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# THERMODYNAMIC PROPERTIES OF POLAR FLUIDS FROM A PERTURBED-DIPOLAR-HARD-SPHERE EQUATION OF STATE

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ABSTRACT

Based on theoretical results for a system of hard spheres with dipoles, a new equation of state is applied to the correlation of thermodynamic properties for four fluids: argon, ammonia, water, and acetonitrile. The reference system has the same dependence on density as that given by the Carnahan-Starling equation, but the coefficients are now functions of temperature through the reduced dipole moment. These coefficients are chosen to match the Padé approximant developed by Stell, Rushbrooke and Hoye for the Helmholtz energy of dipolar hard spheres. The reference system proposed here shows a phase transition for reduced dipole moments greater than 1.9. A simple, empirical perturbation term is added to the reference system to account for induction and dispersion forces. For polar fluids, the equation gives results significantly better than those obtained from conventional cubic equations of state, when using the same limited experimental data for determining equation-of-state parameters.

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# INTRODUCTION

While much attention has been given to the equation of state for nonpolar fluids, relatively little work has been reported on the equation of state for those fluids whose molecules possess an appreciable dipole moment. For practical applications to systems containing polar fluids, it has become common practice to use empirical extensions of methods originally intended for nonpolar fluids (e.g. Soave(1980), Lüdecke and Prausnitz(1985), Guo, et al (1985a, 1985b), Ikonomou and Donahue (1986), Vimalchand and Donahue (1985), and Huron et al(1978)) or else to use "chemical" equations of state such as those of Grenzheuser and Gmehling(1986, 1981), Gmehling et al (1979), Wenzel et al (1982), Kulasinska, et al (1983), and others.

Recently, however, there has been much interest in the use of perturbation theory to describe properties of polar fluids. Perturbation theories have been reported for dipolar hard spheres (Stell, et al (1974), (1973), and (1972)) and multipolar Lennard-Jones fluids (Annath et al (1974), Twu and Gubbins (1975), Flytzani-Stephanopoulos, et al (1975), and Gray, et al(1978)). These theories have led to some successful applications for representing the properties of real fluids (Gubbins and Twu (1978), Twu, et al (1978), and (1976), Winkelmann (1983), (1981), and (1979), and Chung, et al (1984)). All of these perturbation theories use a reference system which exhibits only repulsive forces: typical reference systems are assemblies of hard spheres or other rigid convex bodies. However, for highly polar fluids, these reference systems can lead to difficulties in convergence of the perturbation series. Among others, Chung et al (1984) state the need for a more sophisticated reference system to surmount this obstacle.

In this work, we use a reference system containing orientation-averaged attractive (dipole-dipole) forces in addition to repulsive forces; this reference system is combined with a semi-empirical perturbation term to represent thermodynamic properties of real polar fluids.

## EQUATION OF STATE FOR POLAR FLUIDS

We use an equation of state of the van der Waals form where compressibility factor z is the sum of two contributions, one from the reference system and one from a perturbation,

$$z = \frac{Pv}{RT} = z^{ref} + z^{pert} \qquad (1)$$

It has been customary to use for the reference system an assembly of convex bodies (usually spheres) which exhibit only repulsive forces at contact. Attractive forces, at somewhat larger distances, are taken into account in the perturbation term.

In a departure from previous practice, we use here a reference system that contains hard spheres with ideal dipole moments at their centers. This reference system therefore includes not only the usual forces of repulsion but, in addition, dipole-dipole forces which, on average, are attractive. The perturbation term takes into account attractive forces arising from induction and dispersion.

For the compressibility factor of the reference system, we write a generalized Carnahan-Starling expression:

$$z^{ref} = \frac{1 + f^{(1)}\eta + f^{(2)}\eta^2 - f^{(3)}\eta^3}{(1 - \eta)^3} \qquad (2)$$

where the reduced density is:

$$\eta = b\rho/4 = \pi\rho\sigma^3/6 \qquad (3)$$

and the coefficients depend on reduced dipole moment $\tilde{\mu}$:

$$f^{[1]} = 1 - 0.61357\tilde{\mu} + 3.06030\tilde{\mu}^2 - 4.63519\tilde{\mu}^3 + 0.86956\tilde{\mu}^4 \qquad (4)$$

$$f^{[2]} = 1 + 2.79108\tilde{\mu} - 12.6917\tilde{\mu}^2 + 15.8026\tilde{\mu}^3 - 2.77528\tilde{\mu}^4 \qquad (5)$$

$$f^{[3]} = 1 + 2.98994\tilde{\mu} - 13.1452\tilde{\mu}^2 + 14.5664\tilde{\mu}^3 - 2.50544\tilde{\mu}^4 \qquad (6)$$

Here $\rho$ is density and $\sigma$ is the hard-sphere diameter. In the original Carnahan-Starling equation, all coefficients $f^{[1]} = f^{[2]} = f^{[3]} = 1$. In this work, however, these coefficients are functions of temperature through the reduced dipole moment $\tilde{\mu} = \mu/(\sigma^3 kT)^{1/2} = (2\pi\mu^2/3bRT)^{1/2}$. When $\mu$ is in Debye, b in $cm^3$/mole, and T in Kelvins, $\tilde{\mu} = 95.59\,\mu/(bT)^{1/2}$.

Dimensionless dipole moment $\tilde{\mu}$ depends on dipole moment, temperature, and molecular size. For the fluids examined here, at their normal boiling points, the values of $\tilde{\mu}$ are: argon (0.00), ammonia (1.33), water (1.41), and acetonitrile (1.42); at their critical temperatures, they are: argon (0.00), ammonia (1.02), water (1.07), and acetonitrile (1.14).

The coefficients in equation (2) were determined by fitting to a complex equation of state for hard spheres with point dipoles at their centers. That equation was developed by Stell, Rushbrooke, and Hoye (1973) who devised a Padé approximant to the Helmholtz energy of a system of hard spheres using the perturbation theory of Stell, Rasaiah, and Narang (1974, 1972). Their Padé approximant ("Stell's equation"), discussed in Appendix I, gives the Helmholtz energy of a system of dipolar hard spheres as a function of reduced density $\eta$ and reduced dipole moment $\tilde{\mu}$; it is valid for values of $\tilde{\mu}$ to at least 2.00 and perhaps slightly higher.

The Helmholtz energy obtained from Stell's equation is in good agreement with Monte-Carlo calculations for dipolar hard spheres. The third and fifth columns of Table 1 show "experimental" (Monte-Carlo) Helmholtz energies and those calculated from Stell's equation. Monte-Carlo calculations are taken from Patey and Valleau (1974).

Table 1. Effect of Reduced Dipole Moment on the Helmholtz Energy of a System of Dipolar Hard Spheres. Results from Monte-Carlo Simulation, from Dipole-Dipole Carnahan-Starling (DDCS), and from Stell's (SRH) Equations

| | | $-(A - A^{HS})/RT$ | | |
|---|---|---|---|---|
| $\eta$ | $\tilde{\mu}$ | Monte-Carlo | DDCS | SRH |
| 0.474 | 0.24 | 0.0037 | 0.0042 | 0.0034 |
| " | 0.47 | 0.052 | 0.053 | 0.051 |
| " | 0.71 | 0.22 | 0.24 | 0.23 |
| " | 0.95 | 0.58 | 0.61 | 0.62 |
| " | 1.19 | 1.2 | 1.2 | 1.3 |
| " | 1.42 | 2.1 | 2.1 | 2.2 |
| " | 1.66 | 3.3 | 3.4 | 3.5 |
| 0.437 | 0.24 | 0.0035 | 0.0039 | 0.0030 |
| " | 0.71 | 0.21 | 0.22 | 0.20 |
| " | 1.19 | 1.1 | 1.1 | 1.2 |
| " | 1.66 | 3.2 | 3.2 | 3.2 |

$A^{HS}$ is the Helmhotz energy at the same $\eta$ with $\tilde{\mu} = 0$

As discussed in the Appendix I, Stell's equation for the Helmholtz energy gives an equation of state that is mathematically complex. To simplify the reference system, the Carnahan-Starling (1969) form is retained here as shown by equation (2). Functions $f^{[1]}$, $f^{[2]}$, and $f^{[3]}$ (Equations (4) - (6)) reduce to the Carnahan-Starling values when $\tilde{\mu} = 0$. These functions are determined by fitting to "data" generated from Stell's equation. The compressibility factors calculated from equations (2), (4), (5), and (6) are in good agreement with those calculated from Stell's equation, as shown in Figure 1.

Although not immediately apparent by visual inspection, Figure 1 shows that when $\tilde{\mu} \geq 1.90$, dipolar hard spheres exhibit a phase transition. This behavior was also noted by Stell, Rushbrooke, and Hoye (1973), who made representative VLE calculations but did not report the critical dipole moment (or, equivalently, critical temperature) for dipolar hard spheres. When Stell's equation is used, the critical reduced dipole moment is 1.91, again showing excellent agreement with equations (2), (4), (5), and (6). Figure 2 shows the phase transition more clearly in an expanded view of a portion of Figure 1; an isotherm at $\tilde{\mu} = 2.5$ is included to show the behavior at high reduced dipole moments (low temperatures).

Table 1 compares our results for the Helmholtz energies of dipolar hard spheres (equations (2), (4), (5), and (6)) to those obtained from Stell's equation and by Monte-Carlo simulation.

The dipole-dipole Carnahan-Starling (DDCS) equation provides a reference system that represents the behavior of dipolar hard spheres. For the perturbation term we use a semi-empirical form, suggested by Wong and Prausnitz (1985), similar to that of Redlich and Kwong (1949). The proposed equation of state is:

$$z = \frac{1 + f^{[1]}\eta + f^{[2]}\eta^2 - f^{[3]}\eta^3}{(1-\eta)^3} - \frac{a}{RT(v + 0.2b)} \qquad (7)$$

where the second term on the RHS is a form intermediate between the well-known attractive forms proposed by van der Waals and by Redlich and Kwong.

At the critical temperature $T_c$, parameters a and b in Equation (7) can be determined from the usual criteria; at the critical point,

$$\left(\frac{\partial P}{\partial v}\right)_{\tilde{\mu}_c, T_c} = 0 \qquad (8)$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{\tilde{\mu}_c, T_c} = 0 \qquad (9)$$

where $\tilde{\mu}_c = \mu/(\sigma^3 k T_c)^{1/2}$.

Equations (8) and (9) give values of $(b_c/v_c)$ and $(a_c/RT_c v_c)$. Since accurate experimental values for $v_c$ are often not available, parameters $a_c$ and $b_c$ are here determined by:

$$a_c = \left(\frac{a_c}{RT_c v_c}\right) z_c^{theo} \left(\frac{R^2 T_c^2}{P_c}\right) \qquad (10)$$

and:

$$b_c = \left(\frac{b_c}{v_c}\right) z_c^{theo} \left(\frac{RT_c}{P_c}\right) \qquad (11)$$

where $z_c^{theo}$ is the compressibility factor calculated from equation (7) at the critical point; that is, the point where equations (8) and (9) are satisfied. When applied to argon, equation (11) gives a value for $b_c$ which is about 10% smaller than that which gives the most accurate calculated values for the critical compressibility and the liquid molar volumes. Since these properties are extremely sensitive to $b_c$, the direct use of equation (11) leads to poor results. Therefore, the value of $b_c$ was adjusted upward by 10%, providing an improvement for all calculated properties for all fluids examined, especially liquid molar volumes. The calculation of properties from Equation (10) is further improved if $b_c$ is fixed so as to match a single experimental value of the liquid molar volume. The procedure for matching $b_c$ to experimental liquid molar volumes is explained in detail by Panagiotopoulos and Kumar (1985), who demonstrate the technique for three popular two-parameter equations of state. Appendix II describes application of this technique to Equation (7).

Reduced values of $b_c$ (adjusted) and $a_c$ can be found from:

$$\tilde{b}_c = b_c P_c / RT_c = 0.178 + 1.124\,\mu / (RT_c^2/P_c)^{1/2} \qquad (12)$$

$$\tilde{a}_c = a_c P_c / R^2 T_c^2 = 0.5352 + 0.1288\,\mu_c - 0.1783\,\mu_c^2 \qquad (13)$$

(For dimensional consistency, equation (12) must have $\mu$ in Debye, $T_c$ in Kelvins, $P_c$ in bars, and $R = 83.14$ cm$^3$-bar/mole-K)

For our engineering-oriented purposes, parameter b, however determined, is independent of temperature to a good approximation. Parameter a, on the other hand, increases markedly with falling temperature. This dependence must be given accurately, especially for the calculation of vapor pressures, where an error of a few percent in a can lead to an error of 100% in the calculated vapor pressure. Soave (1972) showed that, for

the Redlich-Kwong equation of state, a plot of $(a/a_c)^{1/2}$ vs. $(T/T_c)^{1/2}$ is linear for non-polar fluids at temperatures below the critical. An examination of the properties of argon with Equation (7) confirms this linearity, but the plot of $(a/a_c)^{1/2}$ vs. $(T/T_c)^{1/2}$ gives one line for $(T/T_c) \leq 0.8$ and another for $(T/T_c) \geq 1.0$, with nonlinear behavior in the intermediate region $0.8 \leq (T/T_c) \leq 1.0$. Therefore, we propose that the dependence of a on T be given by:

$$(a/a_c)^{1/2} = (0.41 + 0.075(T/T_c)^{1/2})(1-\Phi) + (\alpha + \beta(T/T_c)^{1/2})(1+\Phi) \quad (14)$$

where the weighting function $\Phi$ is defined by:

$$\Phi \equiv \tanh[10((T_c/T) - 1)] \quad (15)$$

Function $\Phi$ approaches +1 as $T/T_c$ approaches zero, and approaches -1 as $T/T_c$ approaches infinity. The transition between these two values occurs almost entirely in a small temperature range near $T/T_c = 0.9$.

The first expression on the RHS of Equation (14) represents the high-temperature $(T/T_c > 1.0)$ behavior of a. The constants shown are suitable for all of the substances examined here; these values should be used unless a large body of data is available at high temperatures over a wide range of densities.

The second expression on the RHS of equation (14) represents the low-temperature $(T/T_c < 0.8)$ behavior of a. Constants $\alpha$ and $\beta$ can be determined in many ways but, for engineering purposes, the most convenient is to use data for the vapor pressure and enthalpy of vaporization at a single specified temperature, most commonly the normal boiling point. The appendix describes the procedure for fixing $\alpha$ and $\beta$ from such data.

Function $\Phi$, defined by Equation (15), blends the high- and low-temperature functions for a smoothly together in the range of temperatures just below the critical temperature.

RESULTS

Figure 3 shows calculated and experimental results for ammonia; the data were taken from the compilation of Haar and Gallagher (1978). Calculations are based exclusively on experimental data for critical temperature, critical pressure, dipole moment, normal boiling point, and enthalpy of vaporization at the normal boiling point. The calculations are in good agreement with experiment, although there is some discrepancy in the near-critical region, as is common with equations of state of the Van der Waals form. The calculated boundaries of the two-phase region are also in good agreement with experiment, again with the exception of the critical region.

Figure 4 compares calculated and experimental vapor pressures for ammonia (Haar and Gallagher (1978)), water (Keenan, et al (1978)), argon (Angus and Armstrong (1971)), and acetonitrile (Francesconi, et al (1975)). Required input data are the same as those indicated above. Agreement is excellent; about the same as would be obtained with the original Soave-Redlich-Kwong (SRK) equation for argon (and other non-polar fluids), and somewhat better than that from the SRK equation for polar fluids. With more experimental data as input, an even better correlation for a (and hence vapor pressure) can be obtained, as suggested by Soave (1980).

Figure 5 shows that calculated saturated-liquid molar volumes are also in good agreement with experimental data for ammonia (Haar and Gallagher (1978)), water (Keenan, et al (1978)), and argon (Angus and Armstrong (1971)), even though no volumetric data were used to determine the parameters. The calculated liquid volumes for acetonitrile are less accurate, for reasons that are not clear. Calculations for other highly polar fluids give much better results, suggesting that the polarity of acetonitrile alone does not fully explain the relatively poor performance of Equation (7) in predicting its saturated-liquid molar volume. Better values of b, and hence of liquid volume, can be obtained if a single liquid-volume datum is available to fix parameter b.

Figure 6 compares calculated second virial coefficients with experimental results taken from the compilation of Dymond and Smith (1980). Agreement is excellent for argon, good for ammonia and water, and fair for acetonitrile. The results are surprisingly good, in view of the well-known difficulty of **simultaneously** correlating high-density properties (vapor pressures and liquid volumes) and low-density properties (second virial coefficients) with a simple equation of state. Appendix III discusses a fundamental problem concerning calculation of the second virial coefficient from Equation (7).

## COMPARISON WITH CONVENTIONAL EQUATIONS

To determine the effect of dipolar forces in the reference system, calculations were performed for polar fluids with and without reduced dipole moment $\tilde{\mu}$. For polar fluids, the change in reference system has almost no effect on the accuracy of the calculated vapor pressures, because parameter a is determined from vapor-pressure data. However, there is significant improvement in calculated saturated-liquid molar volumes and in second virial coefficients when the dipolar reference system is used. Table 2 compares the accuracy of Equation (2) with and without a dipole moment in the reference system.

The results obtained here suggest that, when using a semi-empirical perturbed hard-sphere equation, it is worthwhile to include the effect of reduced dipole moment on the reference term. For polar fluids, significant improvement is obtained with little additional computational effort and without adding any additional adjustable parameters.

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Table 2. Influence of Dipole Moment on Calculated Liquid Volumes and on Second Virial Coefficients for Ammonia and for Water (constants are determined from critical and vapor-pressure data)

| Property | Temperature (K) | Average Absolute Deviation Between DDCS Equation and Experimental Data | |
|---|---|---|---|
| | | $\mu = \mu^{exptl}$ | $\mu = 0$ |
| | | Percent | |
| $v^{sat\ liq}(NH_3)$ | 197 - 400 | 2.2 | 7.1 |
| $v^{sat\ liq}(H_2O)$ | 273 - 590 | 1.9 | 8.4 |
| | | $cm^3$/mole | |
| $B(NH_3)$ | 273 - 523 | 32 | 86 |
| $B(H_2O)$ | 323 - 723 | 97 | 203 |

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# APPENDIX I

## DIPOLAR-HARD-SPHERE EQUATION OF STATE OF STELL, ET AL

For Helmholtz energy A, the Padé approximant of Stell, et al (1973) is:

$$\frac{A - A^{HS}}{RT} = \frac{-4/3\,\tilde{\mu}^4 \eta\, I_2(\eta)}{1 + 5/6\,\tilde{\mu}^2\, I_3(\eta)/I_2(\eta)} \qquad \text{(I-1)}$$

where $A^{HS}$ is the Helmholtz energy of a system of hard spheres (no dipoles) at temperature T and reduced density $\eta$. Here:

$$I_2(\eta) = \frac{1 - 0.6910\,\eta - 1.1690\,\eta^2 + 0.7510\,\eta^3}{(1 - \eta)^3} \qquad \text{(I-2)}$$

$$I_3(\eta) = \frac{1 + 1.1913\,\eta - 0.4252\,\eta^2}{1 - 1.1279\,\eta - 0.7317\,\eta^2} \qquad \text{(I-3)}$$

and the reduced dipole moment $\tilde{\mu}$ is defined by $\tilde{\mu} = \mu/(\sigma^3 kT)^{1/2} = (2\pi\mu^2/3bRT)^{1/2}$. The equation of state is obtained from:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T \qquad \text{(I-4)}$$

# APPENDIX II

## DETERMINATION OF EQUATION-OF-STATE PARAMETERS

In dimensionless form, the Perturbed DDCS equation (Equation (7)) is:

$$\tilde{P} = \frac{Pb}{4RT} - f(\eta,\tilde{\mu}) - \frac{5a}{bRT}\,\frac{\eta}{1.25+\eta} \qquad \text{(II-1)}$$

If pressure, temperature, and dipole moment are known, the only remaining variables are parameters a and b and reduced density $\eta$. To fit an experimental vapor-pressure datum, we use two criteria, equality of pressure and equality of chemical potentials in the two phases; both criteria must be satisfied. For the perturbed DDCS equation, the vapor-liquid-equilibrium (VLE) criterion may be conveniently stated as:

$$\frac{5a}{bRT} = F(\eta^{\text{sat liq}}) - F(\eta^{\text{sat vap}}) \qquad \text{(II-2)}$$

where function F is defined by:

$$F(\eta) = \frac{\ln\eta + (1-f^{[3]})\ln(1-\eta) + \dfrac{(3+f^{[1]}-3f^{[3]}) + \eta(-4f^{[3]}+2f^{[2]}-2)}{2(1-\eta)}}{\ln(1.25+\eta)} \qquad \text{(II-3)}$$

If we know the saturated-liquid molar volume corresponding to the vapor-pressure datum, we can determine the unique pair of parameters a and b that simultaneously satisfies the VLE criterion and gives the proper value of $\eta$ for the liquid phase by the following procedure:

1. Make initial estimates of a and b.
2. Compute $\tilde{\mu}$.
3. Compute $\eta^{sat\ liq}$ and $\eta^{sat\ vap}$ from (II-1).
4. Compute new value of a from (II-2) and (II-3).
5. New value of a = old value of a ?

   NO : Replace old value of a with new value and go to step 3.

   YES : Go to step 6.
6. $\eta^{sat\ liq}$ (calculated) = $\eta^{sat\ liq}$ (experimental) ?

   NO : Adjust value of b and go to step 2.

   YES : Exit. The values of a and b are consistent with the experimental values for $p^{sat}$ and $v^{sat\ liq}$.

The algorithm described above is only an example; for converging the "inner loop" (steps 3 - 5), there may be more efficient methods than the resubstitution scheme described, and there are many formulae for adjusting b in the "outer loop" (steps 2 - 6). The procedure indicated above is tedious but, with sufficient repetition, it is possible to develop tables and/or equations relating the dimensionless groups Pb/4RT, 5a/bRT, $\tilde{\mu}$, and $\eta^{sat\ liq}$ (and, if desired, $\eta^{sat\ vap}$) to one another.

This repetition has been carried out by Panagiotopoulos and Kumar (1985) for three popular two-parameter equations of state. The Perturbed DDCS equation, however, has one more independent dimensionless group in addition to those in popular equations of the Van der Waals or Redlich-Kwong type.

Instead of fitting simultaneously a and b, it is more convenient to fix b at the critical value and to develop a simple method for determining the temperature dependence of a. When b is known, there are a number of simple ways to determine constants $\alpha$ and $\beta$ in equation (14), and hence to fix the temperature dependence of a in the sub-critical region:

(1) The original approach of Soave (1972) can be applied to the DDCS equation if the acentric factor is known.

(2) If the vapor pressure is known at two different temperatures, Equations (II-1) - (II-3) allow calculation of a at each temperature. Constants $\alpha$ and $\beta$ are then obtained by straightforward algebra.

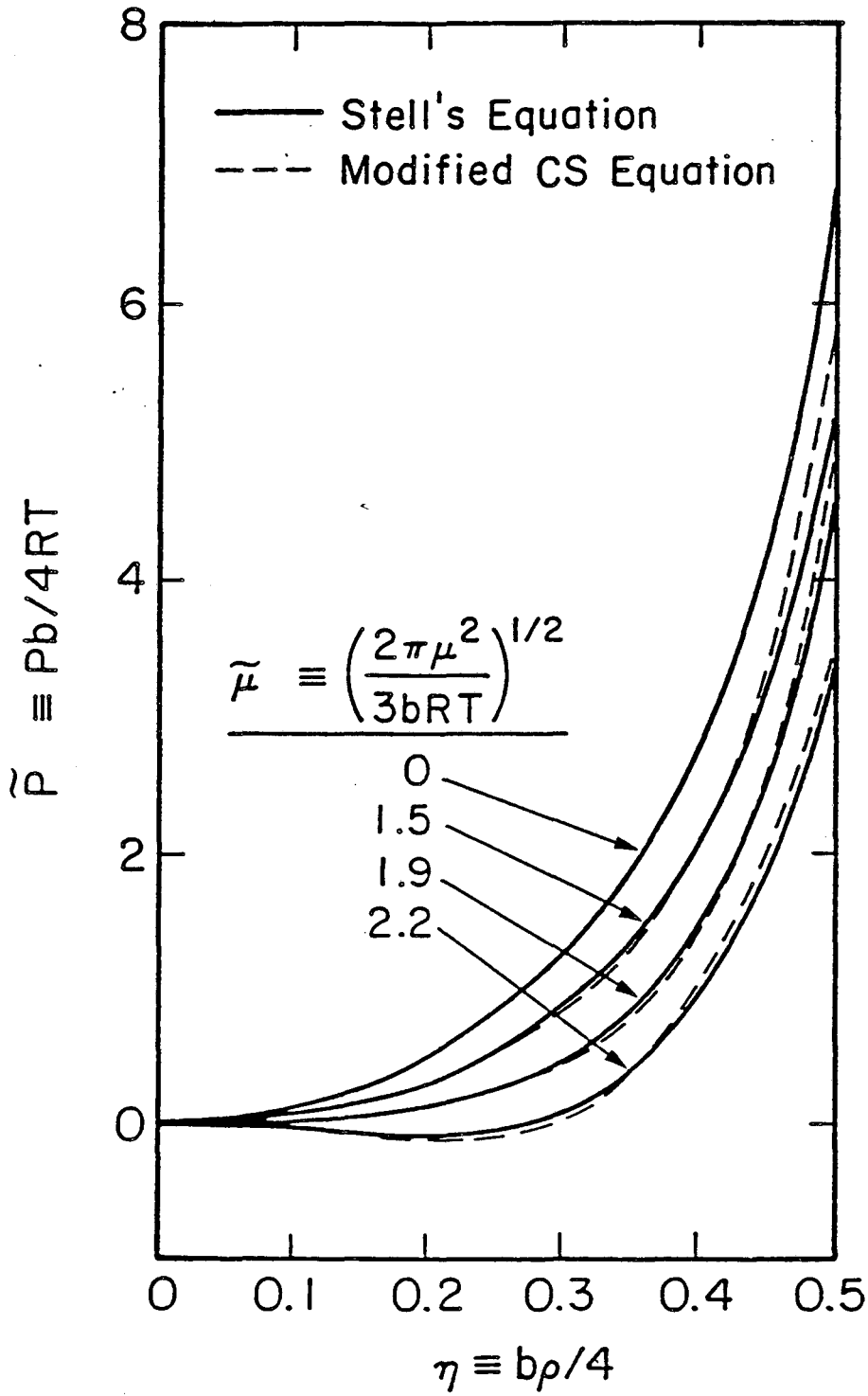
(3) If the vapor pressure and the enthalpy of vaporization are known at a given temperature (such as the normal boiling point), the value of a can be fixed at that point from the vapor-pressure datum, and from the derivative (da/dT) which is related to the enthalpy of vaporization. The latter relation is a complex one which requires solution by numerical methods. When such data are used, it is much simpler to use the enthalpy of vaporization with the Clausius-Clapeyron equation to estimate vapor pressures at temperatures a few degrees above and below the temperature of interest. These estimated vapor pressures are used to calculate a at each point; da/dT is calculated from these two values by finite-difference approximation. In either case, $\alpha$ and $\beta$ are easily calculated when a and its derivative with respect to temperature are known.

# APPENDIX III

## CALCULATION OF SECOND VIRIAL COEFFICIENTS

The relatively large errors in the calculated second virial coefficients follow from a fundamental problem. Neither Stell's equation nor equation (2) give the correct second virial coefficient for a system of dipolar hard spheres, as determined by Keesom (1912). It is possible to relate the function $f^{[1]}$ to this theoretical value by: $f^{[1]} = B^{theo} - 3$, where $B^{theo}$ is the reduced theoretical second virial coefficient ($B^{theo} = 3B/2\pi\sigma^3$), which is equal to 4 for non-polar hard spheres and decreases with increasing dipole moment. If $f^{[1]}$ is determined in this way, agreement between experimental second virial coefficients and those calculated from the resulting equation is excellent, even for acetonitrile. However, since the virial series converges slowly or not at all for liquid-like densities, use of the theoretical second virial coefficient leads to serious problems in the calculation of high-density fluid properties. In this work, it was considered more important to represent accurately the high-density behavior. Therefore, Keesom's result was not used in the development of the DDCS equation.

Figure 1




Isotherms for a Dipolar-Hard-Sphere Fluid. Comparison of Dipole-Dipole Carnahan-Starling Equation to Stell's Equation

# NOTATION

a = equation-of-state constant reflecting attractive forces
b = equation-of-state constant reflecting repulsive forces
B = second virial coefficient
k = Boltzmann constant
P = pressure
R = gas constant
T = absolute temperature
v = molar volume
z = compressibility factor

## Greek Letters

$\alpha, \beta$ = constants reflecting temperature dependence of parameter a
$\rho$ = molar density
$\Phi$ = function providing smooth transition for temperature dependence of parameter a between super- and sub-critical temperatures
$\eta$ = $b\rho/4$ = dimensionless density
$\sigma$ = hard-sphere diameter
$\mu$ = dipole moment

## Superscripts

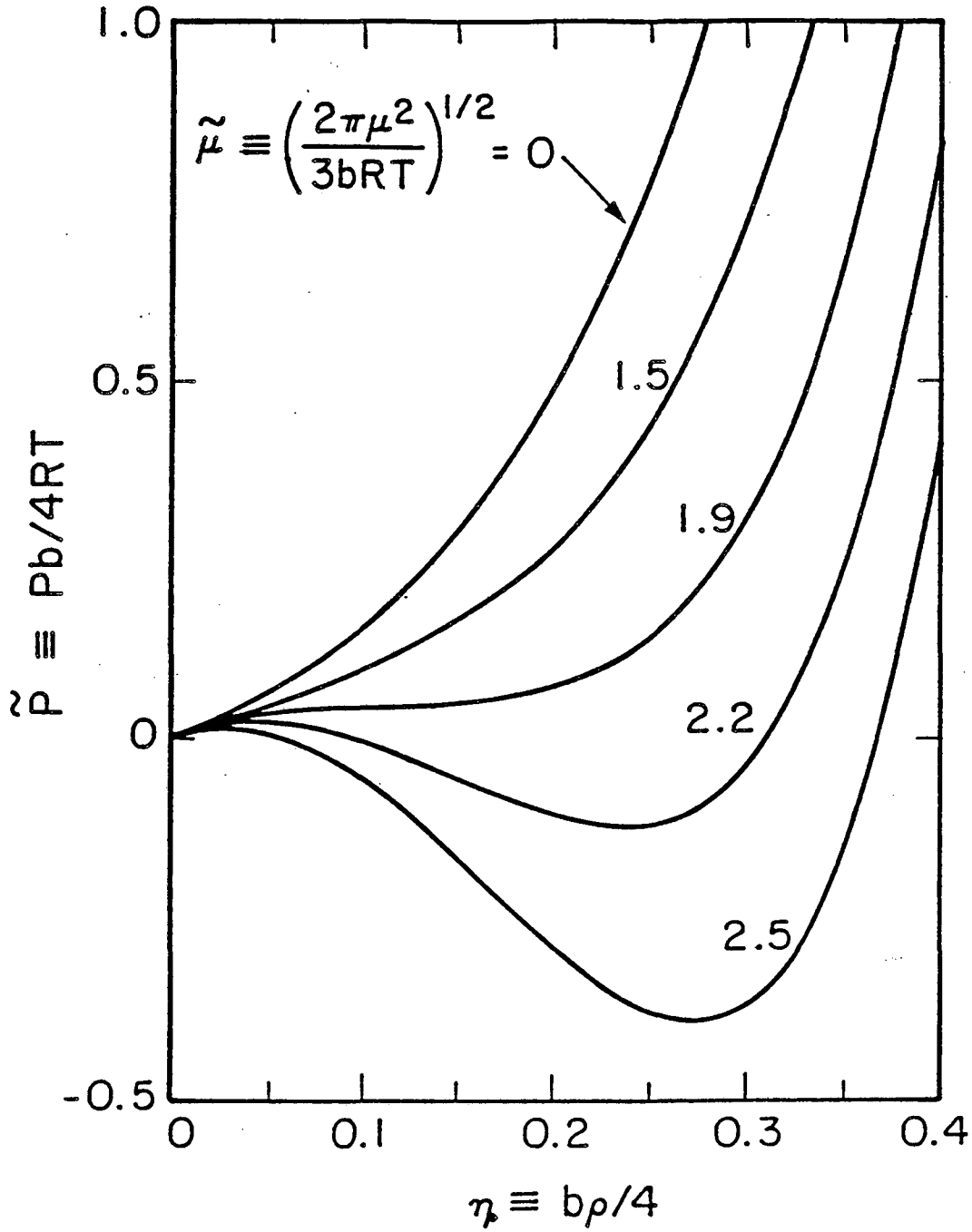
ref = reference part of equation of state
pert = perturbation part of equation of state
theo = theoretically calculated
expt = experimentally determined
HS = hard sphere
= dimensionless

## Subscript

c = critical

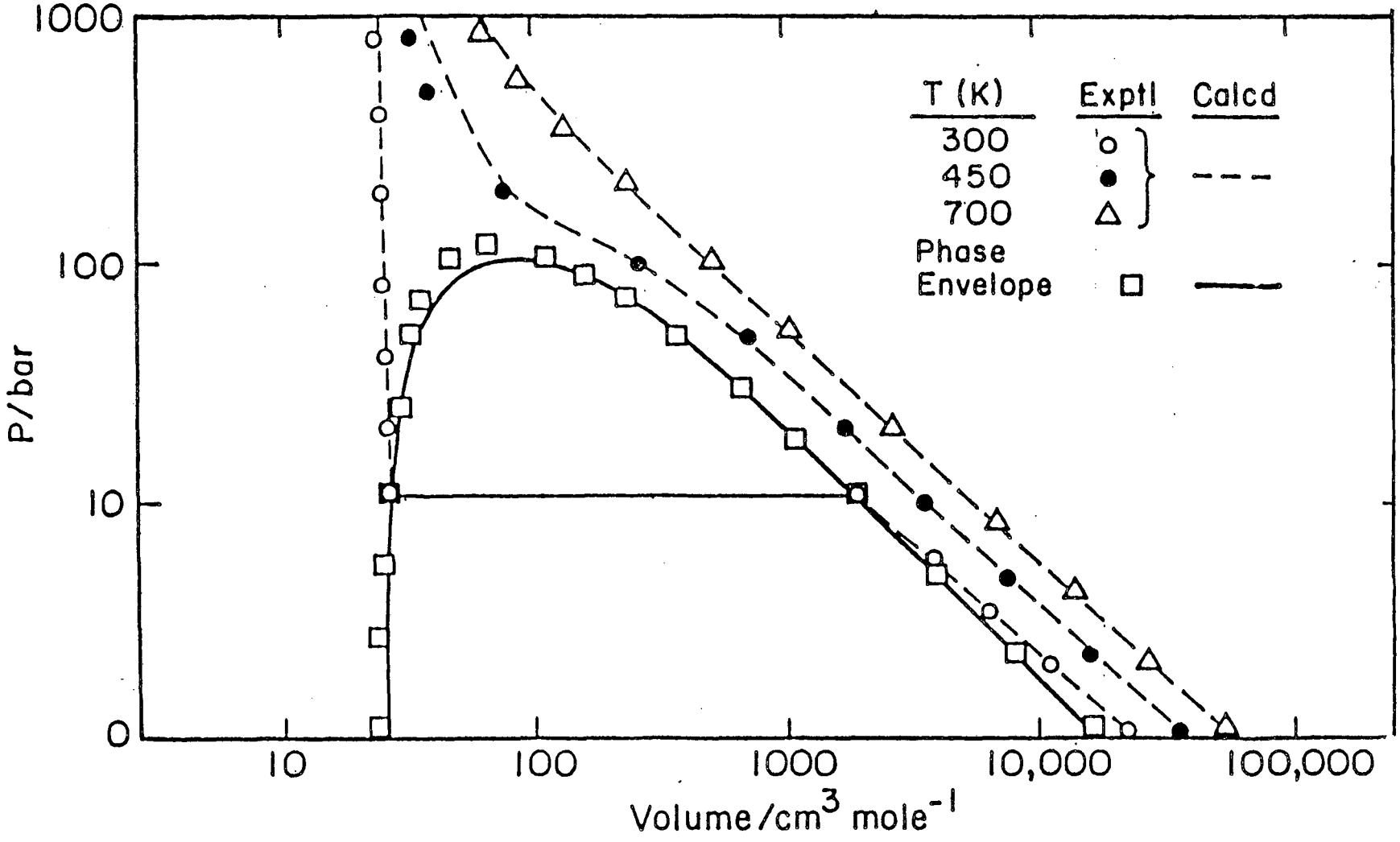
Figure 2





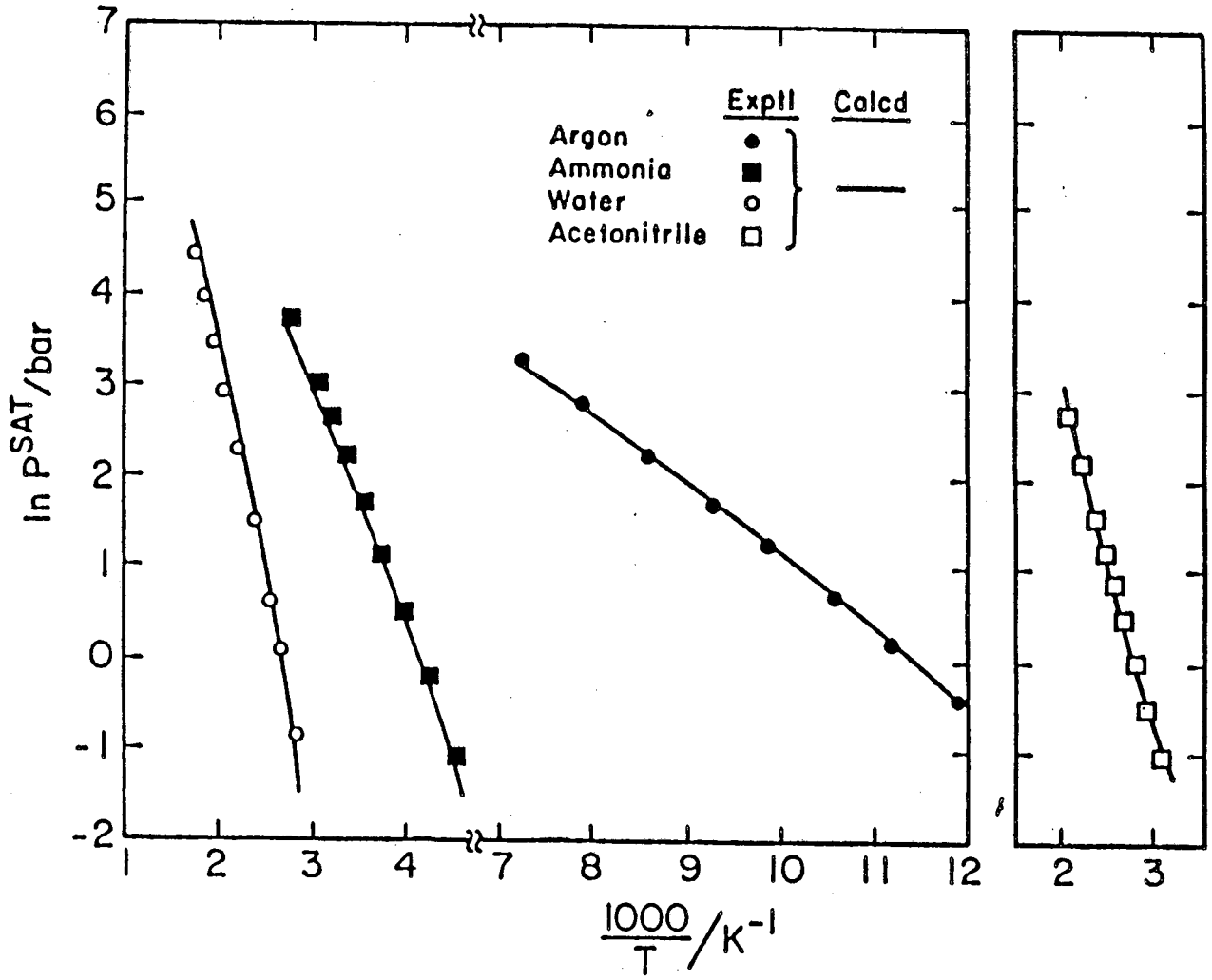

Isotherms for a Dipolar-Hard-Sphere Fluid Calculated by Modified Carnahan-Starling Equation. A Phase Transition occurs when the Reduced Dipole Moment is at Least 1.90.

Figure 3




Calculated and Observed Ammonia Isotherms

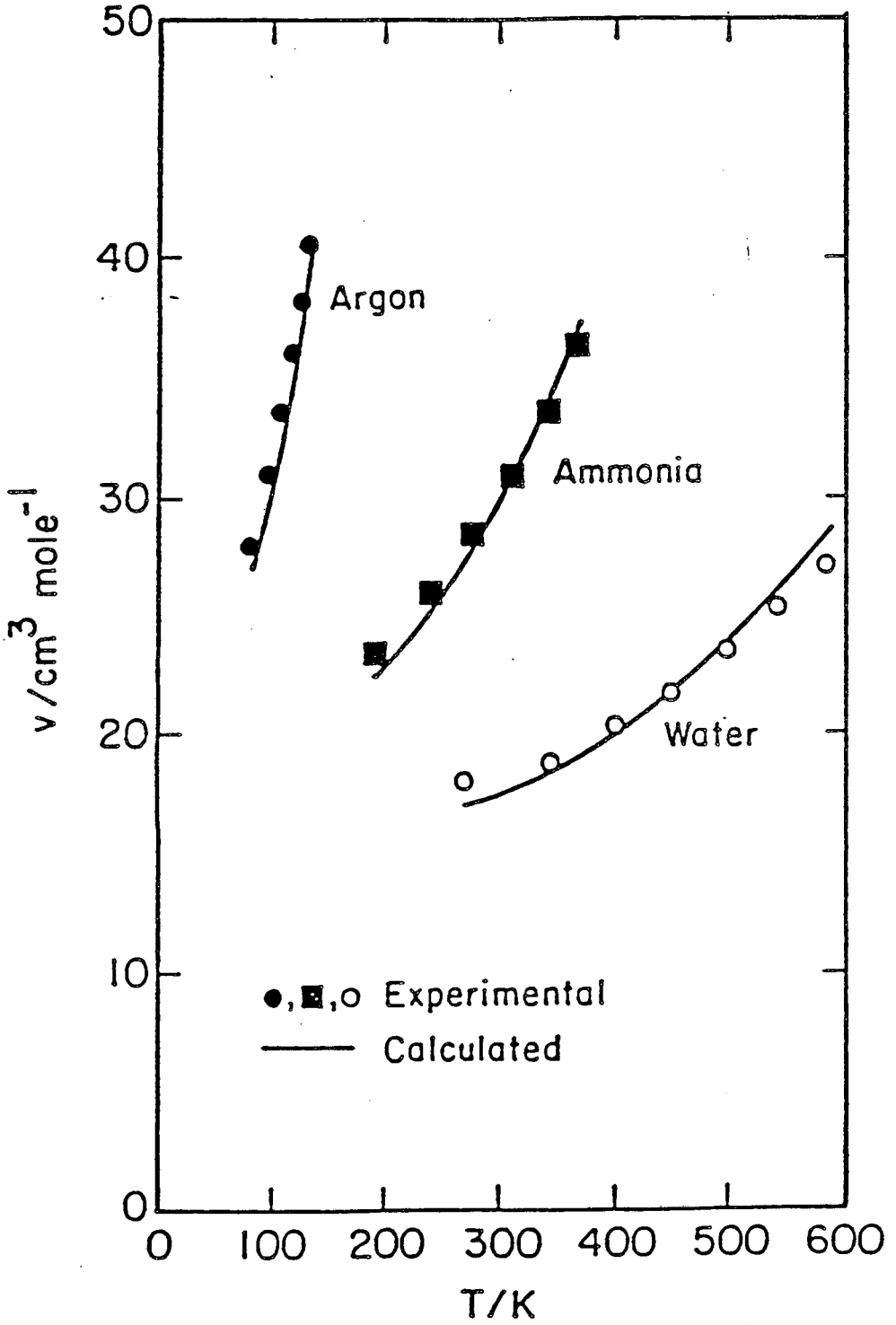
Figure 4




Calculated and Observed Vapor Pressures

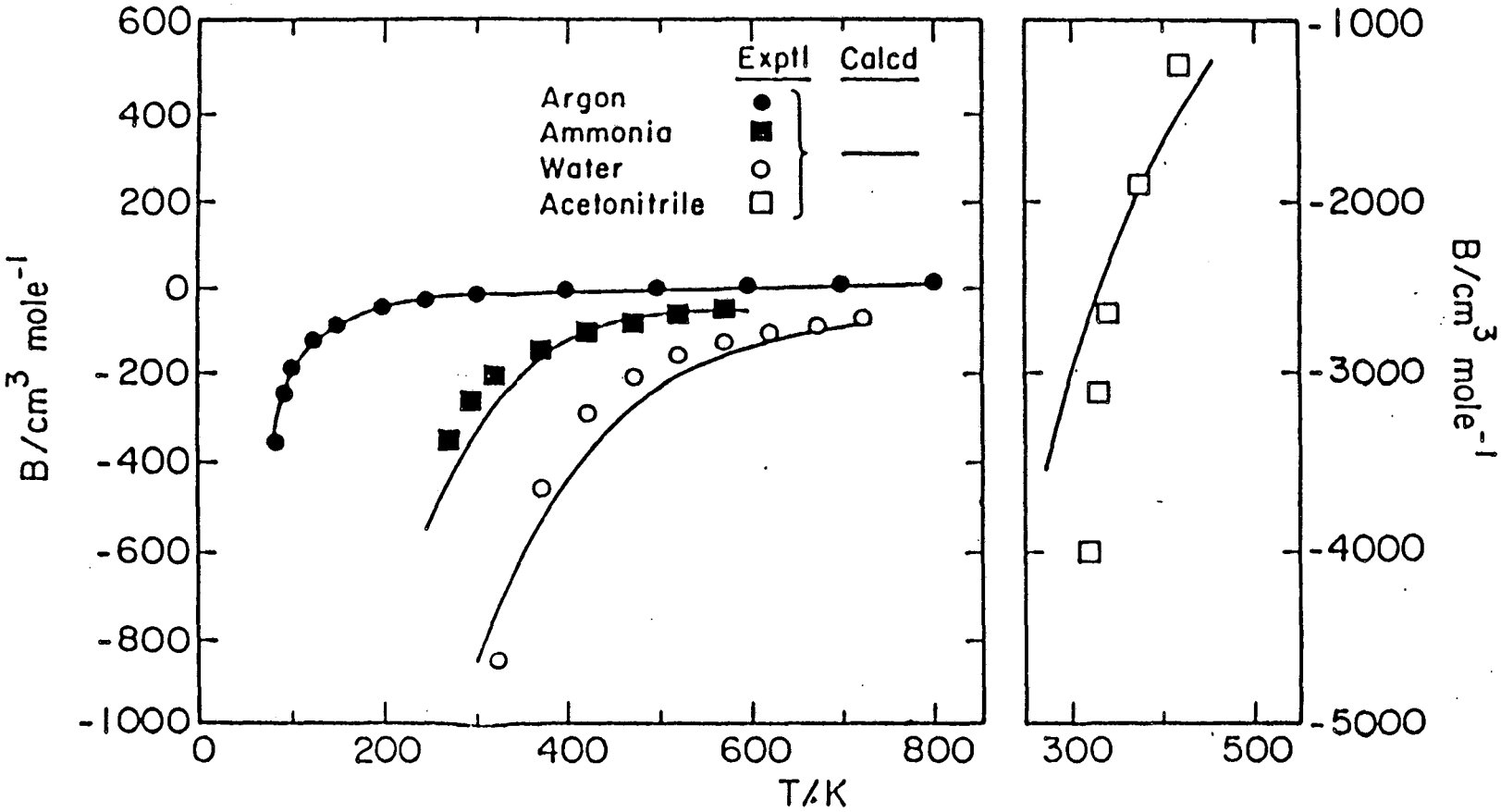
Figure 5






Calculated and Observed Saturated-Liquid Molar Volumes

Figure 6




Calculated and Observed Second Virial Coefficients

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