

Thermodynamic Equations of State for Real Gases and Liquids

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The quantitative thermodynamic description of fluids has presented an analytical problem for scientists which has resulted in an elaborate development of formulations. These have provided varying degrees of adequacy for the user of thermodynamic data. Both theoretical and empirical treatments encounter limitations which ultimately impose bounds on the accuracy and completeness for any formulation. Nevertheless, the experience provided by the many attempts to deal with this problem can be consolidated to establish a coordinated description based on the most desirable characteristics of the best theoretical and empirical treatments.

The quantities of basic concern in thermodynamics are pressure, temperature, density, and the several energy functions. In accord with well established practice, density and temperature will be accepted as the primary independent variables in the following discussion. In addition, the secondary independent variables are suitable composition parameters. The present treatment will be essentially independent of variations in composition. It is recognized, of course, that in process analysis, pressure is more useful than density as a basic parameter. The transfer, however, from density and temperature to pressure and temperature can be accomplished in actual analysis by direct application of a suitable P-V-T relation.

The complete thermodynamic description of any fluid is known if quantitative values of the free energy

are known. Other thermodynamic quantities are derivable from this free energy:

$$\text{Entropy} \quad S = - \left(\frac{\partial A}{\partial T} \right)_\rho \quad (2)$$

$$\text{Pressure} \quad p = \rho^2 \left(\frac{\partial A}{\partial \rho} \right)_T \quad (3)$$

$$\text{Internal Energy} \quad U = A + T \left(\frac{\partial A}{\partial T} \right)_\rho \quad (4)$$

$$\text{Heat Capacity} \quad C_V = -T \left(\frac{\partial^2 A}{\partial T^2} \right)_\rho \quad (5)$$

If pressure, p , 3), and heat capacity, C_V , 4), are known as functions of density and temperature, then by integration the free energy, A , may be sufficiently well established for the determination of any other quantity. It is also useful to make use of the two derived quantities, pressure and heat capacity, to provide a separation of information into that dependent on intermolecular interactions—the pressure—and that dependent primarily on molecular structure—the heat capacity.

In the present discussion, attention will be restricted to the formulation of and the information provided by the P-V-T, pressure-density-temperature, relation, 3).

An established starting point for this examination is that the P-V-T equation of state for real fluids—including the complete liquid region from the critical

$$A = U - TS \quad (1)$$

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density to the solid phase boundary-can in principle be expressed by either one of two extensions of the perfect gas equation:

$$p = \rho R T \quad (6)$$

These extensions are:

I The Virial Equation:

$$p = \rho R T (1 + B\rho + C\rho^2 + D\rho^3 + \dots) \quad (7)$$

where in general the virial coefficients B, C, D, \dots are functions of temperature and composition.

II The Imperfect Gas Equation:

$$p = \rho R T + \rho^2 R (-\alpha' + T \beta' - \gamma_0' \theta_0 - \varphi_1) \quad (8)$$

where $\alpha', \beta', \gamma_0'$ are density functions; θ_0 is a temperature function becoming small when temperature becomes very large, and φ_1 is a small quantity dependent on both density and temperature.

Of these two very general equations, the Virial is by far the best known and the most extensively studied. It is of a form readily indicated by theoretical studies and much effort has been devoted to the theoretical development of the virial coefficients. Their determination becomes difficult beyond the first two or three and also becomes quite sensitive to the precise structure of the molecular interaction. In addition to this problem, the virial equation series converges slowly except for very low densities. As a consequence of these constraints its principal useful application has been in a density region near the perfect gas and well removed from liquid phase densities greater than the critical. Its value, however, is fundamental in view of the sound theoretical foundation. As the application and theory of the Virial Equation is well set forth in many references, it will not be considered further here except to the extent it may be correlated with the second general

equation.

The Imperfect Gas Equation, 8), has been developed primarily by correlation and extension of a variety of semi-empirical equations. However, as indicated in the analysis to follow, in its general form it can be shown to be fully compatible with the Virial Equation and consequently of equal theoretical validity.

The oldest and most familiar extensions of the equation of state to imperfect gases are the Clausius and Van der Waals equations. These may be written respectively as:

$$p = \rho R T / (1 - b\rho) \quad (9)$$

and

$$p + a \rho^2 = \rho R T / (1 - b\rho) \quad (10)$$

The Van der Waals equation, 10), which generalizes the Clausius equation, 9), can also be written:

$$p = \rho R T + \rho^2 R \left(\frac{Tb}{1 - b\rho} - \frac{a}{R} \right) \quad (11)$$

By inspection, this is a special case of the general Imperfect Gas Equation, 8), with the density and temperature functions assuming the values:

$$\begin{aligned} \alpha' &= a/R & \beta' &= b/(1 - b\rho) \\ \theta_0 &= 0 & \varphi_1 &= 0 \end{aligned} \quad (12)$$

In a similar manner a very large number of well known semi-empirical equations can also be shown to be special cases of the general equation, 8).

Among these are:

Bertholet

$$\begin{aligned}\alpha' &= 0, & \beta' &= b/(1-b\rho) \\ \gamma_0' &= 1, \quad \theta_0 = a/RT, & \varphi_1 &= 0\end{aligned}\quad (13)$$

Redlich-Kwong

$$\begin{aligned}\alpha' &= 0, & \beta' &= b/(1-b\rho) \\ \gamma_0' &= \frac{1}{1+b\rho}, \quad \theta_0 = a/RT^{1/2}, \quad \varphi_1 = 0\end{aligned}\quad (14)$$

Beattie-Bridgeman

$$\begin{aligned}\alpha' &= A_0(1-a\rho)/R \\ \beta' &= \beta_0(1-b\rho) \\ \gamma_0' &= 1 - \beta_0 \rho (1-b\rho) \\ \theta_0 &= c/T^2, \quad \varphi_1 = 0\end{aligned}\quad (15)$$

Benedict-Webb-Rubin

$$\begin{aligned}\alpha' &= (A_0 + a\rho + a\alpha\rho^4)/R \\ \beta' &= \beta_0 + b\rho \\ \gamma_0' &= 1 - c/c_0 \rho (1 + \gamma_0 \rho^2) e^{-r_0 \rho^2} \\ \theta_0 &= c/RT^2, \quad \varphi_1 = 0\end{aligned}\quad (16)$$

Martin-Hu

$$\begin{aligned}\alpha' &= \frac{A_2}{(1-b\rho)^2} + \frac{A_3\rho}{(1-b\rho)^3} + \frac{A_4\rho^2}{(1-b\rho)^4} \\ \beta' &= \frac{b}{1-b\rho} + \frac{B_2/R}{(1-b\rho)^2} + \frac{B_3\rho/R}{(1-b\rho)^3} + \frac{B_4\rho^2/R}{(1-b\rho)^4} \\ \gamma' &= \frac{1}{(1-b\rho)^2} + \frac{c_3\rho/c_2}{(1-b\rho)^3} \\ \theta_0 &= c_3 \exp(-5.475T/T_c), \quad \varphi_1 = 0\end{aligned}\quad (17)$$

It is of interest to note that in all these common

semi-empirical equations, the residual function, φ_1 , is set identically equal to zero. It is not possible, in general, to make this assumption without theoretical basis. In fact, even empirical evidence indicates this assumption cannot be made. One can, however, with no loss in generality, write

$$\varphi_1 = \rho \gamma_1' \theta_1 + \rho^2 \gamma_2' \theta_2 + \dots \quad (18)$$

where γ_i' are density functions and θ_i are temperature functions. This series convergence very rapidly so that one or two terms will provide very high accuracy for the entire fluid region. The basic approach to the Imperfect Gas Equation appeared in the author's *Engineering Thermodynamics* (Prentice-Hall, 1960). The same concept with extensive examination of the rate of convergence has appeared in publications of the Academy of Sciences of the Soviet Union: *Thermo-physical Properties of Gaseous and Liquid Methane*, V. A. Zagoruchenko and A. M. Zhuravlev, and *Thermophysical Properties of Air and Air Components*, A. A. Vasserman, Ya. K. Kazavchinskii, and V. A. Rabinovich.

The several density functions occurring in the Imperfect Gas Equation 8) and 18) can be written in the most general case as power series in density:

$$\alpha' = a_0 + a_1 \rho + a_2 \rho^2 + \dots = \sum_n a_n \rho^n \quad (19)$$

$$\beta' = b_0 + b_1 \rho + b_2 \rho^2 + \dots = \sum_n b_n \rho^n \quad (20)$$

$$\gamma_1' = 1 + c_{11} \rho + c_{21} \rho^2 + \dots = \sum_n c_{n1} \rho^n \quad (21)$$

The functions, θ_i , are temperature functions in general of a complex nature. However, as noted, empirically they can be approximated by relatively simple forms. In general these functions will satisfy the conditions:

$$\lim_{T \rightarrow \infty} \theta_i = 0, \quad \lim_{T \rightarrow \infty} \theta_{i+1}/\theta_i = 0 \quad (22)$$

If the Imperfect Gas Equation, 8), is rearranged, using 18), 19), 20), and 21), as a power series in density, a comparison with the Virial Equation, 7), indicates that the virial coefficients will be given by:

$$TB = -a_0 + Tb_0 - \theta_0 \quad (23)$$

$$TC = -a_1 + Tb_1 - c_{10} \theta_0 - \theta_1 \quad (24)$$

$$TD = -a_2 + Tb_2 - c_{20} \theta_0 - c_{11} \theta_1 - \theta_2 \quad (25)$$

It is thus evident that in final detail these two general equations are essentially equivalent.

The application of the Imperfect Gas Equation in its general form:

$$p = \rho R T + \rho^2 R (-\alpha' + T \beta' - \gamma_0' \theta_0 - \rho \gamma_1' \theta_1 \dots) \quad (26)$$

$$= \rho R T + \rho^2 R \left(-\alpha' + T \beta' - \sum_{n=0}^{\infty} \rho^n \gamma_n' \theta_n \right)$$

requires knowledge of the numerical values of the density functions:

$$\alpha', \beta', \gamma_0', \gamma_1', \dots \quad (27)$$

and the temperature functions:

$$\theta_0, \theta_1, \dots \quad (28)$$

As noted above, conventional semi-empirical equations of state provide initial approximations for only the first three density functions and the first temperature function.

The studies referenced above indicate that the addition of information on values of the fourth density function and the second temperature function will suffice to indicate with very high quantitative accuracy the behavior of real gases and liquids throughout the fluid region. In order to obtain a

high degree of accuracy at high densities, attention needs to be given particularly to the several density functions.

Empirical methods for obtaining formulations for all these functions have been described by various authors. These are well summarized in *The Properties of Gases and Liquids*, Robert C. Reid and Thomas K. Sherwood, (McGraw-Hill, 2nd ed., 1966) and in *Design Data for Industry-Property Prediction with Computer Systems*, R.C. Reid and L.B. Evans, (AIChE Today Series, 1970).

While there are many variations in the empirical approach, essentially the compressibility factor, Z , is first computed. Since:

$$Z = \frac{p}{\rho R T} = 1 + \frac{\rho}{T} (-\alpha' + T \beta' - \gamma_0' \theta_0 - \rho \gamma_1' \theta_1 \dots) \quad (29)$$

it follows from the general behavior of θ_i at large temperatures that:

$$\alpha' = \lim_{T \rightarrow \infty} \frac{T^2}{\rho} \frac{\partial z}{\partial T} \quad (30)$$

$$\beta' = \lim_{T \rightarrow \infty} \frac{z-1}{\rho} \quad (31)$$

Consequently a graphical correlation with respect to the reciprocal of the temperature will give the density functions α' and β' from the slope and intercept of compressibility factor isochores. Once α' and β' are determined, the residual quantity

$$\varphi_0 = \gamma_0' \theta_0 + \varphi_1 \quad (32)$$

may be computed from empirical data. In 32) φ_1 will be a small quantity becoming zero at $\rho=0$, consequently, since by 21) $\gamma_1'(0)=1$:

$$\theta_0(T) = \varphi_0(0, T) \quad (33)$$

It then follows from 22) that

$$\gamma_0 = \lim_{T \rightarrow \infty} \varphi_0(\rho_1 T) / \varphi_0(0, T) \quad (34)$$

Successive terms in φ_1 can be similarly developed. The very rapid convergence of the series formulation

$$\varphi_1 = \rho \gamma_1' \theta_1 + \dots \quad (35)$$

is such, however, that even the first term may be sufficient in most cases to give good quantitative accuracy at high liquid densities.

Most available discussions of the several density and temperature functions have either been of limited range and of specialized form, as indicated by the listed semi-empirical equations above, or have been applied to specific substances. There is a clear need for a more general treatment of these single variable functions.

The two density functions α' and β' can be made dimensionless by introducing the critical temperature and density. The resulting reduced functions

$$\alpha_r' = \alpha' \frac{\rho_c}{T_c}, \quad \beta_r' = \beta' \rho_c \quad (36)$$

along with the dimensionless functions γ_0' , γ_1' may be plotted or tabulated against reduced density, $\rho_r = \rho / \rho_c$. Such reduced functions for pure substances in accordance with the law of corresponding states will vary only slightly in value subject to their dependence on the reduced compressibility factor, Z_c , or other suitable parameter.

The temperature functions θ_0 and θ_1 will also have reduced forms

$$\theta_{0r} = \theta_0 \rho_c / T_c, \quad \theta_{1r} = \theta_1 \rho_c^2 / T_c \quad (37)$$

They will be functions of reduced temperature, $T_r = T / T_c$, and will similarly be dependent on parameters such as the compressibility factor, Z_c .

The density and temperature functions may also be expressed in terms of composition for fluid mixtures. Such data can be assembled in graphical form or by semi-empirical formulations.

In summary, the general Imperfect Gas Equation, 26), which has been described, has several advantages to be emphasized:

1. It is compatible with all the most widely accepted existing semi-empirical imperfect gas equations.
2. It is analytically equivalent to the Virial Equation of State.
3. By making provision for very accurate determination of a limited number of general density functions, as much accuracy as may be desired at high densities is attainable.
4. Temperature functions which occur may be determined empirically or by reference to semi-theoretically determined virial coefficients.
5. Density and temperature functions occurring in the general equation may be expressed in reduced form. They can also consolidate dependence on the critical compressibility or equivalent factors as well as on composition.

Further investigation to give explicit attention to the general nature of the several density and temperature functions will be a promising approach to substantial advance in the development of equations of state for real gases and liquids.

