

M3.8 (5.4a, 7th Ed.) - ANSWER

Express  $\left(\frac{\partial S}{\partial V}\right)_T$  in terms of  $\alpha$  and  $\kappa_T$ .

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad \boxed{\text{M.R.}}$$

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1 \quad \boxed{\text{CR}}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = - \frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}$$

$$\alpha = \frac{1}{V} \cdot \left(\frac{\partial V}{\partial T}\right)_p$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \boxed{+\frac{\alpha}{\kappa_T}}$$

M.3.8b (5.4b, 7th Ed.)

$\left(\frac{\partial S}{\partial p}\right)_T$  in terms of  $\alpha$

$$\left(\frac{\partial S}{\partial p}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_p = - \frac{V}{V} \left(\frac{\partial V}{\partial T}\right)_p = \boxed{-V\alpha}$$

M3.10a (5.14a, 7th Ed)

Molar Helmholtz energy of a gas given as:

$$A_m = -\frac{a}{V_m} - RT \ln(V_m - b) + f(T)$$

Obtain EOS of gas.

$$\boxed{\text{FET}} \quad dA_m = -SdT - pdV_m$$

$$\boxed{\text{ThD.}} \text{ of } p: \quad p = -\left(\frac{\partial A_m}{\partial V_m}\right)$$

Hence, substitute in for  $A_m$  to make the EOS:

$$p = -\frac{\partial}{\partial V_m} \left[ -\frac{a}{V_m} - RT \ln(V_m - b) + f(T) \right]$$

$$= -\frac{a}{V_m^2} + RT \frac{1}{V_m - b} = \boxed{-\frac{a}{V_m^2} + \frac{RT}{V_m - b}}$$

note: this is the vdW eqn!

M3.10b (5.14b, 7th)

$$G = RT \ln p + A + Bp + \frac{1}{2} Cp^2 + \frac{1}{3} Dp^3. \text{ Find EOS.}$$

$$dG = -SdT + Vdp, \text{ so ThD. } V = \left(\frac{\partial G}{\partial p}\right)_T$$

$$V = \frac{d}{dp}(G) = \boxed{\frac{RT}{p} + B + Cp + Dp^2} \quad \text{VIRIAL EQUATION}$$