Problem 16

a) $$\frac{dP}{dT} = \frac{\Delta h}{T\Delta v} \qquad 2$$

$$v_g \gg v_l \Rightarrow \Delta v \approx v_g = \frac{RT}{P}$$

$$\frac{dP}{dT} \approx \frac{P\Delta h}{RT^2} \qquad 1$$

$$\frac{dP}{P} = \frac{dT}{RT^2}$$

$$\ln\frac{P}{P_0} = -\frac{\Delta h}{RT} + \frac{\Delta h}{RT_0}$$

$$P(T) = P_0\, e^{-\frac{\Delta h}{RT} + \frac{\Delta h}{RT_0}} \qquad 2$$

b) $$P_0\, e^{-\frac{mgh}{RT_{air}}} = P_0\, e^{-\frac{\Delta h}{RT} + \frac{\Delta h}{RT_0}}$$

$$\Rightarrow \frac{mgh}{T_{air}} = \frac{\Delta h}{T} - \frac{\Delta h}{T_0} \qquad 2$$

$$\frac{29 \cdot 9.81 \cdot 1609}{300} \frac{g}{mol} \frac{m \cdot m}{s^2\, K} = \frac{\Delta h}{T} - \frac{\Delta h}{T_0} \qquad 1$$

$$\frac{29 \cdot 9.81 \cdot 1609}{300 \cdot 10 \cdot 4.186} \frac{g \quad m\, m\, mol}{mol\, s^2\, K\, kJ} = \frac{1}{T} - \frac{1}{373K}$$

$$\frac{1}{T} = \frac{1}{373K} + 3.65 \cdot 10^{-5} \frac{1}{K}$$

$$\Rightarrow T = 368\,K \qquad 2$$

Problem 17:

2 a) exchange 1 and 2 ($\leftrightarrow x \Rightarrow 1-x$)

$$\mu_1(P,T,x) = \mu_1^{(0)}(P,T) - \lambda(1-x)^2 + RT\ln x$$

2 b)
$$\mu_1(P,T,x_\alpha) = \mu_1(P,T,x_\beta)$$
$$\mu_2(P,T,x_\alpha) = \mu_2(P,T,x_\beta)$$

c) from b):

$$-\lambda(1-x_\alpha)^2 + RT\ln x_\alpha = -\lambda(1-x_\beta)^2 + RT\ln x_\beta$$
$$-\lambda x_\alpha^2 + RT\ln(1-x_\alpha) = -\lambda x_\beta^2 + RT\ln(1-x_\beta)$$

use $x_\alpha = 1 - x_\beta$:

1 $$-\lambda(1-x_\alpha)^2 + RT\ln x_\alpha = -\lambda x_\alpha^2 + RT\ln(1-x_\alpha)$$

second equation gives the same.

$$RT\left[\ln(1-x_\alpha) - \ln x_\alpha\right] = -\lambda\left[(1-x_\alpha)^2 - x_\alpha^2\right]$$

(*) $$T = -\frac{\lambda}{R}\,\frac{(1-x_\alpha)^2 - x_\alpha^2}{\ln(1-x_\alpha) - \ln x_\alpha} = -\frac{\lambda}{R}\,\frac{1-2x_\alpha}{\ln(1-x_\alpha) - \ln x_\alpha} \qquad g(x_\alpha)$$

$$g(x_\alpha) \geq 0 \qquad \lim_{x_\alpha \to 0} g(x_\alpha) = 0$$

$\Rightarrow$ if $\lambda < 0$ and TR small enough we can solve

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$$T = -\frac{\lambda}{R}\,g(x_\alpha) \text{ for } x_\alpha$$

d) T_c is the largest temperature for which coexistence is still possible

$$T_c = -\frac{\lambda}{R} \max_{x_\alpha \in [0,1]} q(x_\alpha)$$

$$q'(x_\alpha) = \frac{-2\left[\ln(1-x_\alpha) - \ln x_\alpha\right] + (1-2x_\alpha)\frac{1}{x_\alpha(1-x_\alpha)}}{\left[\ln(1-x_\alpha) - \ln x_\alpha\right]^2}$$

$$\frac{d}{dx_\alpha}\left[-2\left[\ln(1-x_\alpha) - \ln x_\alpha\right] + (1-2x_\alpha)\frac{1}{x_\alpha(1-x_\alpha)}\right]$$

$$= \frac{2}{x_\alpha(1-x_\alpha)} + \frac{-2x_\alpha(1-x_\alpha) - (1-2x_\alpha)(1-2x_\alpha)}{x_\alpha^2(1-x_\alpha)^2}$$

$$= \frac{2x_\alpha(1-x_\alpha) - 2x_\alpha + 2x_\alpha^2 - 1 + 4x_\alpha - 4x_\alpha^2}{x_\alpha^2(1-x_\alpha)^2}$$

$$= \frac{-4x_\alpha^2 + 4x_\alpha - 1}{x_\alpha^2(1-x_\alpha)^2} = -\frac{(1-2x_\alpha)^2}{x_\alpha^2(1-x_\alpha)^2} \leq 0$$

$\Rightarrow$ q' decreases monotonously $\Rightarrow$ q is concave

$\Rightarrow$ q' has at most one zero

$q'(x_\alpha = \frac{1}{2})$ is the only zero and $x_\alpha = \frac{1}{2}$ is maximum of q

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$$\Rightarrow T_c = -\frac{\lambda}{R} q(x_\alpha = \tfrac{1}{2}) = \left.\frac{-2}{-\frac{1}{(1-x_\alpha)x_\alpha}}\right|_{x_\alpha = \frac{1}{2}} = \frac{1}{2}$$

$$\Rightarrow \boxed{RT_c = -\frac{\lambda}{2}}$$ 1

Problem 18:

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

T_c given by $\left(\frac{\partial P}{\partial v}\right)_{T=T_c} = 0 \qquad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = 0$ (1)

$$0 = \left(\frac{\partial P}{\partial v}\right)_{T=T_c} = -\frac{RT_c}{(v_c-b)^2} + \frac{2a}{T_c v_c^3} \Rightarrow \frac{2RT_c}{(v_c-b)^3} = \frac{4a}{T_c v_c^3 (v_c-b)} \quad (1)$$

$$0 = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = \frac{2RT_c}{(v_c-b)^3} - \frac{6a}{T_c v_c^4} \quad (1)$$

$$\Rightarrow \frac{2}{v_c-b} = \frac{3}{v_c} \Rightarrow 2v_c = 3v_c - 3b \Rightarrow \boxed{v_c = 3b} \quad (1)$$

$$T_c^2 = \frac{2a(v_c-b)^2}{Rv_c^3} = \frac{8a}{27Rb} \Rightarrow T_c = \sqrt{\frac{8a}{27Rb}} \quad (1)$$

$$P_c = \frac{RT_c}{v_c-b} - \frac{a}{T_c v_c^2} = \frac{R\sqrt{\frac{8a}{27Rb}}}{2b} - \frac{a}{\sqrt{\frac{8a}{27Rb}}\,9b^2} = \sqrt{\frac{8Ra}{27b^3}}\left[\frac{1}{2} - \frac{3}{8}\right]$$

$$= \frac{1}{4}\sqrt{\frac{2Ra}{27b^3}} \quad (1)$$

b) $$\left(\frac{P}{P_c} + \frac{a\,4b}{Tv^2}\sqrt{\frac{27b^3}{2aR}}\right)\left(\frac{v}{v_c} - \frac{1}{3}\right) = R\frac{T}{T_c}\frac{4\cancel{b}}{3\cancel{b}}\sqrt{\frac{27b^3}{2aR}}\sqrt{\frac{8a}{27Rb}} = \frac{8}{3}\frac{T}{T_c}$$

$$\left(\bar{P} + \frac{a4b}{\bar{T}v^2}\sqrt{\frac{27b^3}{2aR}}\sqrt{\frac{27Rb}{8a}}\right)\left(\bar{v} - \frac{1}{3}\right) = \frac{8}{3}\bar{T}$$

$$\left(\bar{P} + \frac{27b^2}{\bar{T}v^2}\right)\left(\bar{v} - \frac{1}{3}\right) = \frac{8}{3}\bar{T}$$

$$\left(\bar{P} + \frac{3}{\bar{T}\bar{v}^2}\right)(3\bar{v} - 1) = 8\bar{T} \quad (4)$$

Yes, the Berthelot equation satisfies the law of corresponding states.