Problem 13:

Clausius Clapeyron equation:

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{\Delta h}{T\Delta v}$$

Since we are close to T=0°C we can assume that Δh and Δv are constant as temperature changes:

$$dP = \frac{\Delta h}{\Delta v}\frac{dT}{T}$$

$$\Delta P = \frac{\Delta h}{\Delta v}\ln\frac{T}{T_0} \quad 2$$ also accept $\Delta P = \frac{\Delta h}{T\Delta v}\Delta T$

Since they differ only by a constant factor that cancels out anyways we can measure Δh and Δv either both in per mol or both in per g

$v_{water} = 1\ cm^3/g \qquad v_{ice} = \frac{5}{4}\ cm^3/g \Rightarrow \Delta v = -0.25\ \frac{cm^3}{g}$ 2

$$\Delta P = -\frac{80\ cal\ g}{0.25\ g\ cm^3}\ln\frac{271.15}{273.15} = -\frac{80\cdot 4.184\ Nm}{0.25\cdot 10^{-6}\ m^3}\ln\frac{271.15}{273.15}$$

$$= 9.8\cdot 10^6\ \frac{N}{m^2} \quad 2$$

In order to produce this pressure with two masses M they have to fulfil

$$\frac{2gM}{2mm\ 25cm} = 9.8\cdot 10^6\frac{N}{m^2} \qquad M = \frac{9.8\cdot 10^6\cdot 25\cdot 10^{-5}\ N}{9.81\ \frac{m}{s^2}}$$

$$M = 250\ kg$$

2

Problem 14:

a) $g = f + Pv \qquad P = -\left(\frac{\partial f}{\partial v}\right)_T$

solid: $P = \frac{3B}{Tv_s^4} \qquad g_s = \frac{B}{Tv_s^3} + \frac{3B}{Tv_s^3} = \frac{4B}{Tv_s^3}$ (1/2)

$$g_s = \frac{4B}{T}\left(\frac{TP}{3B}\right)^{3/4} = \frac{4B^{1/4}}{3^{3/4}T^{1/4}}P^{3/4}$$ (1)

liquid: $P = \frac{2A}{Tv_\ell^3} \qquad g_\ell = \frac{A}{Tv_\ell^2} + \frac{2A}{Tv_\ell^2} = \frac{3A}{Tv_\ell^2}$ (1/2)

$$g_\ell = \frac{3A}{T}\left(\frac{TP}{2A}\right)^{2/3} = \frac{3A^{1/3}}{2^{2/3}T^{1/3}}P^{2/3}$$ (1)

b) At the coexistence curve the molar Gibbs free energies have to be equal

$$\frac{4B^{1/4}}{3^{3/4}T^{1/4}}P^{3/4} = \frac{3A^{1/3}}{2^{2/3}T^{1/3}}P^{2/3}$$

$$\frac{4^{12}B^3}{3^9T^3}P^9 = \frac{3^{12}A^4}{2^8T^4}P^8$$

$$P = \frac{3^{21}}{2^{32}}\frac{A^4}{B^3}\frac{1}{T}$$ (2)

c) At the coexistence curve the pressures and the molar Gibbs free energies have to be equal

$$\frac{3B}{Tv_s^4} = \frac{2A}{Tv_\ell^3} \quad\wedge\quad \frac{4B}{Tv_s^3} = \frac{3A}{Tv_\ell^2}$$

$$3Bv_\ell^3 = 2Av_s^4 \quad\wedge\quad 4Bv_\ell^2 = 3Av_s^3$$

$$3B\left(\frac{3A}{4B}\right)^{3/2}v_s^{9/2} = 2Av_s^4$$

$$\Rightarrow \quad v_s = \frac{4A^2}{9B^2}\frac{4^3B^3}{3^3A^3} = \boxed{\frac{2^8}{3^5}\frac{B}{A} = v_s}$$ (2)

$$v_e^2 = \frac{3A}{4B} v_s^3 = \frac{3A}{2^2 B}\,\frac{2^{24}}{3^{15}}\,\frac{B^3}{A^3} = \frac{2^{22}}{3^{14}}\,\frac{B^2}{A^2}$$

$$\Rightarrow \quad \boxed{v_e = \frac{2^{11}}{3^7}\,\frac{B}{A}} \quad 2$$

d) $$S_s = -\left(\frac{\partial g}{\partial T}\right)_P = \frac{B^{1/4}}{3^{3/4} T^{5/4}} P^{3/4} \quad 1/2 \quad \overset{\text{coex}}{=} \frac{B^{1/4}}{3^{3/4} T^{5/4}} \left(\frac{3^{21}}{2^{32}}\,\frac{A^4}{B^3}\right)^{3/4} \frac{1}{T^{3/4}}$$

$$= \frac{A^3}{B^2}\,\frac{3^{15}}{2^{24}}\,\frac{1}{T^2} \quad 1$$

$$S_e = -\left(\frac{\partial g}{\partial T}\right)_P = \frac{A^{1/3}}{2^{2/3} T^{4/3}} P^{2/3} \quad 1/2 \quad \overset{\text{coex}}{=} \frac{A^{1/3}}{2^{2/3} T^{4/3}} \left(\frac{3^{21}}{2^{32}}\,\frac{A^4}{B^3}\right)^{2/3} \frac{1}{T^{2/3}} =$$

$$= \frac{A^3}{B^2}\,\frac{3^{14}}{2^{22}}\,\frac{1}{T^2} \quad 1$$

e) $$\left(\frac{dP}{dT}\right)_{\text{coex}} \underset{e}{=} -\frac{3^{21}}{2^{32}}\,\frac{A^4}{B^3}\,\frac{1}{T^2} \quad 1$$

$$\Delta s = s_e - s_s = \frac{A^3}{B^2}\,\frac{1}{T^2}\left[\frac{3^{14}}{2^{22}} - \frac{3^{15}}{2^{24}}\right] = \frac{3^{14}}{2^{24}}\,\frac{A^3}{B^2}\,\frac{1}{T^2}\left[4-3\right] = \frac{3^{14}}{2^{24}}\,\frac{A^3}{B^2}\,\frac{1}{T^2}$$

$$\Delta v = v_e - v_s = \frac{B}{A}\left[\frac{2^{11}}{3^7} - \frac{2^8}{3^5}\right] = \frac{2^8 B}{3^7 A}\left[8-9\right] = -\frac{2^8 B}{3^7 A}$$

$$\frac{\Delta s}{\Delta v} = -\frac{3^{14}}{2^{24}}\,\frac{A^3}{B^2}\,\frac{1}{T^2}\,\frac{3^7 A}{2^8 B} = -\frac{3^{21}}{2^{32}}\,\frac{A^4}{B^3}\,\frac{1}{T^2} = \left(\frac{dP}{dT}\right)_{\text{coex}}$$

1

Problem 15:

a) $d\mu = -s\,dT + v\,dP$

constant temperature: $d\mu = v\,dP$

coexistence condition

$\mu_g(P, T) = \mu_\ell(P, T, x_{solvent})$

$= \mu_\ell^{(0)}(P,T) + RT \ln x_{solvent}$ (2)

$$\Rightarrow \underbrace{\left(\frac{\partial \mu_g}{\partial P}\right)_T}_{= v_g} dP = \underbrace{\left(\frac{\partial \mu_\ell^{(0)}}{\partial P}\right)_T}_{= v_\ell} dP + RT \frac{dx_{solvent}}{x_{solvent}}$$

$$\left(\frac{dP}{dx_{solvent}}\right)_{coex,T} = \frac{RT}{(v_g - v_\ell)\,x_{solvent}} \quad (2)$$

b) $\left.\begin{array}{l} v_g \gg v_\ell \\ P\,v_g \cong RT \end{array}\right\}$ $v_g - v_\ell \approx v_g \approx \frac{RT}{P}$

$$\Rightarrow \left(\frac{dP}{dx_{solvent}}\right)_{coex,T} = \frac{P}{x_{solvent}}$$

$$\frac{dP}{P} = \frac{dx_{solvent}}{x_{solvent}}$$

$$\frac{P}{P_0} = \frac{x_{solvent}}{1} \quad (2)$$

P_0: pressure in absence of solute

c) $\Delta P = P_0 - P = P_0\left(1 - \frac{P}{P_0}\right) = P_0(1 - x_{solvent}) = P_0\, x_{solute}$

$$\boxed{\frac{\Delta P}{P_0} = x_{solute}} \quad (2)$$