

1.)

①

$$C_v = \frac{\partial x_g}{\partial T} u(v_g, T) + x_g \frac{\partial u_g}{\partial T} + \frac{\partial x_e}{\partial T} u_e + x_e \frac{\partial u_e}{\partial T}$$

$$x_g + x_e = 1$$

$$\frac{\partial x_g}{\partial T} = - \frac{\partial x_e}{\partial T}$$

$$C_v = x_g \frac{\partial u_g}{\partial T} + x_e \frac{\partial u_e}{\partial T} + (u_e - u_g) \frac{\partial x_e}{\partial T}$$

$$\left(\frac{\partial u_x}{\partial T} \right)_{\text{coex}} = \frac{\partial u_x}{\partial T} + \left(\frac{\partial u_x}{\partial v_x} \right)_T \left(\frac{\partial v_x}{\partial T} \right)_T$$

• Clausius - Clapeyron

$$\left(\frac{\partial P}{\partial T} \right)_{\text{coex}} = \frac{\Delta h_{e-g}}{T(v_e - v_g)} =$$

$$h_e = u_e + P v_e$$

$$\left(\frac{\partial P}{\partial T} \right)_{\text{coex}} = \frac{u_e - u_g + P(v_e - v_g)}{T(v_e - v_g)}$$

$$\Rightarrow (u_e - u_g) = \left[T \left(\frac{\partial P}{\partial T} \right)_{\text{coex}} - P \right] (v_e - v_g)$$

$$\frac{\partial v_P}{\partial v_g} = 0$$

$$v_P = x_e v_e + x_g v_g$$

$$\frac{\partial x_e}{\partial T} v_e + x_e \frac{\partial v_e}{\partial T} + \frac{\partial x_g}{\partial T} v_g + x_g \frac{\partial v_g}{\partial T} = 0$$

$$\frac{\partial x_e}{\partial T} (v_e - v_g) = -x_e \frac{\partial v_e}{\partial T} - x_g \frac{\partial v_g}{\partial T}$$

$$\frac{\partial x_e}{\partial T} = \frac{1}{(v_e - v_g)} \left[x_e \frac{\partial v_e}{\partial T} + x_g \frac{\partial v_g}{\partial T} \right]$$

(3)

$$C_v = x_g \frac{\partial u_g}{\partial T} + x_e \frac{\partial u_e}{\partial T} + (u_e - u_g) \frac{\partial x_e}{\partial T}$$

$$= x_g \left[c_{vg} + \frac{\partial u_g}{\partial v_g} \frac{\partial v_g}{\partial T} \right] + x_e \left[c_{ve} + \frac{\partial u_e}{\partial v_e} \frac{\partial v_e}{\partial T} \right]$$

$$+ \frac{(u_e - u_g)}{(v_g - v_e)} \left[x_g \frac{\partial v_g}{\partial T} + x_e \frac{\partial v_e}{\partial T} \right]$$

$$= x_g \left[c_{vg} + \frac{\partial u_g}{\partial v_g} \frac{\partial v_g}{\partial T} \right] + x_e \left[c_{ve} + \frac{\partial u_e}{\partial v_e} \frac{\partial v_e}{\partial T} \right]$$

$$+ \left[T \left(\frac{\partial P}{\partial T} \right)_{\text{mix}} - P \right] \left[x_g \frac{\partial v_g}{\partial T} + x_e \frac{\partial v_e}{\partial T} \right]$$

$$= x_g \left[c_{vg} + \left(T \left(\frac{\partial P_g}{\partial T} \right) - P \right) \frac{\partial v_g}{\partial T} \right]$$

$$+ x_e \left[c_{ve} + \left(T \left(\frac{\partial P_e}{\partial T} \right) - P \right) \frac{\partial v_e}{\partial T} \right]$$

$$- \left[T \left(\frac{\partial P}{\partial T} \right)_{\text{mix}} - P \right] \left[x_g \frac{\partial v_g}{\partial T} + x_e \frac{\partial v_e}{\partial T} \right]$$

$$= x_g c_{vg} + x_e c_{ve}$$

$$+ x_g T \frac{\partial P_g}{\partial T} \frac{\partial v_g}{\partial T} + x_e T \frac{\partial P_e}{\partial T} \frac{\partial v_e}{\partial T}$$

$$- T \left(\frac{\partial P}{\partial T} \right)_{\text{mix}} \left[x_g \frac{\partial v_g}{\partial T} + x_e \frac{\partial v_e}{\partial T} \right]$$

$$C_v = x_g \left[c_{vg} - T \left(\frac{\partial P}{\partial v_g} \right)_T \left(\frac{\partial v_g}{\partial T} \right)^2_{\text{mix}} \right]$$

$$+ x_e \left[c_{ve} - T \left(\frac{\partial P}{\partial v_e} \right)_T \left(\frac{\partial v_e}{\partial T} \right)^2_{\text{mix}} \right]$$

2. Ginzburg-Landau theory for the susceptibility

$$\Phi(T, \eta, s) = \Phi_0(T, \eta) + \alpha_2(T, \eta)\eta^2 + \alpha_4(T, \eta)\eta^4 - s\eta$$

$$\frac{\partial \Phi}{\partial \eta} = 2\alpha_2\eta + 4\alpha_4\eta^3 - s = 0$$

order parameter @ $s=0 \rightarrow \eta=0$
 $\eta^2 = \sqrt{-\frac{\alpha_2}{2\alpha_4}}$

$$\alpha_2 = \alpha_0(T - T_c)$$

$$\eta = \pm \sqrt{\frac{\alpha_0(T_c - T)}{2\alpha_4}}$$

susceptibility

$$\lim_{s \rightarrow 0} -\frac{\partial^2 \Phi}{\partial s^2} = \frac{\partial \eta}{\partial s}$$

$$2\alpha_2 \frac{\partial \eta}{\partial s} + 12\alpha_4 \eta^2 \frac{\partial \eta}{\partial s} - 1 = 0$$

above critical point $\eta=0$

$$\eta \rightarrow \chi = \frac{\partial \eta}{\partial s} = \frac{1}{2\alpha_2} = \frac{1}{\alpha_0(T - T_c)}$$

below critical point $\eta = \pm \sqrt{\frac{\alpha_0(T_c - T)}{2\alpha_4}}$

$$\frac{\partial \eta}{\partial s} = \frac{1}{2\alpha_2 + 12\alpha_4\eta^2} = \frac{1}{2\alpha_2 + \frac{12\alpha_4\alpha_0}{2\alpha_4}} = -\frac{1}{4\alpha_2}$$

$$= -\frac{1}{4\alpha_0(T - T_c)} = \frac{1}{4\alpha_0(T_c - T)}$$

$$\text{as } T \rightarrow T_c \quad \frac{\partial \eta}{\partial s} \rightarrow \infty$$

3.) Berthelot Equation of State

$$\left(p + \frac{a}{Tv^2}\right)(v-b) = RT$$

$$p = \frac{RT}{v-b} - \frac{a}{Tv^2}$$

$$\frac{\partial p}{\partial v} = -\frac{RT}{(v-b)^2} + \frac{2a}{Tv^3} = 0 \Rightarrow \frac{RT}{(v-b)^2} = \frac{2a}{Tv^3}$$

$$\frac{\partial^2 p}{\partial v^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{Tv^4} = 0$$

$$= \frac{2}{(v-b)} \left(\frac{2a}{Tv^3}\right) - \frac{3}{v} \left(\frac{2a}{Tv^3}\right) = 0$$

$$2v - 3v + 3b = 0$$

$$\boxed{v_c = 3b}$$

$$\frac{RT_c^2}{4b^2} = \frac{2a}{27b^3}$$

$$T_c = \sqrt{\frac{8a}{27bR}}$$

$$p_c = \frac{2a}{Tv_c^3}(v_c-b) - \frac{a}{Tv_c^3} = \frac{a}{Tv_c^3} [2v_c - 2b - 1] \quad [2v_c - 2b = 1]$$

$$= \frac{a}{Tv_c^3} [v_c - 2b]$$

$$= \frac{a}{T_c 27b^2} = \frac{a}{27b^2} \sqrt{\frac{27bR}{8a}}$$

$$= \sqrt{\frac{aR}{216 \cdot b^3}}$$

to determine whether the law of corresponding states is satisfied $\Rightarrow$ write equation of state in reduced variables and determine whether it depends on parameters a, b, R

$$\bar{P} = \frac{P}{P_c} = \left[\frac{RT_c}{v_c \bar{v} - b} - \frac{a}{T_c \bar{v}^2 v_c} \right] \frac{1}{P_c}$$

$$\bar{P} = \left[\frac{RT_c}{v_c \bar{v} - b} - \frac{a}{T_c \bar{v}^2 v_c} \right] \frac{1}{P_c}$$

$$= \left[\frac{RT_c}{3b\bar{v} - b} - \frac{a}{T_c \bar{v}^2 9b^2} \right] \frac{1}{P_c}$$

$$= \left[\frac{\bar{T}}{3\bar{v} - 1} \frac{(RT_c)}{b} - \frac{1}{\bar{T}\bar{v}^2} \left(\frac{a}{T_c 9b^2} \right) \right] \frac{1}{P_c}$$

$$= \frac{\bar{T}}{3\bar{v} - 1} \left(\frac{RT_c}{bP_c} \right) - \frac{1}{\bar{T}\bar{v}^2} \left(\frac{a}{P_c T_c 9b^2} \right)$$

$$\frac{RT_c}{bP_c} = \frac{R}{b} \left(\frac{8a}{27R} \right)^{1/2} \left(\frac{216b^3}{aR} \right)^{1/2} = 8$$

$$\left(\frac{a}{P_c T_c 9b^2} \right) = \frac{a}{9b^2} \left(\frac{216b^3}{aR} \right)^{1/2} \left(\frac{27aR}{8a} \right)^{1/2} = \frac{27}{a} = 3$$

$$\boxed{\bar{P} = \frac{8\bar{T}}{3\bar{v} - 1} - \frac{3}{\bar{T}\bar{v}^2}}$$

$\Rightarrow$ law of corresponding states is satisfied

4.)

$$G = U - TS + PV = \mu_A N_A + \mu_B N_B$$

• differential:

$$dG = dU - TdS - SdT + PdV + VdP$$

~~for dU =~~

$$\text{Since } U = TS - PV + \sum \mu_i N_i$$

$$dU = TdS + SdT - PdV + \mu_A dN_A + \mu_B dN_B$$

(fundamental equation of thermodynamics)

$$dG = -SdT + VdP + \mu_A dN_A + \mu_B dN_B$$

• Gibbs Duhem equation:

$$SdT - VdP + \sum N_k d\mu_k = 0$$

divide by $N = N_A + N_B$

$$sdT - vdp + \sum x_k dx_k = 0$$

• Clausius-Clapeyron

dg - at two phases (in molar units)

$$dg^I = -s^I dT + v^I dP + (\mu_A^I - \mu_B^I) dx^I$$

$$dg^{II} = -s^{II} dT + v^{II} dP + (\mu_A^{II} - \mu_B^{II}) dx^{II}$$

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{\Delta S}{\Delta V} - \frac{(\Delta \mu_A - \Delta \mu_B)}{\Delta V} \frac{d \Delta x}{dT}$$