

Intermediate Thermodynamics

Lecture 5: Equations of State

PVT behavior

The calculation of the properties, such as enthalpy, entropy, internal energy, etc., for different substances requires knowledge of the PVT (pressure-volume-temperature) behavior of the substance. This can be given in the form of a table, graphs, or analytically. An analytical expression to express PVT behavior is called an *equation of state*.

An example of equation of state is the ideal gas EOS. If the pressure is much lower than the critical pressure, and the temperature much higher than the critical temperature, then the compressibility factor Z is approximately 1 and we can write:

$$p v = \frac{\bar{R}}{M} T = R T \quad (1)$$

$$u = u(T) \quad (2)$$

$$h = h(T) = u(T) + R T \quad (3)$$

For a general substance, however, we will have a much more complex behavior. Fig. 1 shows a pressure-specific volume plot for argon, in terms of the reduced pressure, volume and temperature:

$$P_r = \frac{p}{p_c} \quad v_r = \frac{v}{v_c} \quad T_r = \frac{T}{T_c} \quad (4)$$

We note that an accurate analytical representation of the function of the figure will be difficult to achieve. In general, to develop an EOS we have to decide what is the precision we desire, the range of interest and the amount of data that we will need to determine the adjustable parameters in the equation.

Every EOS must fulfill some criteria common for most substances. At the critical state, the critical isotherm has zero slope and curvature:

$$\left. \frac{\partial p}{\partial v} \right|_{T_c} = 0 \quad \left. \frac{\partial^2 p}{\partial v^2} \right|_{T_c} = 0 \quad (5)$$

Another characteristic is that in a p-T diagram, the isometric curves are almost straight lines, see Fig. 2. In particular, the critical isometric has the slope of the pressure curve (locus of saturation states) at the critical point. This is an additional criterion to follow when developing EOS's.

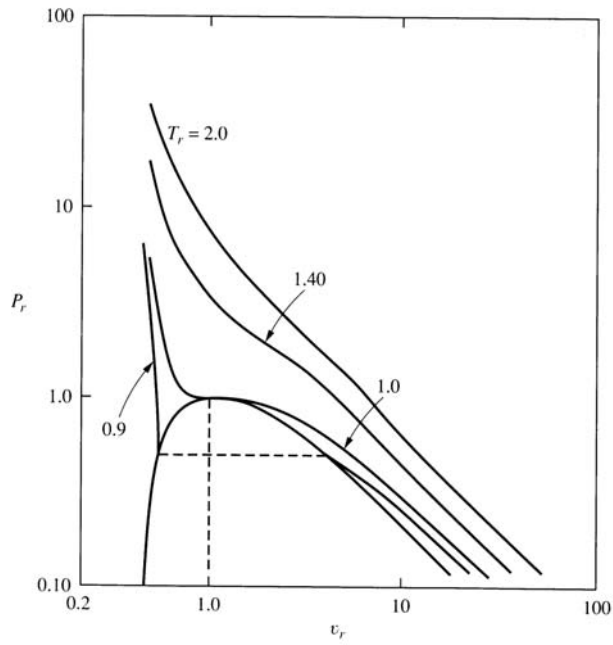


Figure 1: experimental $p_r - v_r$ graph for argon (from Wark).

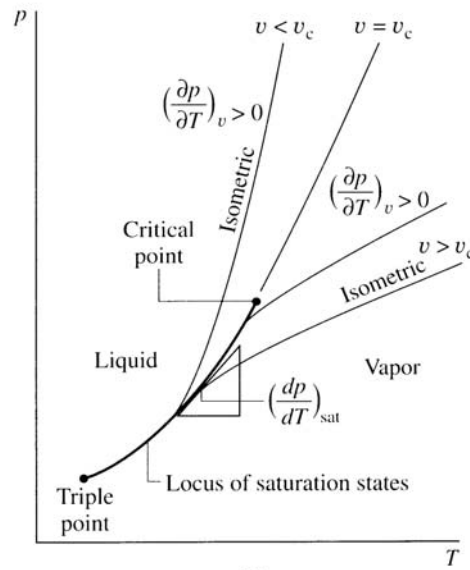


Figure 2: typical phase diagram (from Moran & Shapiro).

The shape of the vapor-pressure curve is nearly a straight line in a plot $\log_{10} P_r^{sat} - 1/T_r$, as shown in Fig. 3. The slope can be calculated as:

$$\frac{d \log_{10} P_r^{sat}}{d(1/T_r)} = -0.434 \left. \frac{T_c}{P_c} \frac{dP}{dT} \right|_{crit} = 0.434 m \quad (6)$$

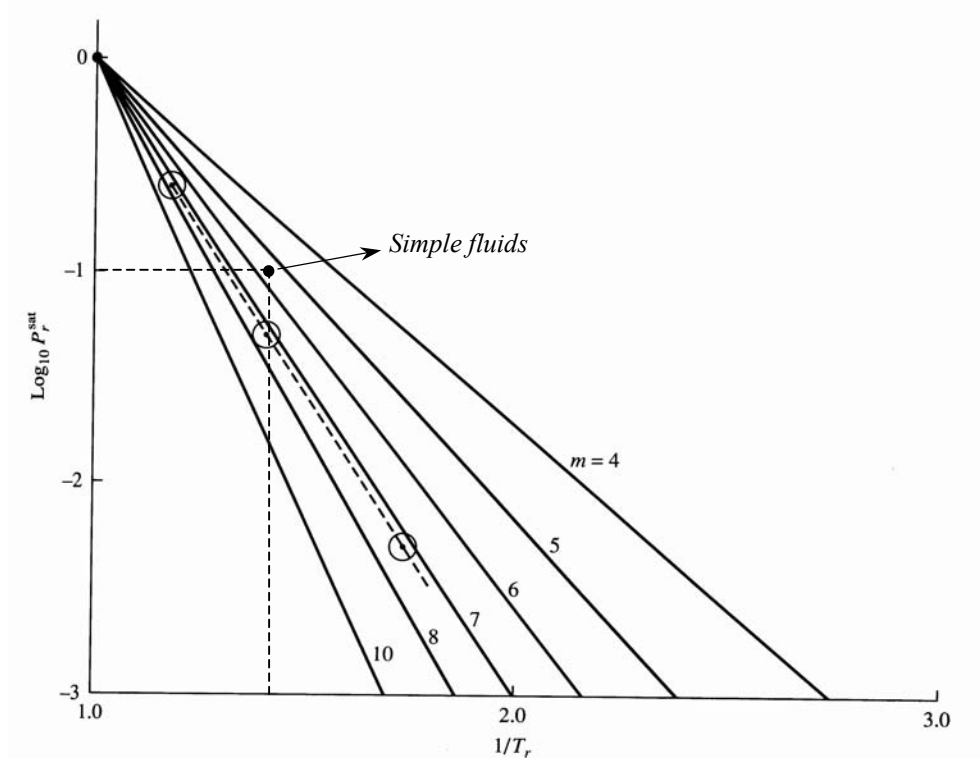


Figure 3: generalized vapor pressure plot (from Wark).

Other characteristics that EOS's should exhibit are:

- 1.- The Z factor approaches to 1 as the pressure approaches zero
- 2.- As the pressure approaches zero, the residual volume (difference between actual specific volume and ideal gas specific volume) approaches a constant value that's only a function of temperature.
- 3.- As the pressure increases, the critical isotherm becomes vertical, with a specific volume approximately equal to $0.26 v_c$ as the pressure goes to infinity.
- 4.- The critical Z factor is in the range of 0.22 - 0.30.
- 5.- As the critical isometric is straight, this results in the requirement for the superheat region:

$$\left. \frac{\partial^2 p}{\partial T^2} \right|_{T_c} = 0 \quad (7)$$

Two-parameter EOS's

Van der Waals proposed in 1873 a correction for the ideal gas model based on two simple ideas. First, van der Waals realized that attractive forces among particles, known as van der Waals forces, would reduce the gas pressure compared to the ideal gas model:

$$P_{act} = P_{ideal} - \frac{a}{v^2} \quad (8)$$

On the other hand, if particle size is finite, the volume available for particle motion reduces, thus for clustered particles we have:

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad (9)$$

that is the van der Waals equation of state. The constants can be evaluated from suitable PVT data, and are constants for each substance.

If no data is available but the most rudimentary, as the pressure, temperature and volume at the critical point, then we can use the criteria described earlier to find the constants. The application of Eqs. (5) to Eq. (9) leads to the following conditions:

$$\left. \frac{\partial p}{\partial v} \right|_{T_c} = \frac{-RT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} = 0 \quad (10)$$

$$\left. \frac{\partial^2 p}{\partial v^2} \right|_{T_c} = \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0 \quad (11)$$

which gives two equations to calculate the two parameters a and b :

$$a = \frac{9RT_c v_c}{8} \quad b = \frac{v_c}{3} \quad (12)$$

Using a and b in Eq. (9) at the critical state, we can calculate the critical pressure:

$$P_c = \frac{3RT_c}{8v_c} \quad (13)$$

Notice that any two of P_c , T_c and v_c can be used to calculate the parameters a and b , and the third variable of the critical state is predicted. The Z factor at the critical state is also a predicted quantity in a van der Waals gas and its value is:

$$Z_c = \frac{P_c v_c}{R T_c} = \frac{3}{8} \quad (14)$$

which is larger than the typical 0.22~0.30 range. As a consequence, if we use the critical pressure and the temperature to calculate the parameters, the critical volume will be roughly 30 % overpredicted by the van der Waals equation.

Van der Waals EOS is qualitatively right, though may have quantitative errors if the pressure is high. In reference to Fig. 4, we see that the predicted isotherms have three roots of volume for a given pressure. For temperatures above the critical, only one root is real (and physically significant). At the critical temperature, the three roots are real and coincident, which results in an inflection point. Below the critical point two roots are real and one is complex. If the saturation pressure is known, the two-phase region can be predicted. In terms of the compressibility factor, the van der Waals EOS is written as:

$$Z^3 - \left(\frac{P_r}{8 T_r} + 1 \right) Z^2 + \left(\frac{27 P_r}{64 T_r^2} \right) Z - \frac{27 P_r^2}{512 T_r^3} = 0 \quad (15)$$

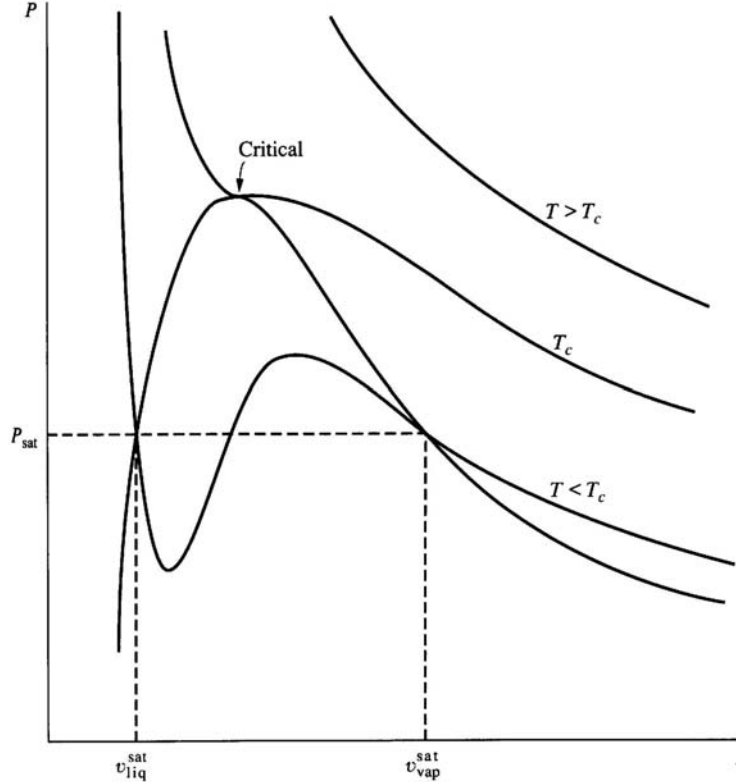


Figure 4: Isotherms predicted by a cubic EOS (from Wark).

An improvement to the van der Waals EOS was proposed 76 years later by Redlich and Kwong (RK), and has the form:

$$p = \frac{RT}{v-b} - \frac{a}{\sqrt{T} v (v+b)} \quad (16)$$

Eq. (16) does a much better job than the original van der Waals EOS, but still predicts a slightly high compressibility factor at the critical state of $Z=1/3$.

The corresponding states principle

The two-parameter EOS's previously described can be written in the form:

$$Z = Z(T_r, P_r) \quad (17)$$

The prediction of this unique relationship between Z and the reduced pressure and temperature is known as the van der Waals *corresponding states principle*. It states that any gas at the same reduced temperature and pressure should have the same compressibility factor. Fig. 5 shows Z as a function of P_r for 10 substances with T_r as the parameter. Excellent quantitative agreement is achieved.

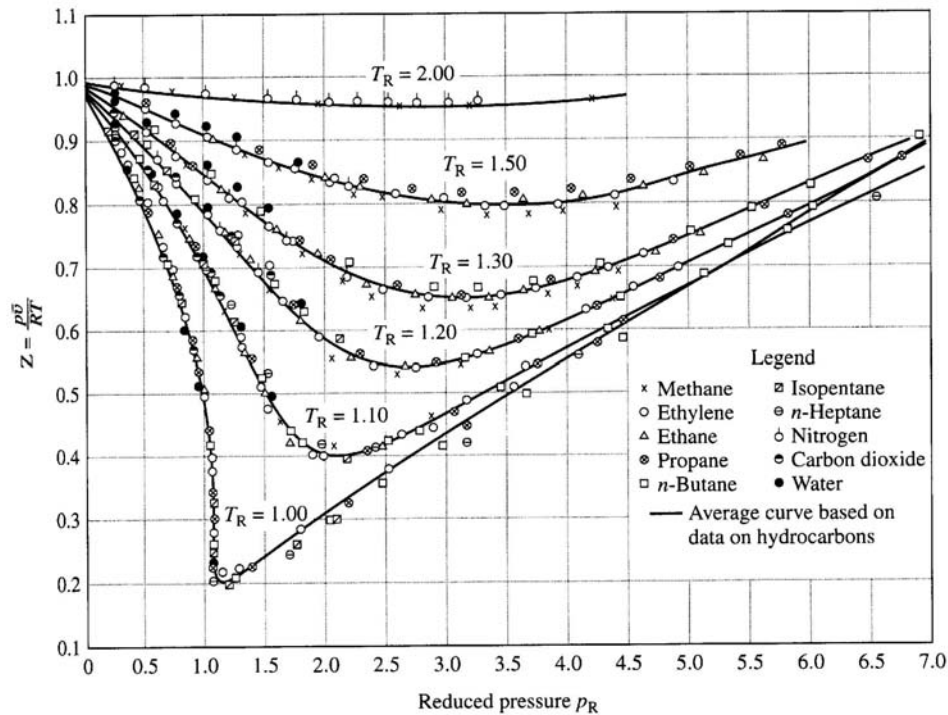


Figure 5: Experimental data and generalized Z chart (from Moran & Shapiro).

Notice that using Eqs. (4) and Eq. (1) we get:

$$Z = \frac{P_r v_r}{T_r} \frac{P_c v_c}{R T_c} = \frac{P_r v_r}{T_r} Z_c \quad (18)$$

which implies that the reduced specific volume will not correlate well since the above described EOS's cannot predict accurately Z_c . The quantity $v_r Z_c$ will however correlate well. Thus a pseudoreduced specific volume is defined as:

$$v_r' \equiv v_r Z_c = \frac{v P_c}{R T_c} = Z \frac{T_r}{P_r} \quad (19)$$

The two-parameter corresponding states principle fails when applied to complex gases, in particular, molecules with strong dipolar moments and/or non-spherical force fields. In these cases a three parameter corresponding principles performs considerably better than the two-parameter one. Two approaches have been followed to choose the third parameter. In the first, the critical compressibility factor has been added, so

$$Z = Z(T_r, P_r, Z_c) \quad (20)$$

This approach provides significant improvement in accuracy, since now the critical compressibility factor can be accurately adjusted in a three-parameter EOS.

Other approach, with a more physical basis, is to include the *acentric factor*, which gives an indication of the deviation from spherical symmetry in a molecule. In *simple fluids*, in which the molecules have spherical symmetry, the acentric factor is zero. In a general fluid, we define the acentric factor in reference to Fig. 3. If the two-parameter corresponding principle was accurate, all the gases should have the same slope. This is obviously not true. It is observed that in simple fluids we have $\log_{10} P_r^{sat} = -1$ at $T_r^{sat} = 0.7$ (see Fig. 3 with $m=5.4$). Using this reference point, the acentric factor ω is:

$$\omega \equiv -1 - \log_{10} P_r^{sat} \Big|_{T_r=0.7} \quad (21)$$

and the corresponding states principle is stated as:

$$Z = Z(T_r, P_r, \omega) \quad (22)$$

with a general expression for the compressibility factor of the form:

$$Z = Z_0 + \omega Z_1 \quad (23)$$

where Z_i are functions of the reduced pressure and temperature only.

Three-parameter cubic equations of state

Cubic EOS's including the acentric factor have been developed for diverse fluids. A widely used equation is the Redlich-Kwong-Soave EOS, which is an extension of the RK EOS and is expressed as:

$$p = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)} \quad (24)$$

$$\text{with } a = \frac{0.42748 R^2 T_c^2}{P_c}, \quad b = \frac{0.08664 RT_c}{P_c} \quad (25)$$

$$\text{and } \alpha = \left[1 + S(1 - \sqrt{T_r})\right]^2, \quad S = 0.48 + 1.574\omega - 0.177\omega^2 \quad (26)$$

where we notice that in the original RK EOS we had $\alpha = 1/\sqrt{T_c}$. A similar EOS with about the same accuracy than the RKS EOS equation of state was developed by Peng & Robinson.

In general, most cubic equations of state can be written in the format:

$$p = \frac{RT}{v-b} - \frac{\gamma}{(v+c)(v+d)} \quad (27)$$

with γ a function of the temperature and b, c and d constants. In terms of the reduced pressure, temperature and pseudoreduced specific volume we have:

$$p = \frac{T_r}{v'_r - B} - \frac{A}{(v'_r + C)(v'_r + D)} \quad (28)$$

where A, B, C and D are written in terms of the critical pressure and temperature and the other parameters present in Eq. (27).

Other EOS's

Other important EOS include the *virial equation*, derived from statistical mechanics, in which the compressibility factor is expressed in terms of a series in $1/v$:

$$Z = \frac{Pv}{RT} = 1 + \frac{C_2}{v} + \frac{C_3}{v^2} + \dots \quad (29)$$

where the *virial coefficients* C_i are only a function of the temperature for a given gas. Eq. (29) is then explicit in pressure. An alternate form explicit in specific volume is:

$$Z = \frac{Pv}{RT} = 1 + B_2 P + B_3 P^2 + \dots \quad (30)$$

where the virial coefficients in Eq. (30) are related to those in Eq. (29). The evaluation of the virial coefficients usually requires empirical data, since theoretical results are scarce and only for the first two or three coefficients. An important EOS derived from virial equations is the *Benedict-Webb-Rubin equation*, that has 8 empirical constants to adjust:

$$P = \frac{RT}{v} + \frac{B_0 RT - A_0 - C_0 / T^2}{v^2} + \frac{b RT - a}{v^3} + \frac{a\alpha}{v^6} + \frac{c}{v^3 T^2} \left(1 + \frac{\gamma}{v^2}\right) e^{-\frac{\gamma}{v^2}} \quad (31)$$

Though Eq. (31) is quite accurate, but today's applications usually require more accuracy, which in practice means more parameters to adjust. A widely used model is the *modified Benedict-Webb-Rubin equation*, which is written as:

$$P = \sum_{n=1}^N \frac{a_n}{v^n} + e^{-\left(\frac{v_c}{v}\right)^2} \sum_{n=N+1}^M \frac{a_n}{v^{in-j}} \quad (32)$$

with the coefficients a_i function of the temperature and i and j constants. These complex EOS's are mostly used to adjust important fluids such reservoir hydrocarbons (natural gas and oil) and refrigerants.

Problems

1. find expressions for A, B, C and D in Eq (28) in terms of the constants in Eq. (27).
2. Given nitrogen at 100 bar and 200 K, find the specific volume by using
 - a) The ideal gas equation of state.
 - b) The truncated virial equation $Pv = RT + bP$ with $b = 39.5 - \frac{10^4}{T} - \frac{1.084 \cdot 10^6}{T^2}$.
 - c) Tabular data.
 - d) Compare the errors.