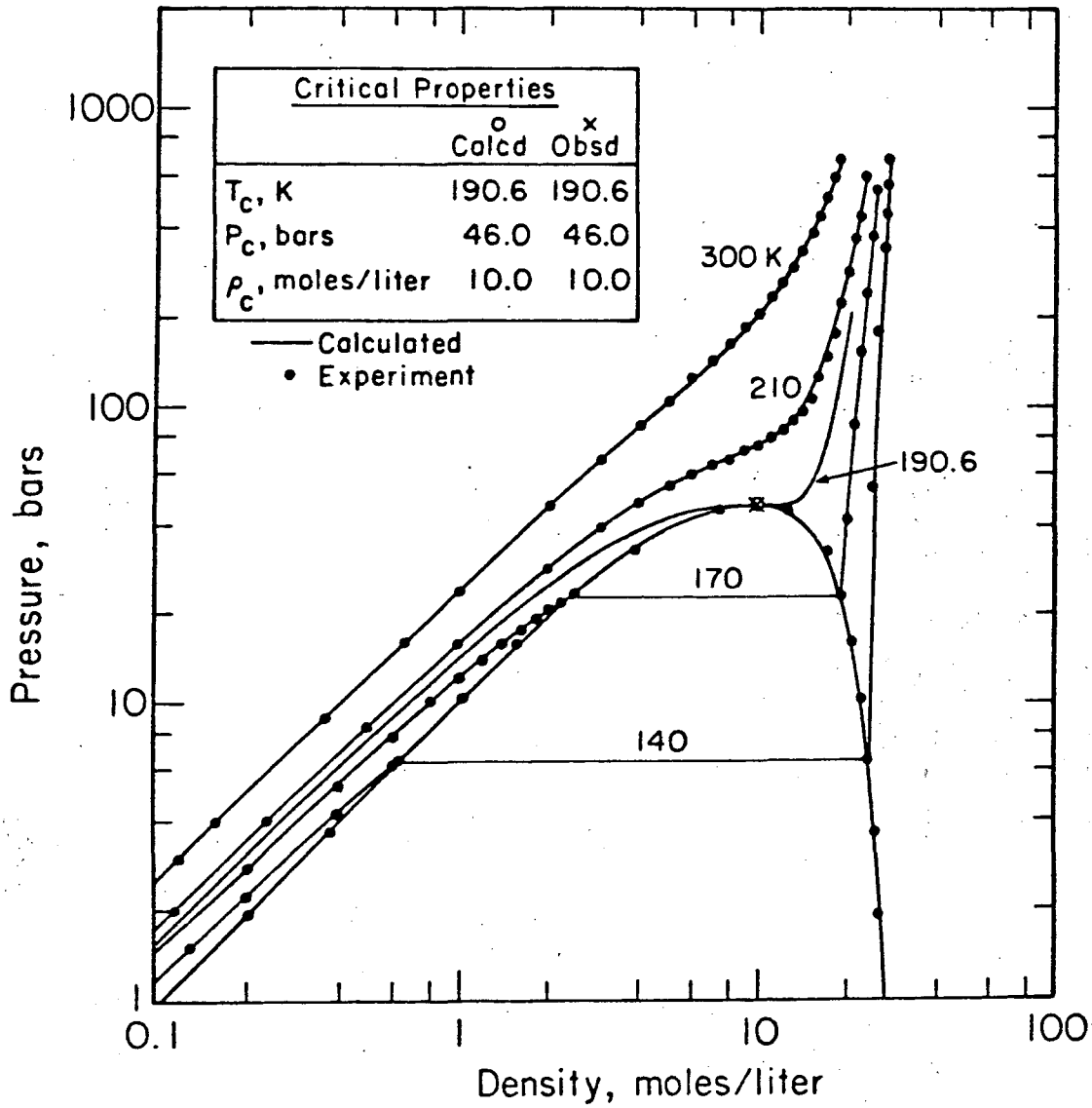CALCULATIONS WITH UNCORRECTED EQUATION
OF STATE

FIGURE 2
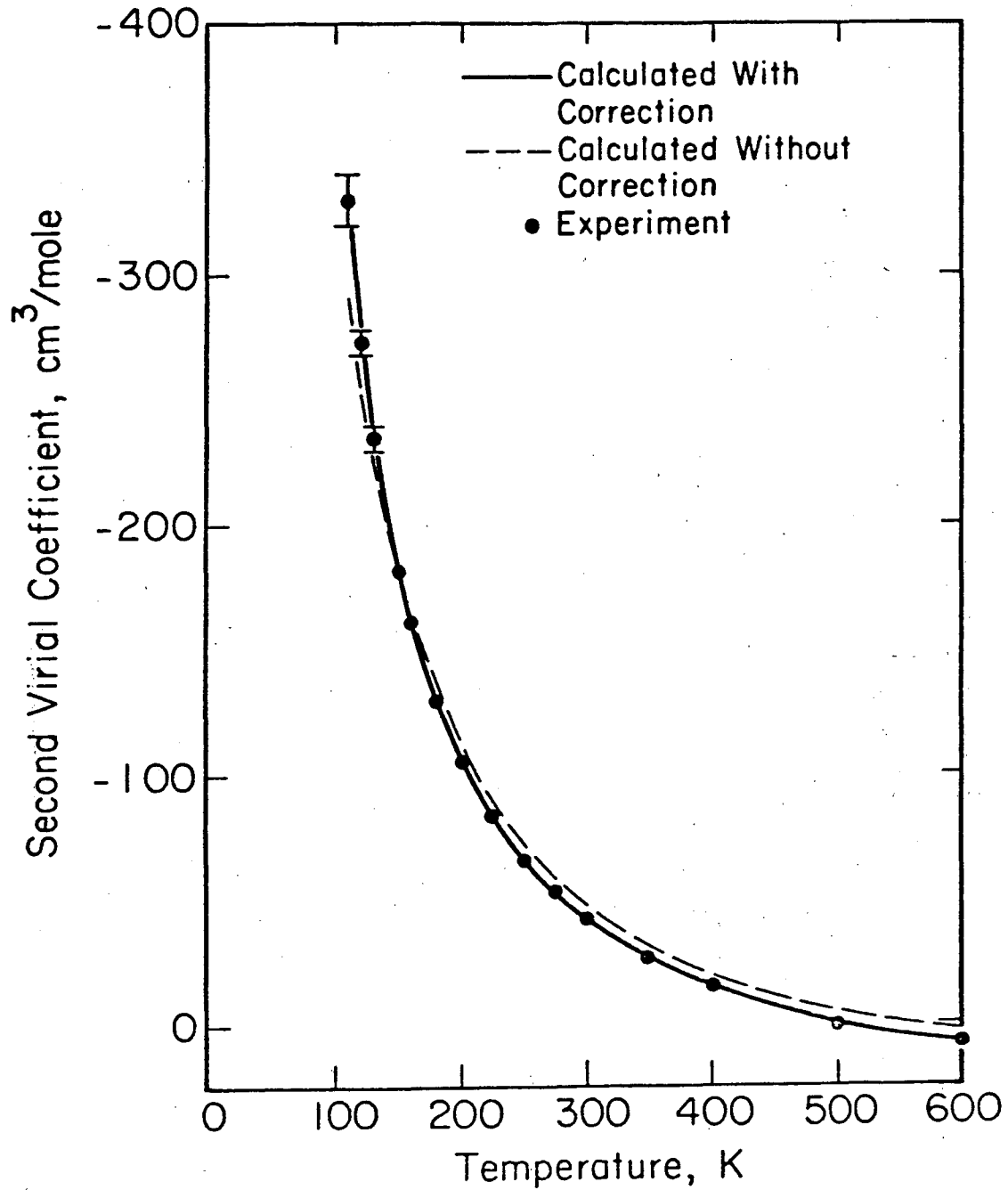
CALCULATED AND OBSERVED SECOND VIRIAL
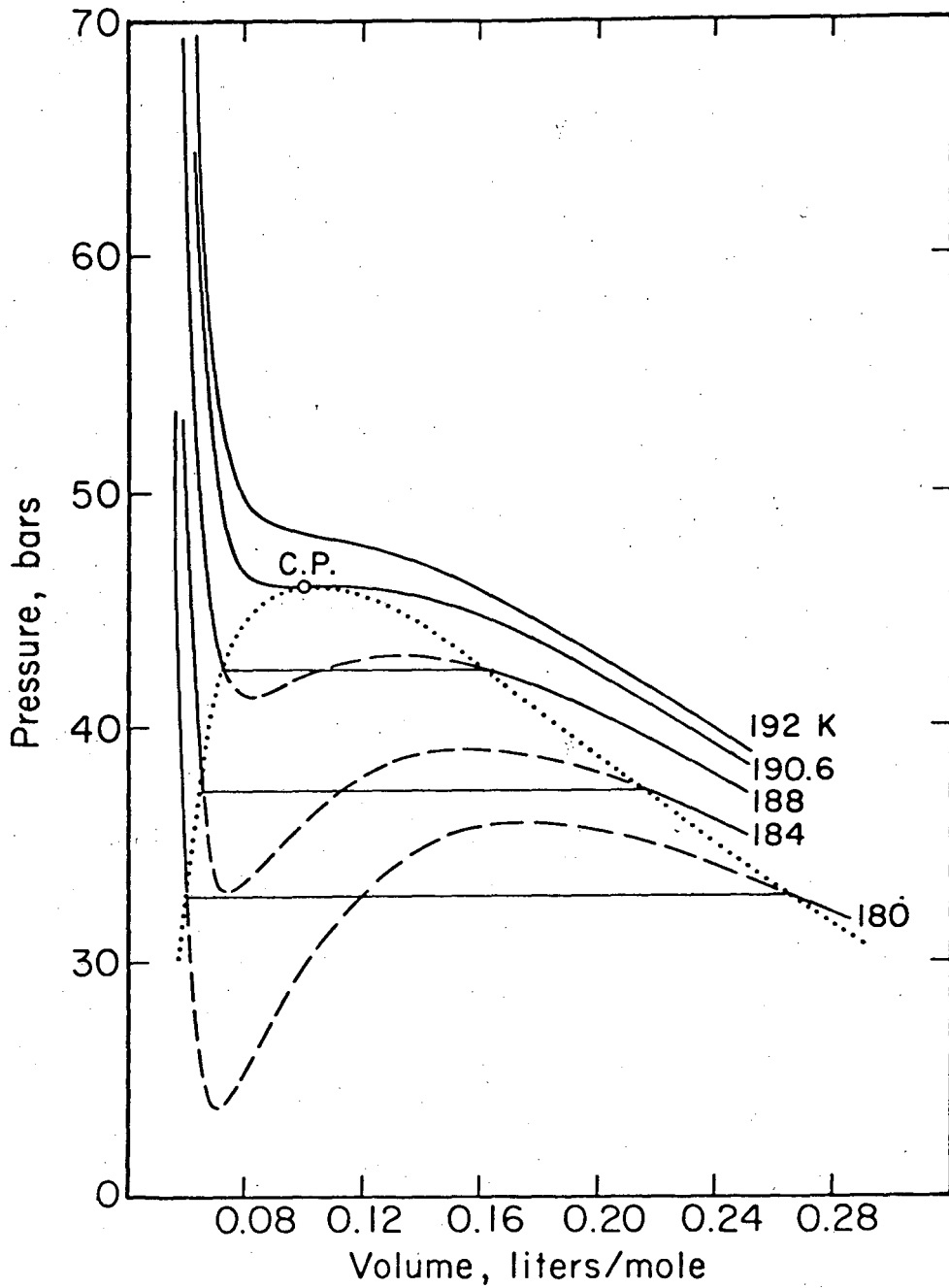COEFFICIENTS FOR METHANE

FIGURE 3

FIGURE 4

-17-

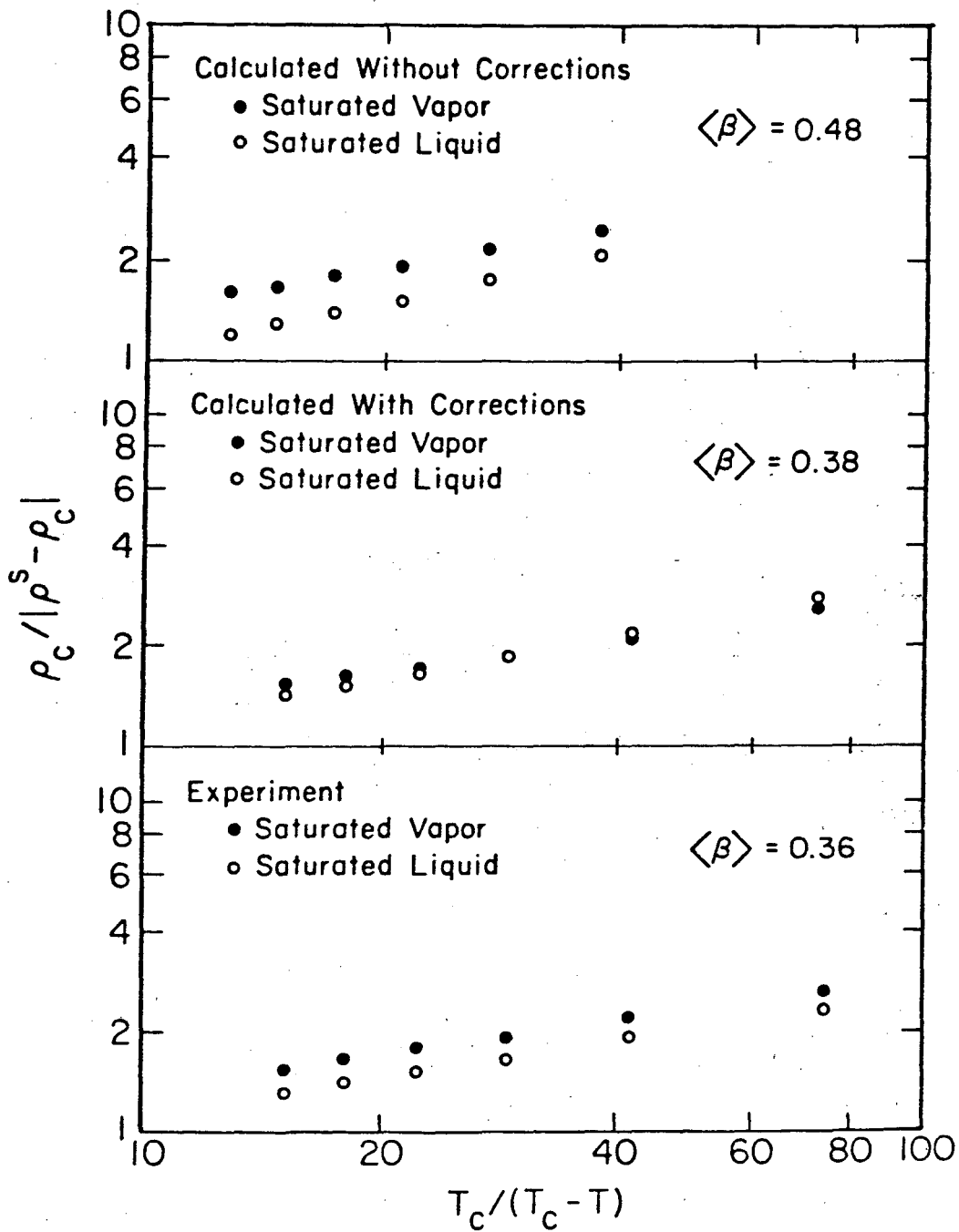CALCULATED AND OBSERVED THIRD VIRIAL COEFFICIENTS FOR METHANE

PRESSURE—DENSITY DIAGRAM FOR METHANE.
CALCULATIONS WITH CORRECTED EQUATION
OF STATE

FIGURE 5

CALCULATED ISOTHERMS AND TWO-PHASE BOUNDARY
FOR METHANE IN THE CRITICAL REGION

FIGURE 6

DETERMINATION OF EXPONENT β IN THE REGION
2–12 K BELOW T_c. (ρ^s IS THE SATURATED DENSITY)

FIGURE 7
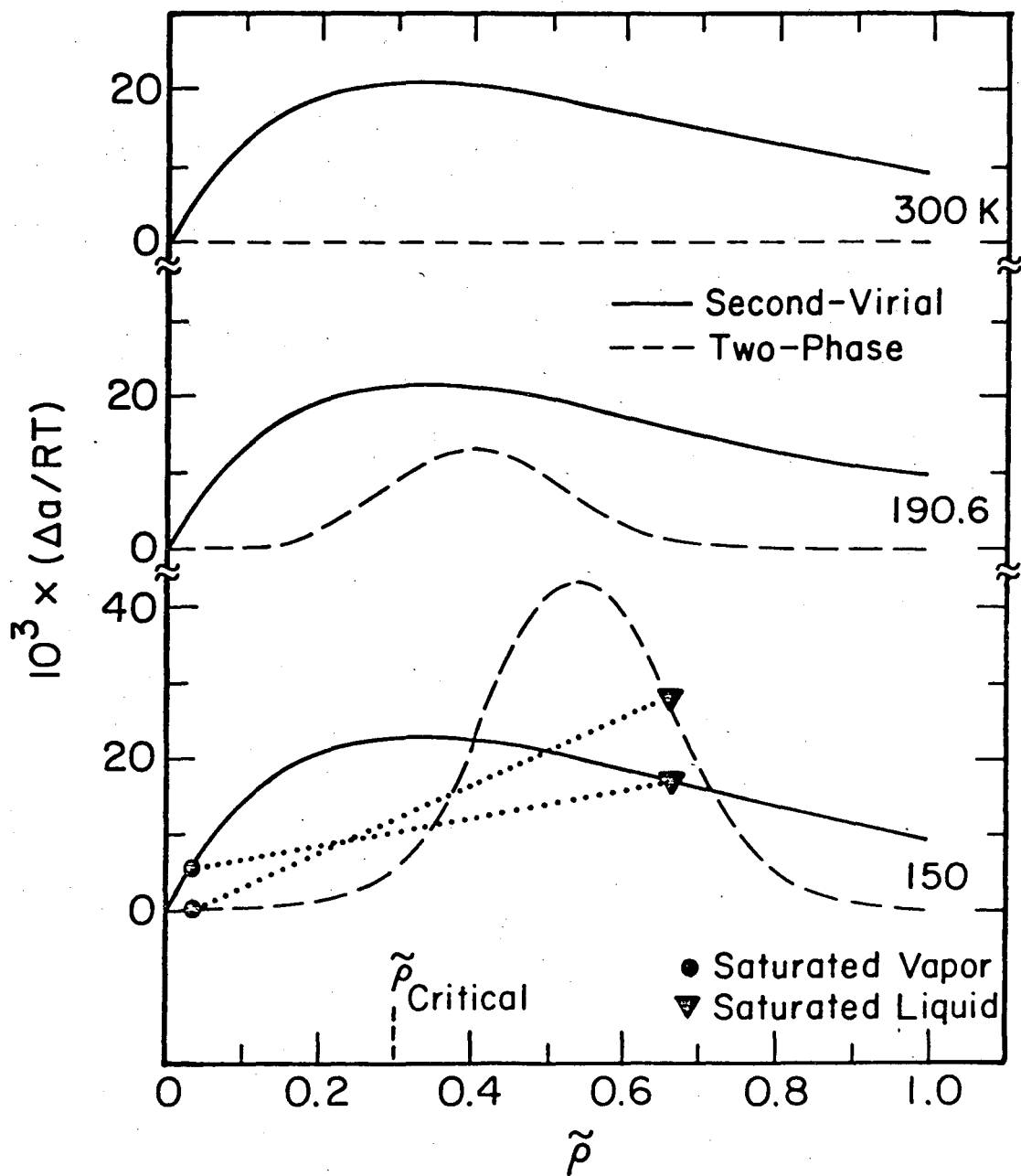
Corrections to the Helmholtz Energy

FIGURE 8