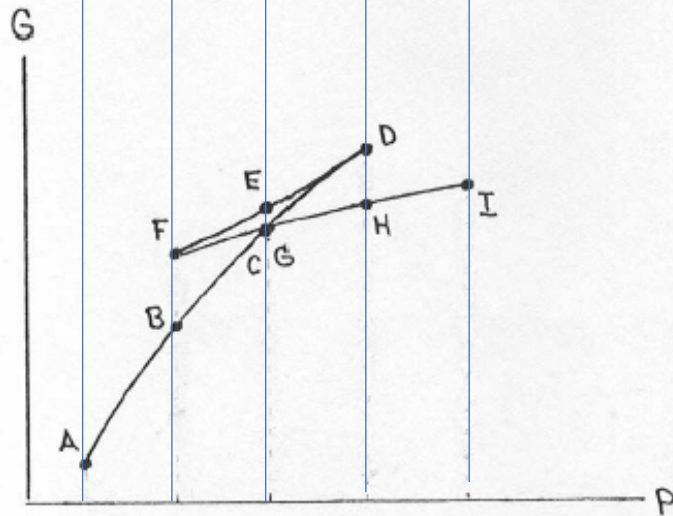
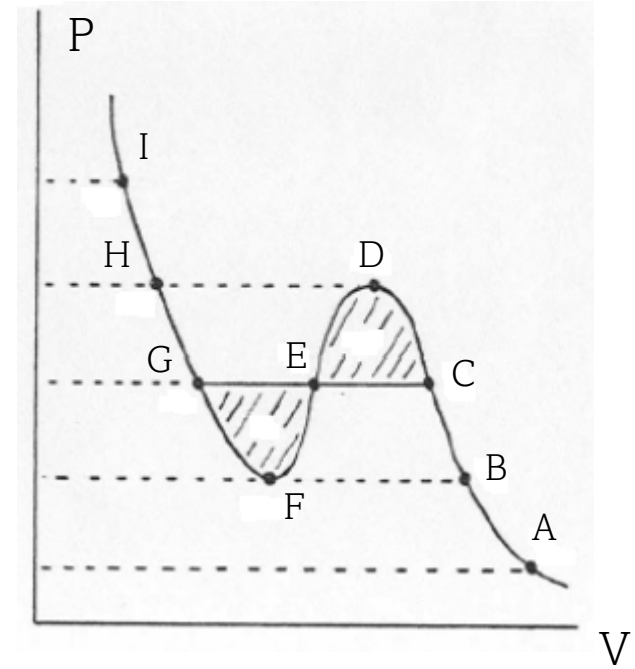
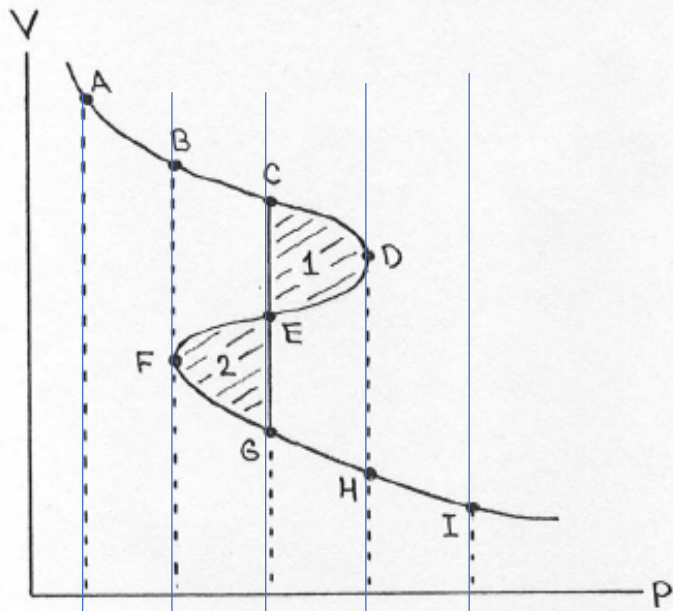
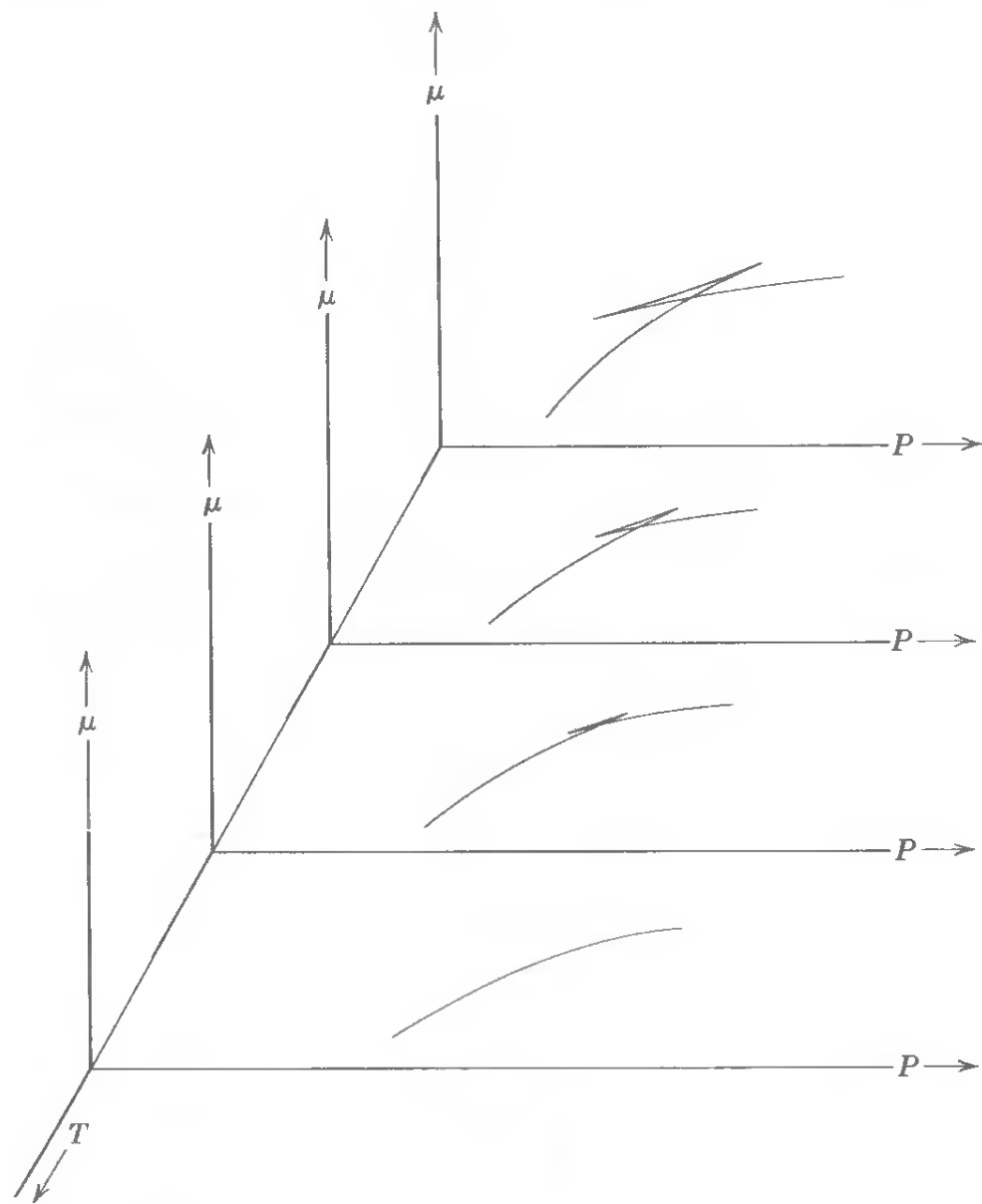


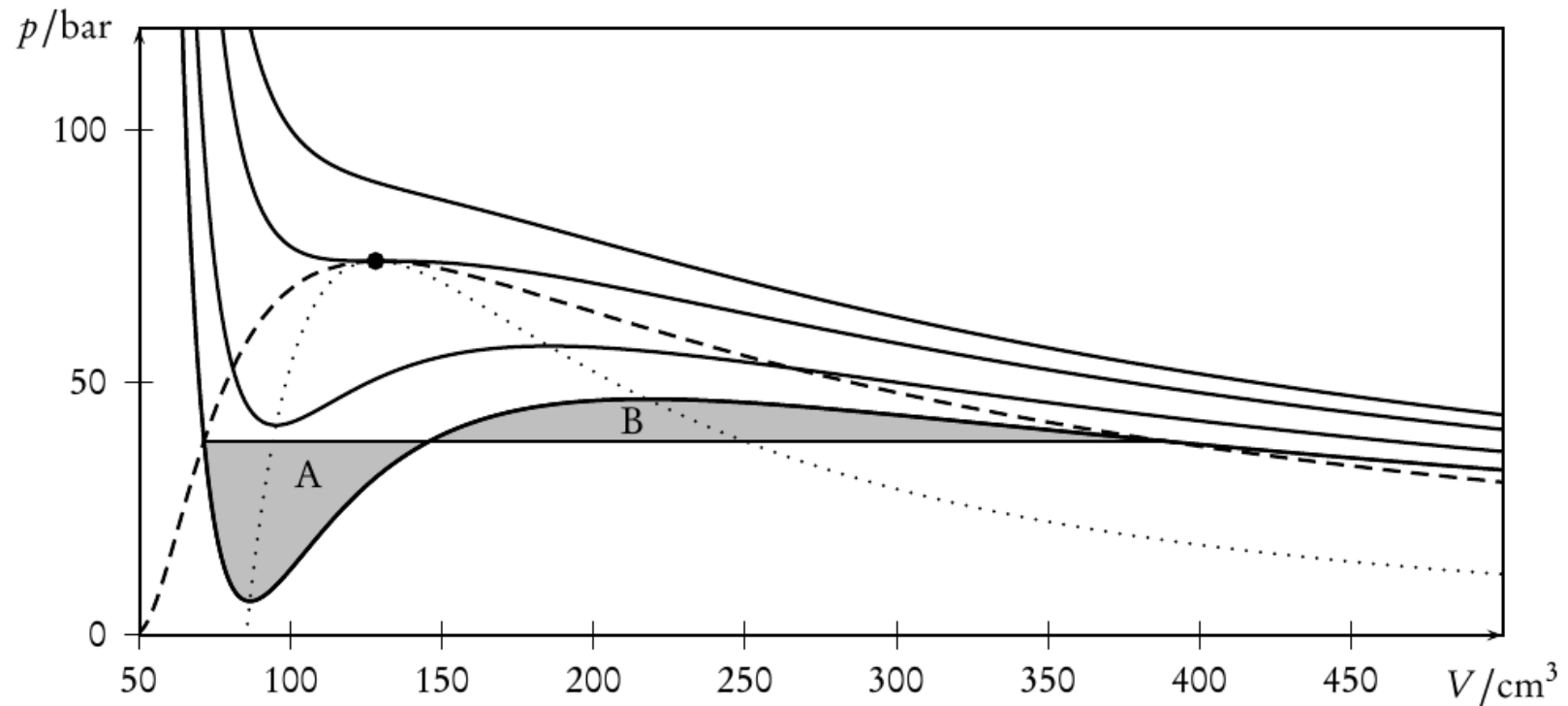
FIGURE 9–1 (a) Sketch of isotherms in the v, p plane according to Eq. (9.2), for $T_4 > T_3 > T_c > T_2 > T_1$. For sufficiently high temperatures, the isotherms are monotonically decreasing functions of v , as they would be for an ideal gas. T_c is the critical temperature and its isotherm has a horizontal point of inflection. For sufficiently low temperatures, the isotherms display multiple values of v for the same value of p . (b) A low temperature isotherm on an exaggerated scale, illustrating a maximum and a minimum value of p . The curve between the maximum and minimum values, p_{\max} and p_{\min} , corresponds to unstable states having negative compressibility, $\kappa_T < 0$.

The Maxwell Construction



It is only after the non-monotonic isotherm has been truncated by this equal area construction that it represents a true physical isotherm.





Isothermal lines of CO_2 around the liquid-gas phase transition modelled by the van-der-Waals equation of state. The solid lines are, listed from top to bottom, isothermals calculated for $T = 320\text{K}$, $T = T_{cr} = 303.998\text{K}$, $T = 280\text{K}$, and $T = 260\text{K}$. The binodal is plotted as a dashed line. It delimits the region where homogeneous states are metastable. The spinodal curve is plotted as a dotted line and it marks the boundary of the region where homogeneous states are unstable. Binodal and spinodal meet in at the critical point, which is marked by a black dot.

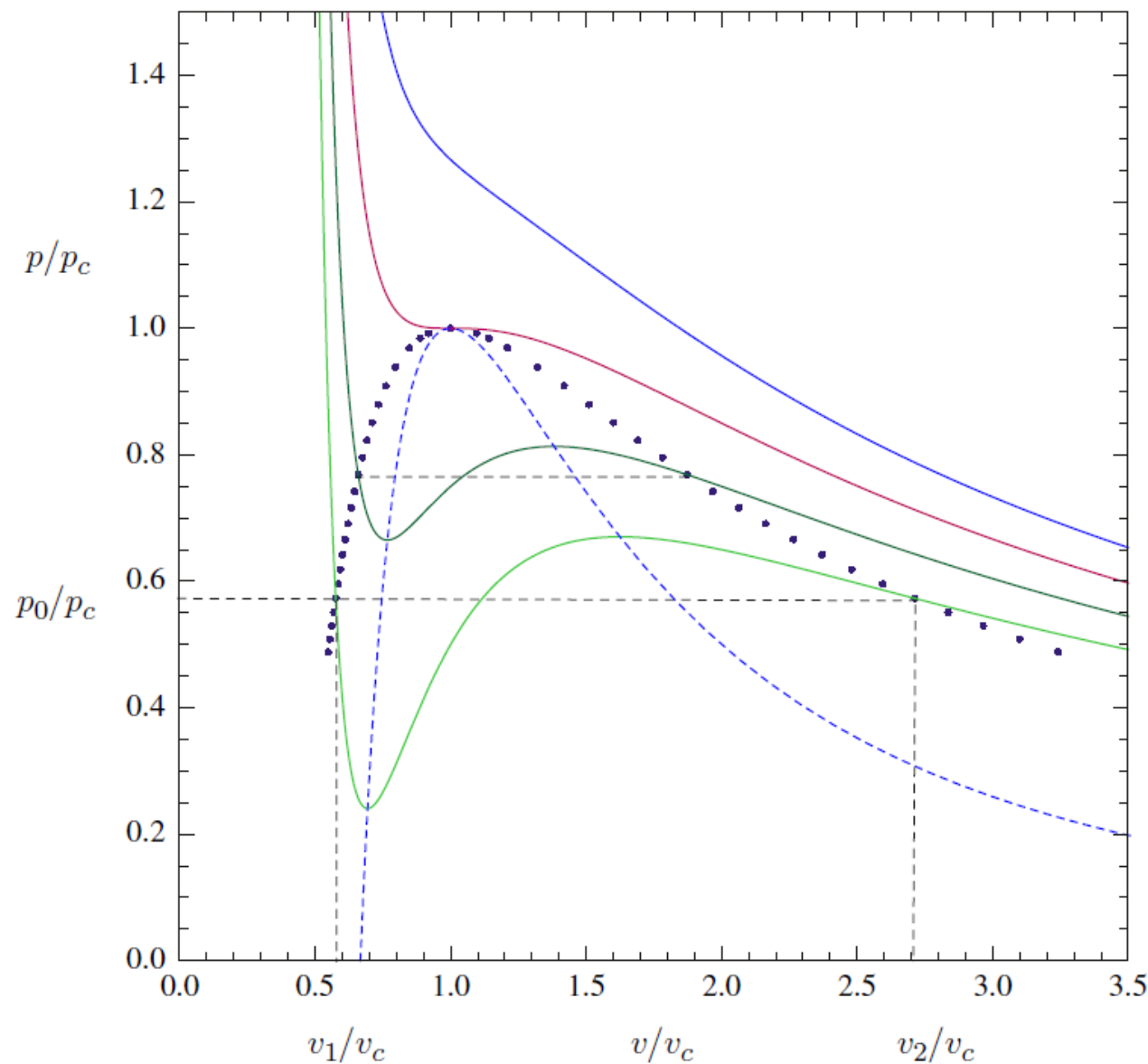


FIGURE 9–8 Maxwell's equal area construction for determining the miscibility gap. The isotherms from top to bottom are $T/T_c = 32/30, 1, 30/32, 28/32$. The dashed curve is the spinodal and the dotted curve is the miscibility gap, computed numerically as discussed in the example problem. The dashed horizontal line at p_0/p_c illustrates the equal-area construction for the lowest isotherm and the shorter horizontal line illustrates the equal area construction for the next lowest isotherm.

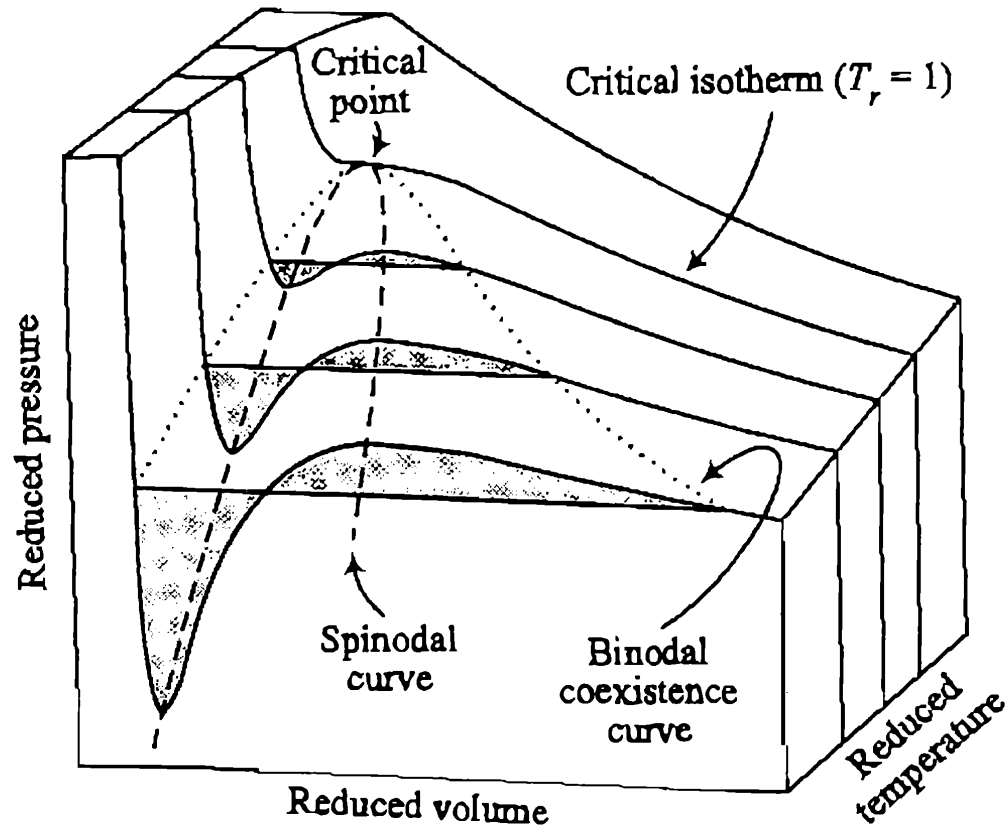
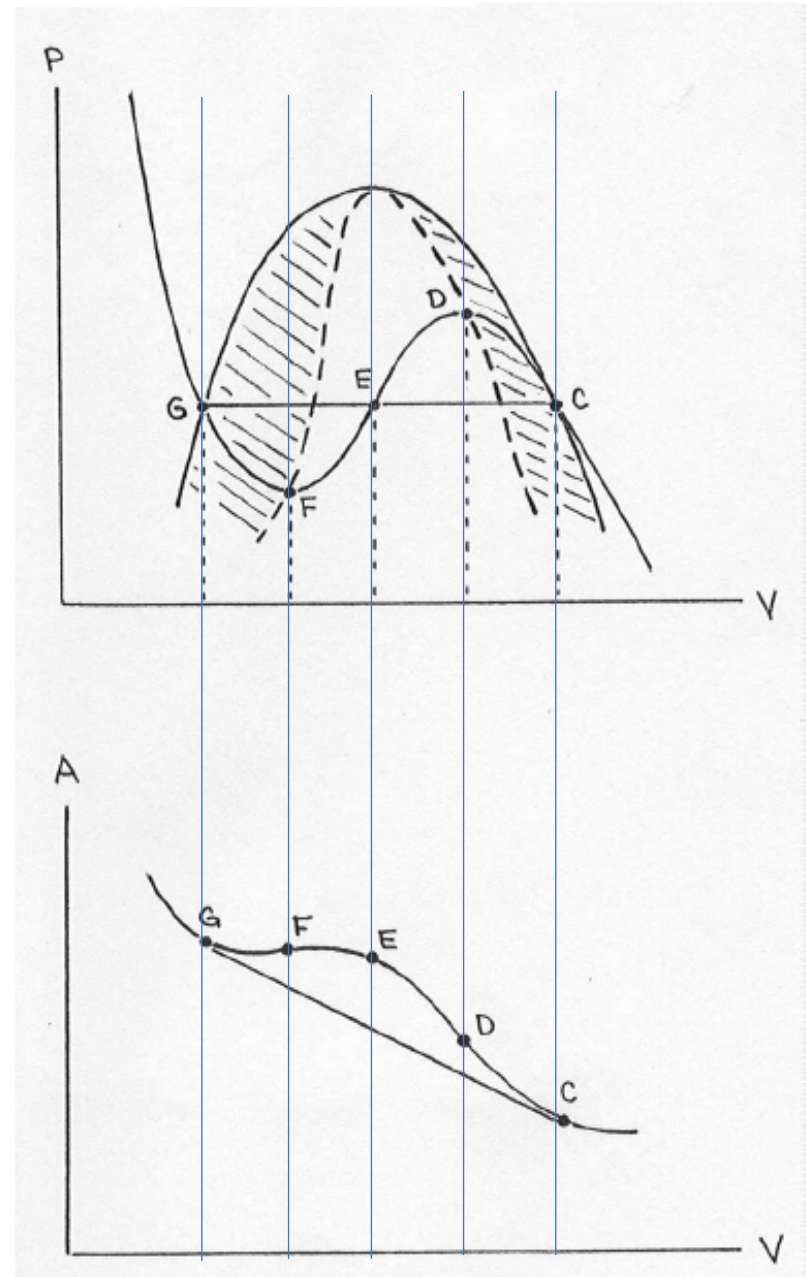


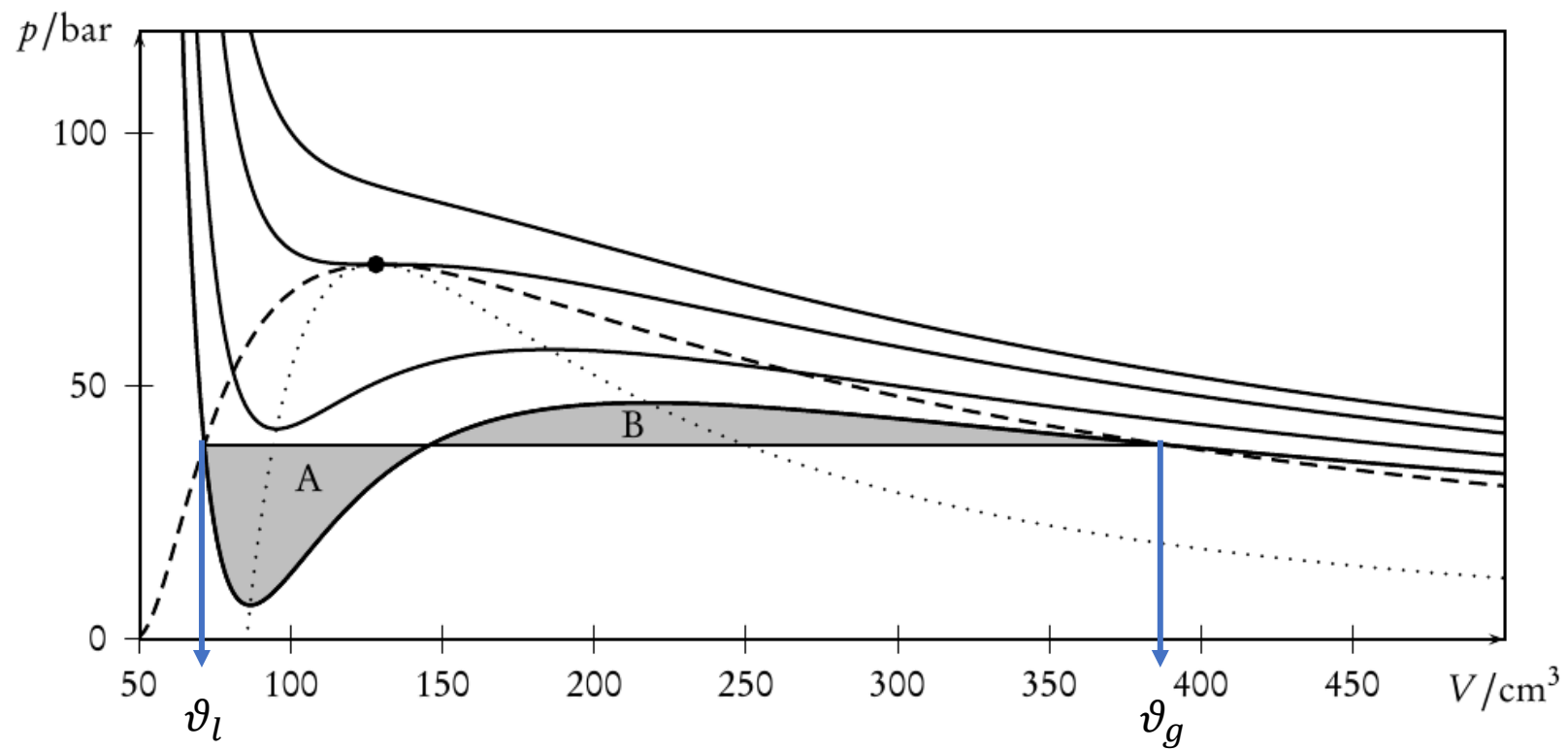
Figure 7.6 *PVT* phase diagram for the reduced form of the van der Waals equation of state. Vapor and liquid equilibrium coexistence (binodal) lines and limits of stability (spinodal) lines shown (see Example 7.2) [produced with EOS program from Jolls (1990)].

Variation of the Helmholtz potential along the subcritical isotherm:

$$dA = -SdT - pdV = -pdV$$

$$A(T, V) = A(T, V_A) - \int_{V_A}^V dv p(V).$$





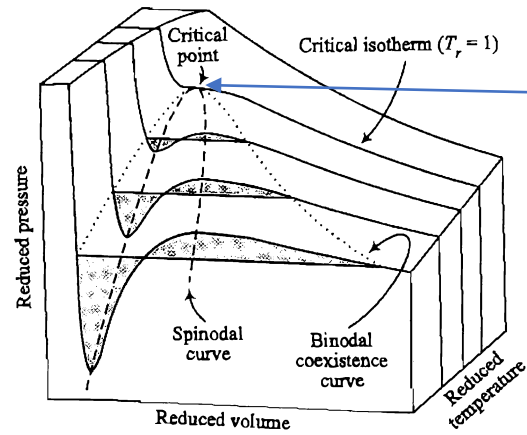
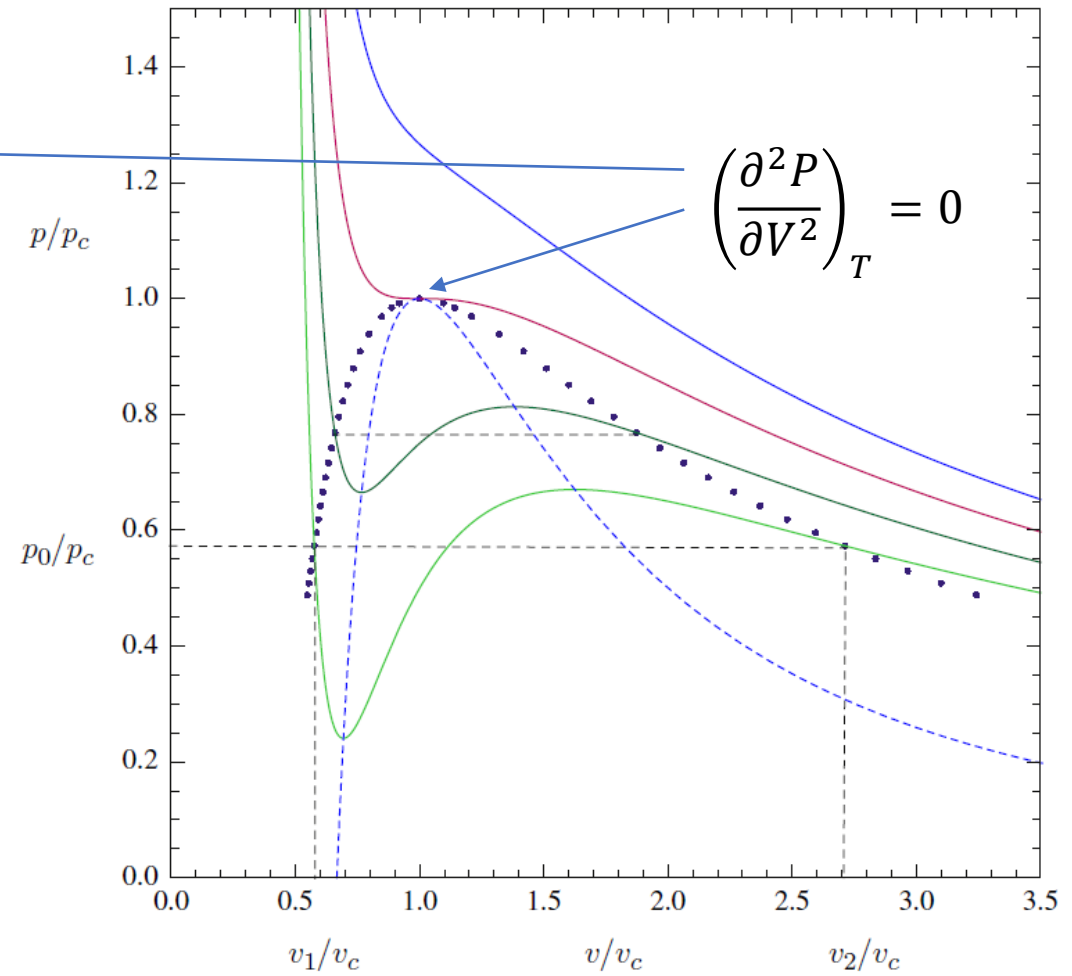
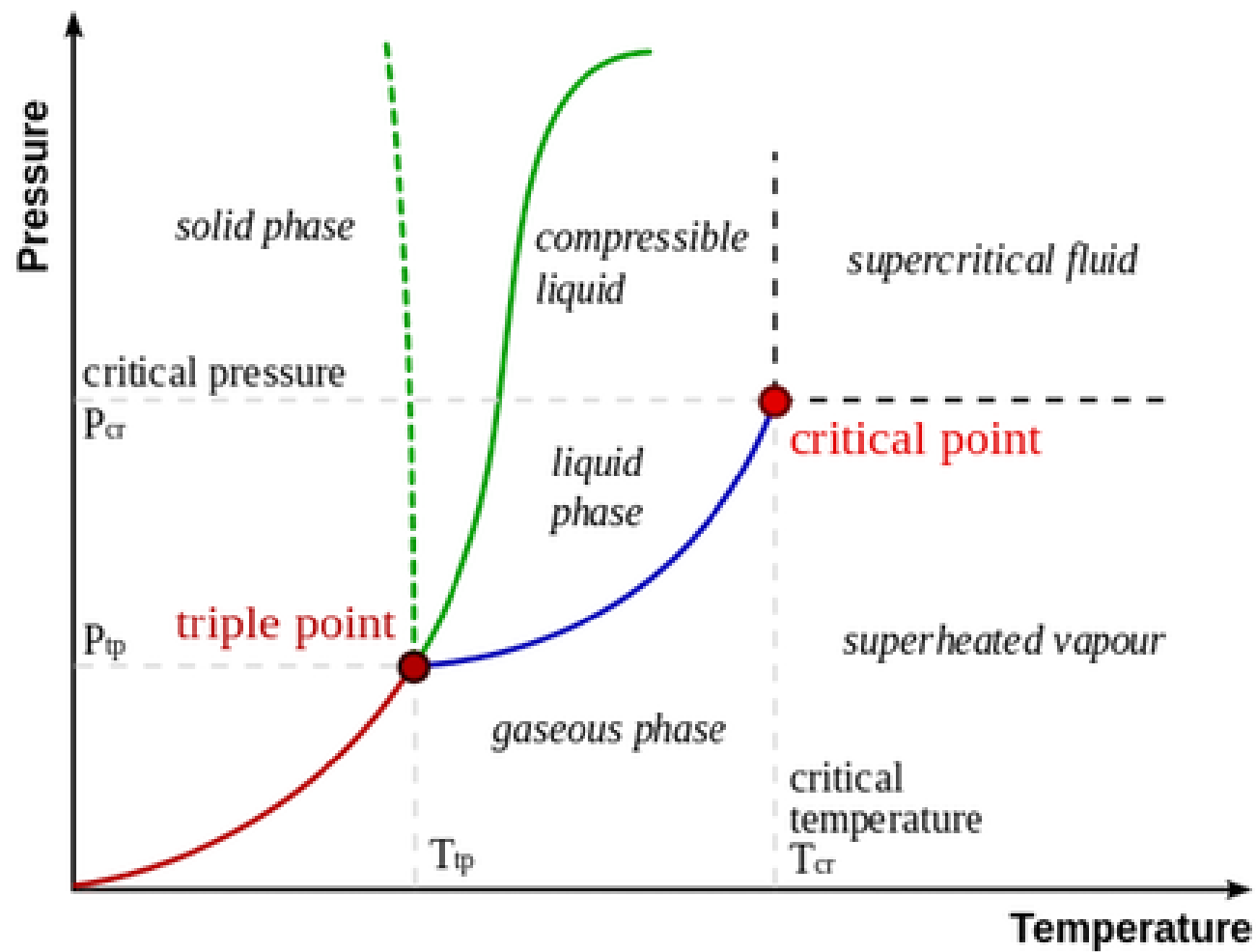


Figure 7.6 PVT phase diagram for the reduced form of the van der Waals equation of state. Vapor and liquid equilibrium coexistence (binodal) lines and limits of stability (spinodal) lines shown (see Example 7.2) [produced with EOS program from Jolls (1990)].





Cubic equations of State

The general form of a cubic equation is:

$$v^3 + f_1(T, P)v^2 + f_2(T, P)v + f_3(T, P) = 0$$

$$P = \frac{RT}{v - b} - \text{Attr}$$

Equation	Year	Attr
van der Waals	1873	$\frac{a}{v^2}$
Redlich–Kwong	1949	$\frac{a/\sqrt{T}}{v(v + b)}$
Soave–Redlich–Kwong	1972	$\frac{a\alpha(T)}{v(v + b)}$
Peng–Robinson	1976	$\frac{a\alpha(T)}{v(v + b) + b(v - b)}$

Redlich–Kwong

$$P = \frac{RT}{v - b} - \frac{a}{T^{1/2}v(v + b)} \quad (4.24)$$

$$a = \left(\frac{1}{9(\sqrt[3]{2} - 1)} \right) \frac{R^2 T_c^{2.5}}{P_c} = \frac{0.42748 R^2 T_c^{2.5}}{P_c} \quad (4.24a)$$

$$b = \left(\frac{\sqrt[3]{2} - 1}{3} \right) \frac{RT_c}{P_c} = \frac{0.08664 RT_c}{P_c} \quad (4.24b)$$

$$P_r = \frac{3T_r}{v_r - 0.2599} - \frac{1}{0.2599\sqrt{T_r}v_r(v_r + 0.2599)} \quad z_c = \frac{1}{3}$$

Peng–Robinson

The **Peng–Robinson equation of state** is given by:

$$P = \frac{RT}{v - b} - \frac{a\alpha(T)}{v(v + b) + b(v - b)} \quad (4.25)$$

with,

$$a = 0.45724 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.07780 \frac{RT_c}{P_c}$$

$$\alpha(T) = [1 + \kappa(1 - \sqrt{T_r})]^2$$

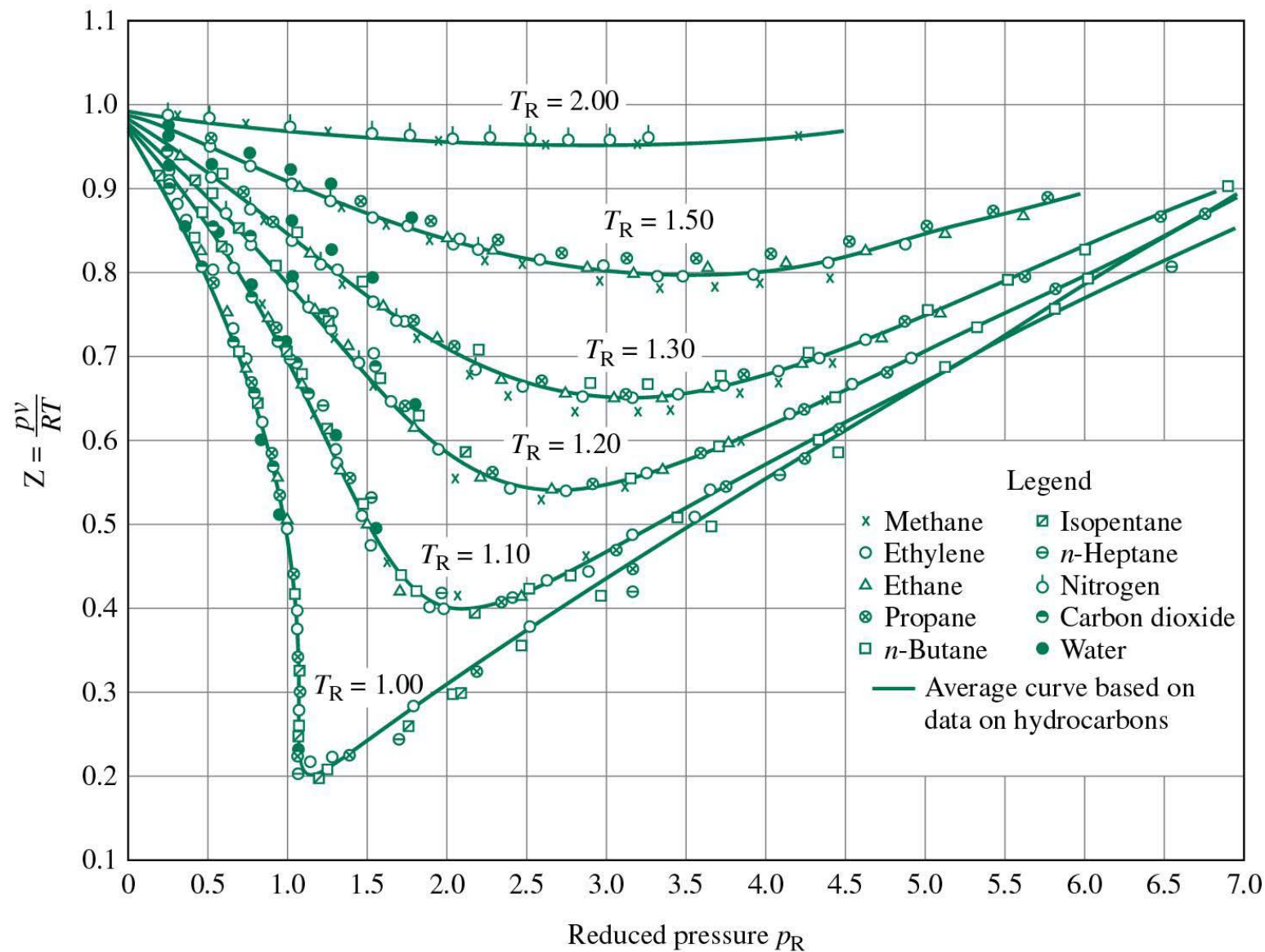
$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

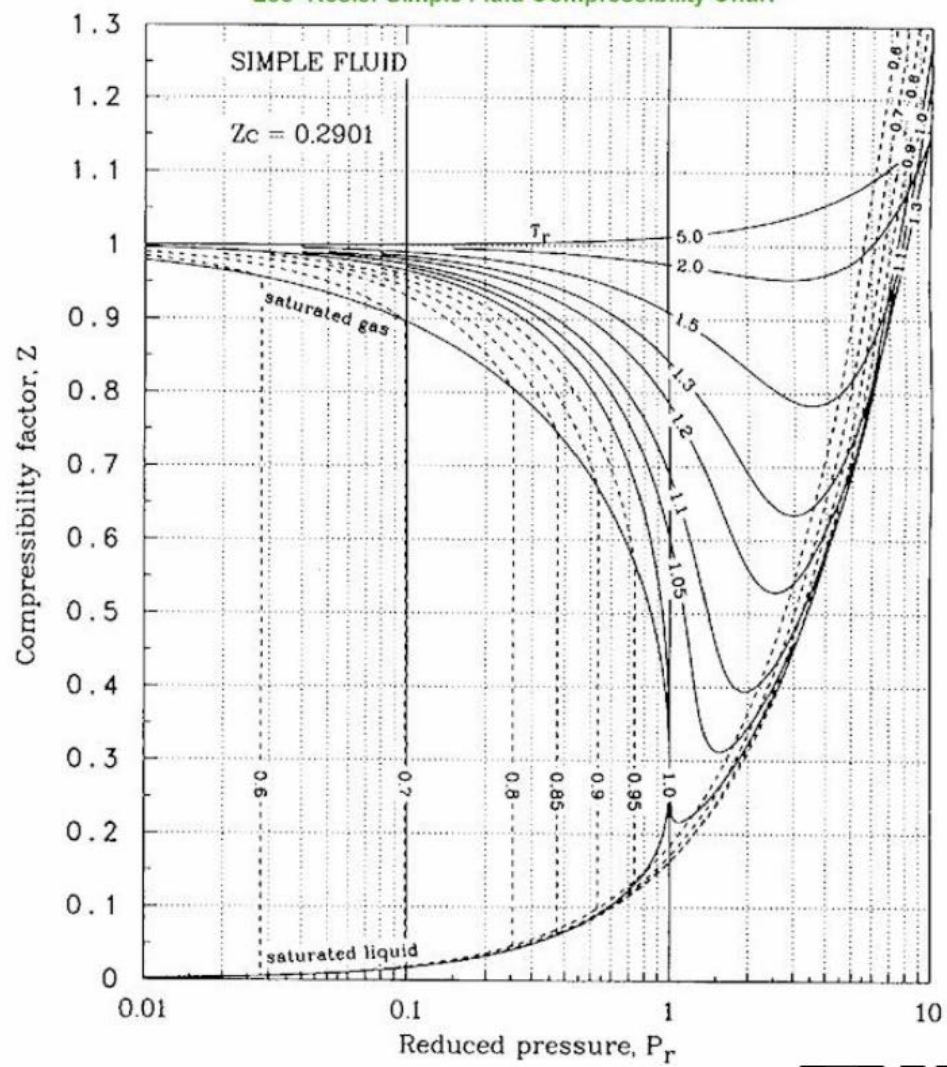
$$z_c = 0.307$$

Acentric factor

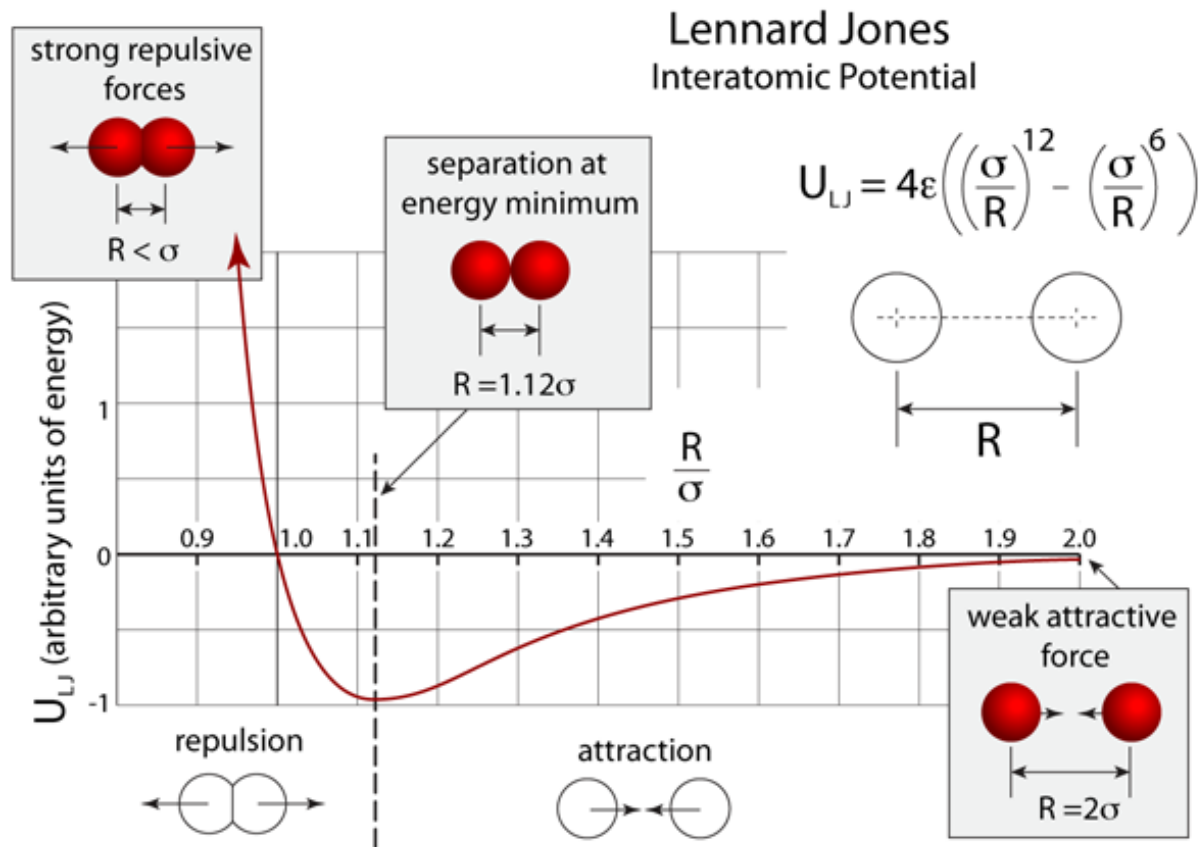
$$\omega \equiv -1 - \log_{10}[P^{\text{sat}}(T_r = 0.7)/P_c],$$

where $P^{\text{sat}}(T_r = 0.7)$ is the saturation pressure at a reduced temperature of 0.7.

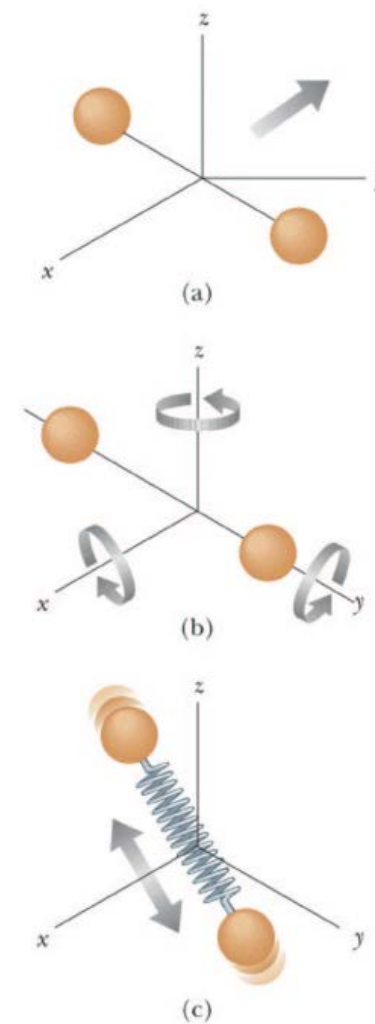
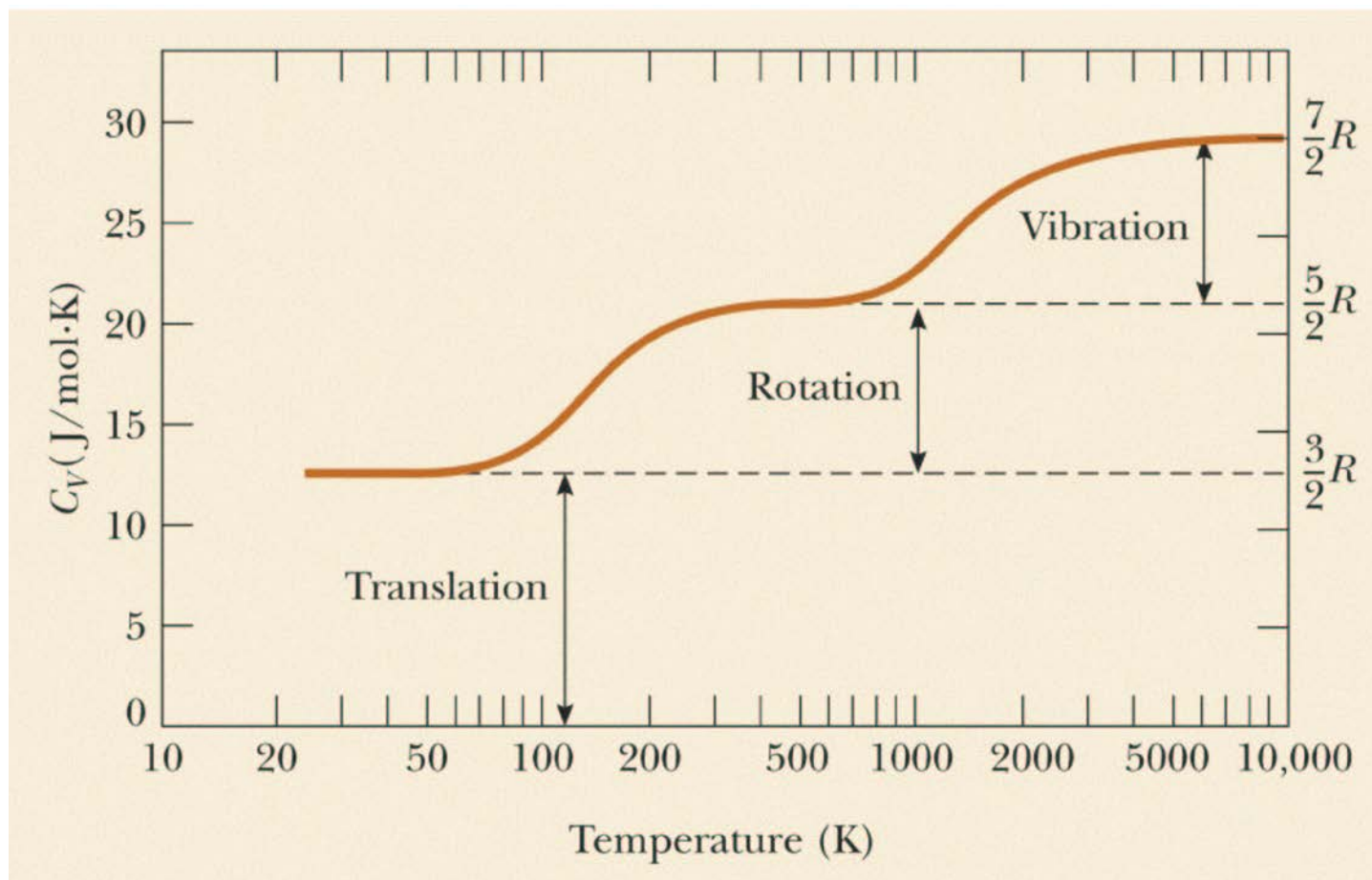




Lenard Jones Potential $W(r) = \frac{C_1}{r^{12}} - \frac{C_2}{r^6}$



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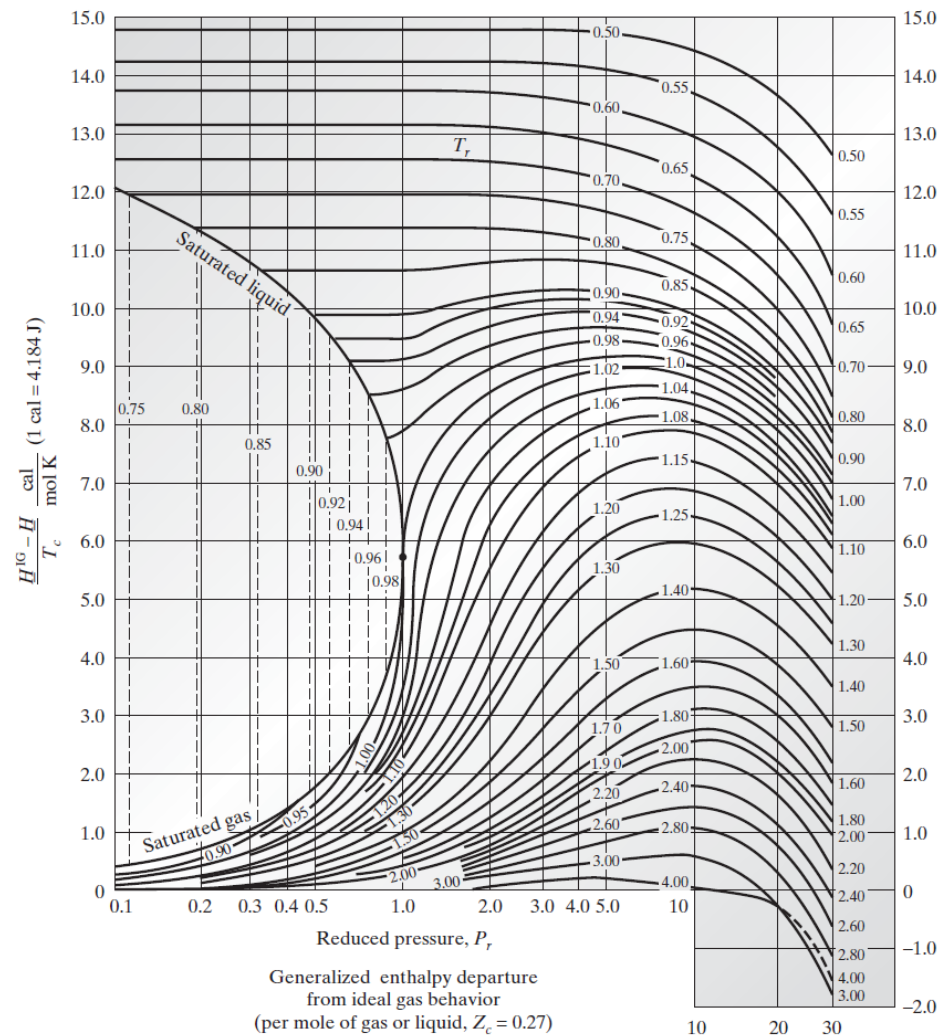


Figure 6.6-4 (Reprinted with permission from O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles Charts*, 2nd ed., John Wiley & Sons, New York, 1960. This figure appears as an Adobe PDF file on the website for this book, and may be enlarged and printed for easier reading and for use in solving problems.)

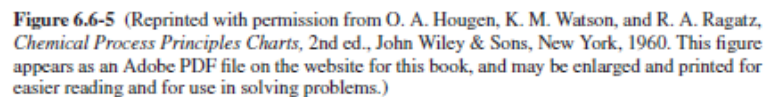


Figure 6.6-5 (Reprinted with permission from O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles Charts*, 2nd ed., John Wiley & Sons, New York, 1960. This figure appears as an Adobe PDF file on the website for this book, and may be enlarged and printed for easier reading and for use in solving problems.)