

PROBLEM 11.55

KNOWN: Three cases are under consideration: (a) an ideal gas, (b) a gas whose equation of state is $p(V-b) = RT$, (c) a gas obeying the van der Waals equation.

FIND: Derive expressions for β and κ for each case.

ANALYSIS: From Eqs. 11.62 and 11.63

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad \text{and} \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

(a) Ideal Gas: $V = RT/p$

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{p} \quad \text{and} \quad \left(\frac{\partial V}{\partial p} \right)_T = -\frac{RT}{p^2}$$

Thus

$$\beta = \frac{1}{V} \left[\frac{R}{p} \right] = \frac{1}{T} \quad \leftarrow (a)$$

$$\kappa = -\frac{1}{V} \left[-\frac{RT}{p^2} \right] = \frac{1}{p} \left[\frac{RT}{pV} \right] = \frac{1}{p}$$

(b) $V = (RT/p) + b$

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{p}, \quad \left(\frac{\partial V}{\partial p} \right)_T = -\frac{RT}{p^2}$$

Thus

$$\beta = \frac{1}{V} \left[\frac{R}{p} \right] = \frac{R}{V} \left[\frac{V-b}{RT} \right] = \frac{1}{T} \left[\frac{V-b}{V} \right] \quad \leftarrow (b)$$

$$\kappa = -\frac{1}{V} \left[-\frac{RT}{p^2} \right] = \frac{1}{p} \left[\frac{RT}{pV} \right] = \frac{1}{p} \left[\frac{RT/V}{RT/(V-b)} \right] = \frac{1}{p} \left[\frac{V-b}{V} \right]$$

Note: When $b=0$ these expressions reduce to those of part (a).

(c) van der Waals: $p = \frac{RT}{(V-b)} - \frac{a}{V^2}$.

As the van der Waals equation is not explicit in V , the required partial derivatives are not so easily found as in parts (a) and (b). Thus, following the procedure explained in Example 11.2, an expression for $(\partial V/\partial T)_p$ is obtained as

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{-R/(V-b)}{[2a/V^3 - RT/(V-b)^2]}$$

So

$$\beta = \frac{-R(V-b)V^2}{2a(V-b)^2 - RTV^3}$$

Using Eqs. 11.15 and 11.16

$$\left(\frac{\partial V}{\partial p} \right)_T = \frac{-\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial p}{\partial T} \right)_V} = \frac{\frac{R/(V-b)}{[2a/V^3 - RT/(V-b)^2]}}{R/(V-b)} = \frac{1}{[2a/V^3 - RT/(V-b)^2]} \quad \leftarrow (c)$$

Thus

$$\kappa = -\frac{1}{V[2a/V^3 - RT/(V-b)^2]} = \frac{-V^2(V-b)^2}{[2a(V-b)^2 - RTV^3]}$$