

from K.S. Pitzer,
Thermodynamics (3rd ed.)
(Mc-Graw Hill, NY, 1995).

Pitzer-9

CHAPTER 9

REAL GASES AND THE FLUID STATE

The ideal gas law is a satisfactory approximation for the P - V - T properties of gases at low pressures with molar volumes large compared to the volumes of the molecules and where the attractive intermolecular potentials are small in comparison to thermal energy. The initial deviations of real gases from ideal behavior are readily represented by simple equations. In the separate range of low temperatures, the properties of liquids can be represented by simple empirical equations giving the linear dependence of density on temperature and pressure. The behavior of a fluid outside of these two regions, however, is complex and no single equation of state has been found that is fully satisfactory for representing the properties of fluids over the full range of temperature and pressure.

In this chapter, we first describe the general pattern of properties of the fluid state ranging from nearly ideal gases to dense liquids. At temperatures near critical or above, the appropriate reference state is the ideal gas. At lower temperatures one uses both the ideal gas and the liquid reference states. General thermodynamic relationships are next illustrated with relatively simple equations of state that further simplify for the low-pressure range. Then, in later sections, other empirical equations

of state that describe the entire P - V - T range from ideal gas to dense liquid are described. Finally, we discuss the problem of estimation of fluid properties for substances for which there are only a few measurements. Only pure fluids are considered in this chapter; fluids with two or more components are treated in later chapters.

Throughout this chapter it will be convenient to consider the quantity z defined as

$$z = PV/nRT = P/\rho RT \quad (9-1)$$

which is called the *compression factor*, or more frequently but less appropriately, the *compressibility factor*. Here $\rho = n/V$ is the molar density. For an ideal gas, $z = 1.0$, and for real gases z may be either greater or smaller than unity. Figure 9-1 shows the typical pattern of the compression factor in the range of low and moderate pressures. At low pressures the isotherms are nearly straight lines with slope negative at low temperature but becoming positive at high temperature. At somewhat higher pressures the isotherms show some curvature downward at low temperatures and upward at higher temperatures. A plot of z vs. ρ shows a similar pattern. This behavior is represented effectively by a power series in either P or ρ .

Throughout this and subsequent chapters and appendices on fluids, we ordinarily use the density rather than the volume as a variable. We believe this has several advantages but note that much of the literature on this field uses the molar volume $V_m = 1/\rho$ instead.

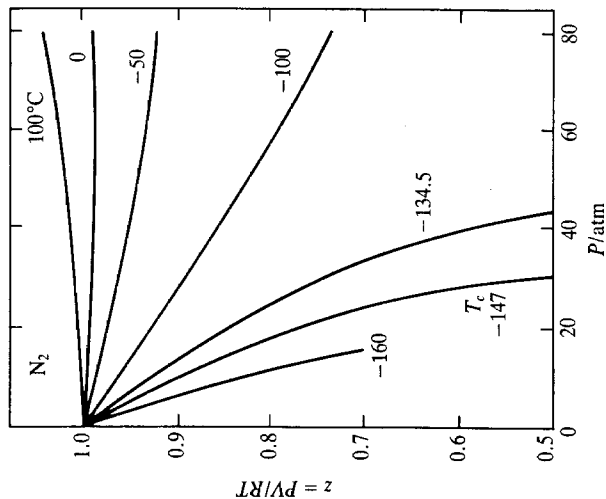


FIGURE 9-1
The compression factor for nitrogen.

Virial Equations of State

In 1901 Onnes first used a power series to express the P - V - T properties of a gas. Such an expression is known as a virial equation of state, and a convenient form is

$$\frac{P}{RT} = \rho + B\rho^2 + C\rho^3 + D\rho^4 + \dots \quad (9-2)$$

The unit coefficient for the first term on the right is the first virial coefficient and represents the ideal gas law. B is the second virial coefficient, C the third, etc.; each is a function of temperature, and is specific to a particular gas or vapor. The dimension of B is volume per mole, of C is $\text{vol}^2 \text{mol}^{-2}$, etc. In terms of the compression factor, this series becomes

$$z = 1 + B\rho + C\rho^2 + D\rho^3 + \dots \quad (9-3)$$

Often it is more convenient to take P and T as the independent variables (instead of ρ and T). Then one adopts the series

$$z = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (9-4)$$

By comparison of Eqs. (9-3) and (9-4) in the limit of small ρ and P , one can show for the second virial coefficient that $B' = B/RT$. The higher coefficients are related, $C' = (C - B^2)/(RT)^2$, but in an increasingly complex manner. In view of their approximate nature, one should use caution in converting the higher coefficients from one series for use in the other.

The coefficients B , C , etc., of Eqs. (9-2) and (9-3) are related in statistical mechanics to molecular properties and, in a strict sense, only they and not B' , C' , etc., should be called virial coefficients.

Fluids Over Wide Ranges of T and P

Figure 9-2 shows a series of isotherms of pressure as a function of density for a fluid. The example is methane but the pattern is universal. At high temperatures, P increases with ρ in a simple, nearly linear manner that is readily expressed by a virial series, Eq. (9-4). With decreasing temperature, the pattern becomes more complex with an intermediate point of minimum slope. The point where this minimum slope becomes zero is designated the critical point; it is the unique point for the entire diagram. The critical conditions are

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0 \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0 \quad (9-5)$$

or

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \quad (9-6)$$

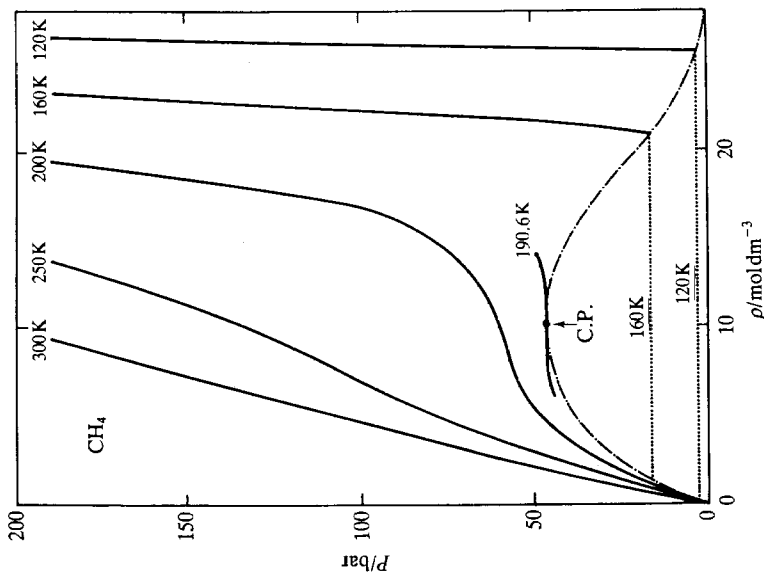


FIGURE 9-2
 P - ρ isotherms illustrating the critical region and differences at other temperatures.

Below the critical temperature one has a range of density in which the homogeneous fluid is unstable and the equilibrium state is that of the coexisting saturated vapor and saturated liquid. The conditions are

$$T_{\text{vap}} = T_{\text{liq}} \quad P_{\text{vap}} = P_{\text{liq}} \quad \mu_{\text{vap}} = \mu_{\text{liq}} \quad (9-7)$$

The pressure equality is obvious; the equality of chemical potential requires a more complex calculation, but we shall see that it is implicit in a comprehensive equation of state.

From Figure 9-2, we see that the vapor isotherms are simple (nearly linear) at temperatures well below critical and have a simple shape below a density one half that of the critical point at any temperature. This is the region in which a simple virial representation is always satisfactory; indeed, the use of just the second virial coefficient frequently suffices. Also, as noted at the beginning of this chapter, the isotherms become simple for small ranges of density near that of the saturated liquid at

temperatures well below critical. But, for the entire range of temperature and density, it is clear that the pattern is complex and may be difficult to represent with an equation.

Reduced Variables and Equations

The critical point is the unique point in the P - V - T diagram, and van der Waals proposed in 1873 that the properties of various fluids might be the same if compared on a reduced basis, i.e., as functions of $T_r = T/T_c$, $P_r = P/P_c$, $V_r = V/V_c$, $\rho_r = \rho/\rho_c$. Figure 9-3 shows isotherms of the compression factor on the reduced basis. It is clear that N_2 , CO_2 , and H_2O have similar reduced isotherms, but that they are not exactly the same. Nevertheless, it has been found to be very useful to compare fluid properties on a reduced basis and to develop equations in terms of reduced properties. It is found that there are small groups of fluids that have quite accurately the same properties on a reduced basis. The simplest and most important group comprises the heavier noble gases (Ar, Kr, Xe) and methane; they are sometimes denoted simple fluids.

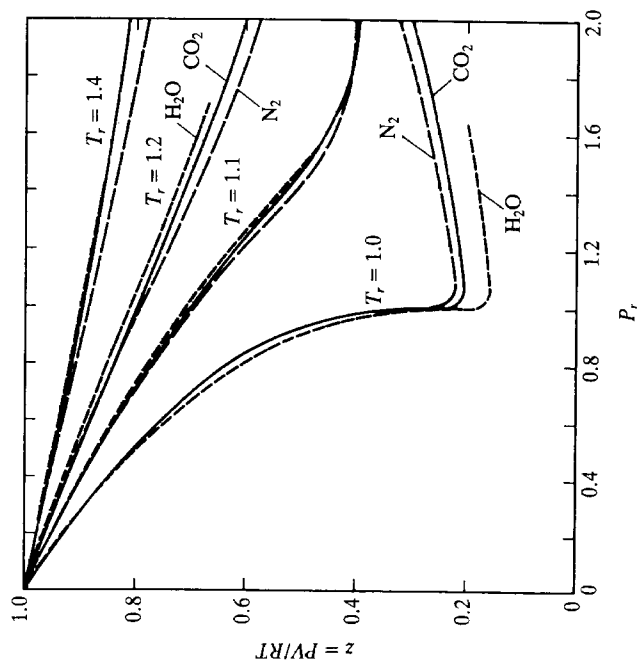


FIGURE 9-3
A test of the hypothesis of corresponding states. Isotherms of nitrogen (long-dashed lines), carbon dioxide (solid lines), and steam (short-dashed lines) as functions of reduced pressure.

Evaluation of Virial Coefficients

Various methods may be used to determine the second virial coefficient or an entire series of virial coefficients from a sequence of pressure-volume measurements at constant temperature. One may select one or another of Eqs. (9-2) to (9-4), retaining an appropriate number of terms, and then carry out a least-squares regression of the data to evaluate the virial coefficients retained, B , C , \dots . It is important to consider the experimental uncertainties and to assign appropriate weights to the measured values. Also, in most cases, one should recalculate with a different number of coefficients in order to ascertain the degree to which the individual coefficients are unambiguously determined.

An alternate procedure is to rearrange Eq. (9-3) to

$$\frac{z-1}{\rho} = B + C\rho + D\rho^2 + \dots \quad (9-8)$$

Then a graph of $(z-1)/\rho$ vs. ρ will give B as the intercept at $\rho = 0$. This shows visually the uncertainty and the possible redundancy of B with C .

One may carry this procedure another step and write

$$\frac{z-1}{\rho^2} - \frac{B}{\rho} = C + D\rho + \dots \quad (9-9)$$

whereupon extrapolation of the left-hand side gives C as the intercept at $\rho = 0$. The work of Douslin¹ on methane is a good example of the use of Eqs. (9-8) and (9-9).

Most investigators, however, have carried out direct regressions of Eq. (9-2) with varying numbers of terms. The work of Michels et al.² on argon is an excellent example that shows clearly that the second virial coefficient is relatively insensitive to the number of terms. The values of the third virial coefficient, however, vary significantly between different treatments of the same data. For example, at 188.15 K, they used a three-term equation (ending in C) fitted to the data up to 50 bar and obtained $B = -54.83 \text{ cm}^3 \text{ mol}^{-1}$ and $C = 1791 \text{ cm}^6 \text{ mol}^{-2}$. They also fitted a seven-term equation to their full array of data extending to 1000 bar. In the latter case, B is almost unchanged at -54.27 while C is greatly decreased to 1416; also the next term D is large and positive and is expressing some of the effect included in C for the shorter equation.

At temperatures well below critical, where the saturated vapor pressure is small, only the second virial coefficient is readily determined. Surface adsorption effects can be more important than those of the third virial coefficient. The study of argon in this range by Fender and Halsey³ indicates how these problems can be handled.

There are now accurate data for the second virial coefficient for many gases; these have been evaluated and summarized by Dymond and Smith,⁴ who also give third virial coefficient values when available.

Second Virial Coefficients: Temperature Dependence and Other Properties

The second virial coefficients for several gases are shown in Fig. 9-4 on a reduced basis. The reduced virial coefficient is

$$B_r = \frac{nB}{V_c} = B\rho_c \quad (9-10)$$

while the reduced temperature is $T_r = T/T_c$. At reduced temperatures above about 2.7, the virial coefficient is positive, reflecting a dominant effect of repulsive forces. The temperature at which $B = 0$ is known as the Boyle point. At lower temperatures, the relative importance of intermolecular attractive forces increases. The pattern of negative values below $T_r \approx 0.8$ represents the increasing proportion of double molecules in the vapor. For normal fluids, this dimerization does not proceed very far

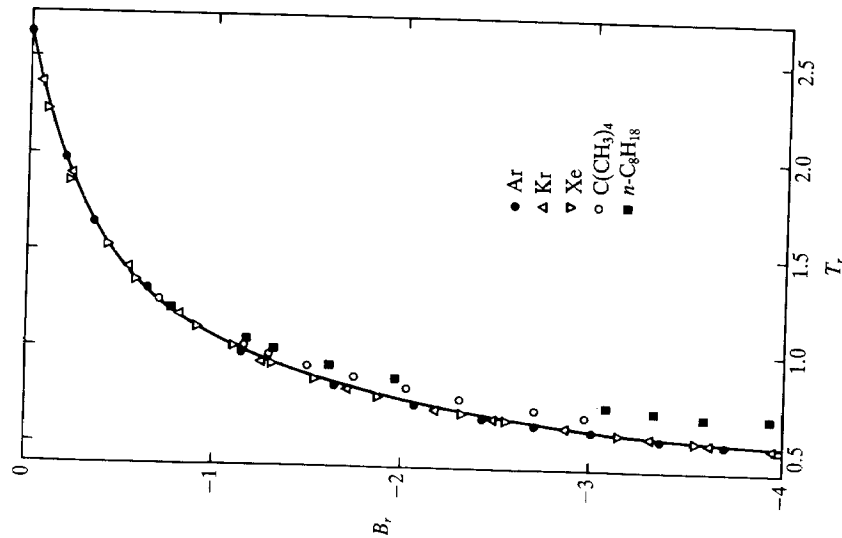


FIGURE 9-4
The reduced second virial coefficient for several gases together with the curve of Eq. (9-12)*, which represents the behavior of the inert gases Ar, Kr, and Xe.

before the vapor condenses to the liquid. Thus, the virial coefficient expression is usually more satisfactory than a dimerization reaction equilibrium treatment because the repulsive-force effects are naturally included in the former but not in the latter.

There are special cases, usually involving hydrogen bonding, where the dimerization or polymerization proceeds to a large extent before liquefaction. Such examples and the appropriate methods of treatment are described in a separate section below where the statistical mechanics of the second virial coefficient is also given.

It is not surprising that the points for Ar, Kr, and Xe fall close to a single curve on Fig. 9-4. For other normal fluids the reduced virial coefficient is even more negative at low T_r , as illustrated by the points for $C(CH_3)_4$ and n -octane. This pattern of behavior can be expressed in a general equation described in a later section and in Appendix 4. For the present, we take as an example the equation⁵ fitting the data for the simple fluids Ar, Kr, and Xe on a reduced basis:

$$B_r = 0.44226 - \frac{0.98097}{T_r} - \frac{0.61114}{T_r^2} - \frac{0.005156}{T_r^6} \quad (9-11)^*$$

If we insert the critical properties, $T_c = 150.86$ K and $\rho_c = 13.41$ mol dm⁻³, the second virial coefficient of argon is

$$B = 32.98 - \frac{1.1036 \times 10^4}{T} - \frac{1.0372 \times 10^6}{T^2} - \frac{4.53 \times 10^{12}}{T^6} \quad \text{cm}^3 \text{ mol}^{-1} \quad (9-12)^*$$

This equation fits the experimental values⁴ over the entire range from 80 to 1000 K within experimental uncertainty.

Expansion and Compression Coefficients

The coefficient of expansion, the compressibility and related quantities are obtained by differentiation after appropriate rearrangement of the virial equations. From Eq. (9-4) after multiplication by RT/P , one obtains

$$\left(\frac{\partial V_m}{\partial T}\right)_P = \frac{R}{P} + RT \left(\frac{dB'}{dT} + P \frac{dC'}{dT} + P^2 \frac{dD'}{dT} + \dots \right) \quad (9-13)$$

$$\left(\frac{\partial V_m}{\partial P}\right)_T = RT \left(-\frac{1}{P^2} + C' + 2D'P + \dots \right) \quad (9-14)$$

As usually defined, the coefficient of expansion α is

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{zT} + RTP \left(\frac{dB'}{dT} + P \frac{dC'}{dT} + P^2 \frac{dD'}{dT} + \dots \right) \quad (9-15)$$

while the compressibility is

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = RTP \left(\frac{1}{P^2} - C' - 2D'P + \dots \right) \quad (9-16)$$

In a similar manner, Eq. (9-2) yields

$$\left(\frac{\partial P}{\partial T}\right)_\rho = R \left[\rho + \left(B + T \frac{dB}{dT} \right) \rho^2 + \left(C + T \frac{dC}{dT} \right) \rho^3 + \left(D + T \frac{dD}{dT} \right) \rho^4 + \dots \right] \quad (9-17)$$

$$\left(\frac{\partial P}{\partial \rho}\right)_T = RT \left[1 + 2B\rho + 3C\rho^2 + 4D\rho^3 + \dots \right] \quad (9-18)$$

The last two results can be combined to obtain $(\partial V/\partial T)_\rho$ as a function of density:

$$\left(\frac{\partial V_m}{\partial T}\right)_\rho = \frac{1}{\rho^2} \frac{(\partial P/\partial T)_\rho}{(\partial P/\partial \rho)_T} \quad (9-19)$$

THERMODYNAMIC RELATIONSHIPS

We now apply the general thermodynamic equations to fluids, both on a general basis and then with the virial equations as examples.

Gibbs and Helmholtz Energies

All of the other thermodynamic properties of a fluid can be expressed very conveniently in terms of the Gibbs energy, if the independent variables are T and P , or in terms of the Helmholtz energy, if the independent variables are T and ρ (or V). For the region of low and moderate pressures shown in Fig. 9-1, either set of variables is fully satisfactory and both methods will be described. When the two-phase, vapor-liquid region is involved, however, the Helmholtz energy is a much more satisfactory basis since A and P remain single-valued functions of T and ρ . In this region ρ (or V) is a multiple-valued function of T and P . One can tabulate or write separate equations for vapor and liquid properties, including the Gibbs energy, as functions of P . But if one wishes a single comprehensive equation of state, one uses T and ρ (or V) as variables and the Helmholtz energy as the parent function.

The parent function in either case is the sum of two functions, one for the ideal-gas or standard-state properties and the other for the departure of the fluid from ideal-gas behavior. Thus, on a molar basis and considering first the ideal gas,

$$G^{\text{id}}(T,P) = G^\circ(T) + RT \ln \left(\frac{P}{P^\circ} \right) \quad (9-20)$$

where P° is the pressure of the standard state, normally 1 bar, and $G^\circ(T)$ is the Gibbs energy in the standard state, which is a function of T . Then, at constant T ,

$$\left[\frac{\partial(G - G^{\text{id}})}{\partial P} \right]_T = V_m - \frac{RT}{P} \quad (9-21)$$

$$G(T,P) - G^{\text{id}}(T,P) = \int_0^P \left(V_m - \frac{RT}{P'} \right) dP' \quad (9-22)$$

$$G(T,P) = G^\circ(T) + RT \left[\ln \left(\frac{P}{P^\circ} \right) + \int_0^P (z-1) d \ln P' \right] \quad (9-23)$$

Insertion of the virial equation for z yields

$$G(T,P) = G^\circ(T) + RT \left[\ln \left(\frac{P}{P^\circ} \right) + B'P + \frac{C'P^2}{2} + \frac{D'P^3}{3} + \dots \right] \quad (9-24)$$

The corresponding treatment for the molar Helmholtz energy also begins with the ideal gas,

$$\begin{aligned} A^{\text{id}}(T,\rho) &= A^\circ(T) + RT \ln \left(\frac{\rho}{\rho^\circ} \right) \\ &= G^\circ(T) + RT[-1 + \ln(\rho RT)] \end{aligned} \quad (9-25)$$

since $\rho^\circ = P^\circ/RT$, $P^\circ = 1$ bar, and $G^\circ = A^\circ + RT$.

The initial formulation of an equation of state is often given for the Helmholtz energy instead of the compression factor. In particular, one first divides A into an ideal and a residual term,

$$A = A^{\text{id}} + A^{\text{res}} \quad (9-26)$$

where A^{id} was given in Eq. (9-25). Then

$$z = 1 + \rho \left[\frac{\partial (A^{\text{res}}/RT)}{\partial \rho} \right]_T \quad (9-27a)$$

If z is initially defined, one has the converse relationship

$$\frac{A^{\text{res}}}{RT} = \int_0^\rho (z-1) d \ln \rho' \quad (9-27b)$$

This yields A^{res} if the equation was first formulated for z , and the complete equation for the Helmholtz energy is

$$A(T,\rho) = G^\circ(T) + RT[-1 + \ln(\rho RT)] + A^{\text{res}} \quad (9-28)$$

If we substitute the virial equation, we obtain from Eqs. (9-27b) and (9-28)

$$A(T,\rho) = G^\circ(T) + RT \left[-1 + \ln(\rho RT) + B\rho + \frac{C\rho^2}{2} + \frac{D\rho^3}{3} + \dots \right] \quad (9-29)$$

Note that, in the last two equations, R must be in bars for the quantity ρRT , while in the factor outside the brackets R has the units used for G° and A .

Other Thermodynamic Functions

The chemical potential, fugacity, entropy, enthalpy and other functions are readily derived from the expressions for the molar Gibbs and Helmholtz energies. All extensive

quantities in this section are for one mole. The results with pressure as the independent variable are

$$\frac{\mu}{RT} = \frac{G}{RT} = \frac{G^\circ}{RT} + \ln\left(\frac{P}{P^\circ}\right) + \int_0^P (z-1) d\ln P' \quad (9-23)$$

$$\ln\left(\frac{f}{P}\right) = \int_0^P (z-1) d\ln P' \quad (9-30)$$

$$\frac{H-H^\circ}{R} = -T^2 \int_0^P \left(\frac{\partial z}{\partial T}\right)_P d\ln P' \quad (9-31)$$

$$\frac{S-S^\circ}{R} = -\ln\left(\frac{P}{P^\circ}\right) + \int_0^P \left[1 - z - T\left(\frac{\partial z}{\partial T}\right)_P\right] d\ln P' \quad (9-32)$$

$$\frac{C_P - C_P^\circ}{R} = -T \int_0^P \left[2\left(\frac{\partial z}{\partial T}\right)_P + T\left(\frac{\partial^2 z}{\partial T^2}\right)_P\right] d\ln P' \quad (9-33)$$

If the virial series in pressure, Eq. (9-5), is substituted, one obtains after integration,

$$\frac{\mu - G^\circ}{RT} = \ln\left(\frac{P}{P^\circ}\right) + B'P + \frac{C'P^2}{2} + \frac{D'P^3}{3} + \dots \quad (9-24)$$

$$\ln\left(\frac{f}{P}\right) = PB' + \frac{P^2C'}{2} + \frac{P^3D'}{3} + \dots \quad (9-34)$$

For calculations with density as the independent variable, we first recall Eqs. (9-25)–(9-27) for the Helmholtz energy. Then the standard relationships yield expressions for other molar functions as follows.

$$\frac{A - G^\circ}{RT} = -1 + \ln(\rho RT) + \int_0^\rho (z-1) d\ln \rho' \quad (9-28)$$

$$\frac{\mu - G^\circ}{RT} = \ln(\rho RT) + z-1 + \int_0^\rho (z-1) d\ln \rho' \quad (9-35)$$

$$\ln\left(\frac{f}{P}\right) = z-1 - \ln z + \int_0^\rho (z-1) d\ln \rho' \quad (9-36)$$

$$\frac{U - U^\circ}{R} = -T^2 \int_0^\rho \left(\frac{\partial z}{\partial T}\right)_\rho d\ln \rho' \quad (9-37)$$

$$\frac{H - H^\circ}{R} = T(z-1) - T^2 \int_0^\rho \left(\frac{\partial z}{\partial T}\right)_\rho d\ln \rho' \quad (9-38)$$

$$\frac{S - S^\circ}{R} = -\ln(\rho RT) + \int_0^\rho \left[1 - z - T\left(\frac{\partial z}{\partial T}\right)_\rho\right] d\ln \rho' \quad (9-39)$$

$$\frac{C_V - C_V^\circ}{R} = -T \int_0^\rho \left[2\left(\frac{\partial z}{\partial T}\right)_\rho + T\left(\frac{\partial^2 z}{\partial T^2}\right)_\rho\right] d\ln \rho' \quad (9-40)$$

Substitution of Eq. (9-27b) yields alternate expressions involving A^{res}/RT .

Now any equation of state may be substituted for z (and A^{res}) and the desired function obtained. For example, if the virial series in density, Eq. (9-3), is chosen, one obtains the following.

$$\frac{A - G^\circ}{RT} = -1 + \ln(\rho RT) + B\rho + \frac{C\rho^2}{2} + \frac{D\rho^3}{3} + \dots \quad (9-29)$$

$$\frac{\mu - G^\circ}{RT} = \ln(\rho RT) + 2B\rho + \frac{3C\rho^2}{2} + \frac{4D\rho^3}{3} + \dots \quad (9-41)$$

$$\ln f = \ln(\rho RT) + 2B\rho + \frac{3C\rho^2}{2} + \frac{4D\rho^3}{3} + \dots \quad (9-42)$$

$$\ln\left(\frac{f}{P}\right) = B\rho + \frac{(C + B^2)\rho^2}{2} + \left(BC + \frac{D}{3}\right)\rho^3 + \dots \quad (9-43)$$

$$U - U^\circ = -RT^2 \left[\rho \left(\frac{dB}{dT}\right) + \frac{\rho^2}{2} \left(\frac{dC}{dT}\right) + \dots \right] \quad (9-44)$$

$$H - H^\circ = RT \left[\rho \left(B - T\frac{dB}{dT}\right) + \frac{\rho^2}{2} \left(C - T\frac{dC}{dT}\right) + \dots \right] \quad (9-45)$$

$$S - S^\circ = -R \left[\ln(\rho RT) + \rho \left(B + T\frac{dB}{dT}\right) + \frac{\rho^2}{2} \left(C + T\frac{dC}{dT}\right) + \dots \right] \quad (9-46)$$

$$C_V - C_V^\circ = -RT \left[\rho \left(2\frac{dB}{dT} + T\frac{d^2B}{dT^2}\right) + \rho^2 \left(\frac{dC}{dT} + \frac{T}{2} \frac{d^2C}{dT^2}\right) + \dots \right] \quad (9-47)$$

The fugacity coefficient $\phi = f/P$ is directly available from Eqs. (9-30), (9-34), (9-36), and (9-43). Also, as noted above, if the standard state is the perfect gas at 1 bar, then R must be in bars for the quantity (ρRT) in these equations. Where R appears elsewhere, it has the same units as the function calculated: A, G , etc.

REAL GASES AT LOW PRESSURE; THE SECOND VIRIAL COEFFICIENT

In many practical situations with gases at or near atmospheric pressure, the deviation from the ideal gas law is small but is significant for accurate work. Under these conditions the higher virial coefficients can be ignored and attention concentrated on the second virial coefficient. The simplification of equations through (9-47) is obvious; in particular, Eq. (9-43) becomes

$$\frac{f}{P} = \exp(B\rho) \cong 1 + B\rho \quad (9-43)^*$$

where the second equality arises from the expansion of the exponential. But from Eq. (9-3) we see that in this approximation

$$\frac{f}{P} = z = \frac{P}{\rho RT} \quad (9-48)^*$$

and, if we note that the ideal pressure at ρ and T is $P_i = \rho RT$, we find

$$\frac{f}{P} = \frac{P}{P_i} \quad (9-49)^*$$

Thus, the actual pressure lies between the fugacity and the pressure calculated from the ideal-gas law and is the geometrical mean of the two.

Very simple and useful equations are obtained by making the substitution $\rho = P/RT$, which is valid at the second virial level, into Eq. (9-45) and then differentiating:

$$H - H^0 = P \left(B - T \frac{dB}{dT} \right) \quad (9-50)^*$$

$$C_P - C_P^0 = -PT \frac{d^2B}{dT^2} \quad (9-51)^*$$

It is interesting to test the error caused by the omission of the third virial coefficient. In an earlier section, the values $B = -54.8 \text{ cm}^3 \text{ mol}^{-1}$ and $C = 1791 \text{ cm}^6 \text{ mol}^{-2}$ were given for argon at 188.15 K, which is somewhat above the critical temperature at 150.86 K. At 188 K and 10 bar, the density is about $6.4 \times 10^{-4} \text{ mol cm}^{-3}$ and the second virial term reduces z by 3.5%. For these conditions, the third virial term raises z by 0.07%, which is negligible for many purposes.

An example of application of the equation in pressure is obtained from the work of Otto, Michels, and Wouters⁶ for nitrogen to 200 bar. Their expression for 0°C may be converted to the basis of pressure in bars and density in mol cm^{-3} .

$$\begin{aligned} \frac{P}{\rho} &= 22712 - 10.281P + 0.064337P^2 + 4.9943 \times 10^{-7}P^4 \\ &\quad - 1.2318 \times 10^{-11}P^6 + 9.20 \times 10^{-17}P^8 \end{aligned} \quad (9-52)^*$$

From Eqs. (9-4), and (9-34)*, we then obtain

$$\begin{aligned} \ln \left(\frac{f}{P} \right) &= \ln \phi = -4.527 \times 10^{-4}P + 1.4164 \times 10^{-6}P^2 + 5.497 \times 10^{-12}P^4 \\ &\quad - 9.039 \times 10^{-17}P^6 + 5.06 \times 10^{-22}P^8 \end{aligned} \quad (9-53)^*$$

The change of heat capacity with pressure in the low-pressure range is sometimes of interest and its calculation will serve as an example of other derived quantities. If, for example, we substitute Eq. (9-12)* for argon into Eq. (9-51)* and express the results as C_p/R , we obtain in bar^{-1}

$$\left(\frac{\partial C_p/R}{\partial P} \right)_T = \frac{265.5}{T^2} + \frac{7.485 \times 10^4}{T^3} + \frac{2.29 \times 10^{12}}{T^7} \quad (9-54)^*$$

This effect for argon is only 0.1 bar^{-1} at 100 K and decreases rapidly with increase in temperature. For larger and more complex molecules, the effect is larger, as we show in a later section.

EQUATIONS OF STATE VALID OVER THE FULL RANGE OF T AND P

The simplest equation that yields all of the qualitative features of real fluids is that of *van der Waals*. In terms of density, it is

$$P = \frac{RT\rho}{1 - b\rho} - a\rho^2 \quad (9-55)^*$$

Here a and b are parameters to be adjusted for each substance. The first term involving b includes the repulsive interactions, while the second term represents the intermolecular attractive forces.

It is interesting to apply certain transformations to this simple case. The conditions for the critical point Eq. (9-5) yield values for the parameters in terms of the critical temperature T_c and density ρ_c :

$$b = \frac{1}{3\rho_c} \quad a = \frac{9RT_c}{8\rho_c} \quad \text{also} \quad \rho_c = \frac{8P_c}{3RT_c}$$

The molar Helmholtz energy is readily obtained from Eqs. (9-27b) and (9-28):

$$\frac{A^{\text{res}}}{RT} = -\ln(1 - b\rho) - \frac{a\rho}{RT} \quad (9-56)^*$$

$$A = G^0 + RT[-1 + \ln(\rho RT) - \ln(1 - b\rho)] - a\rho \quad (9-57a)^*$$

The chemical potential or molar Gibbs energy is then

$$\mu = G = A + \frac{P}{\rho}$$

$$P = \mu^0 + RT \left(\ln(\rho RT) - \ln(1 - b\rho) + \frac{b\rho}{1 - b\rho} \right) - 2a\rho \quad (9-57b)^*$$

Other properties can now be calculated as desired using Eq. (9-56)*.

