Chemistry 553

Problem set 5

Due: 11 March 2011

From your text,

1. 14.1
2. 14.6
3. 15.3 use a graphics package
4. 16.2
5. 16.5
6. 16.21
7. 25.3
8. 25.10
9. a few more to come

Problem set 5

1. 14.1

a) $\left(\frac{\partial \ln P}{\partial T}\right) = \frac{\Delta H}{RT^2} \Rightarrow \left(\frac{\Delta \ln P}{\Delta T}\right) = \frac{\ln(760/23)}{373 - 300}$

$\Delta H \sim RT^2(0.048) = (8.315 \frac{J}{K})(373)(0.048) \sim 55.4 kJ$

or $\frac{\partial \ln P}{\partial(1/T)} = -\frac{\Delta H}{R} \therefore \frac{\Delta \ln P}{\Delta(\frac{1}{T})} = 44.6$ kJ/mole

b) $\ln(P_2/P_1) = \frac{z w_{AA}}{2R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ lattice model

$\frac{\Delta H}{R} = -\frac{z w_{AA}}{2R}$, since $\frac{\partial \ln P}{\partial(1/T)} = \frac{z w_{AA}}{2R}$

and $w_{AA} = \frac{2}{z}\Delta H = \frac{1}{2}\Delta H(L \to G) = -22.3$ kJ/mole

2. 14.6 $P = P^0_{int} \exp(z w_{AA}/2RT)$

but $\Delta H_{vap} = -z w_{AA}/2$ given above

$P = P_0 \exp(-\Delta H_{vap}/k_B T) \Rightarrow$ if the P_0's are the same then

$\left.\frac{\Delta H_{vap}}{T}\right|_{\text{fluid a}} = \left.\frac{\Delta H_{vap}}{T}\right|_{\text{fluid b}}$

and $\frac{T_b}{T_a} = \frac{\Delta H_{vap,b}}{\Delta H_{vap,a}} = \frac{15 \text{ kcal}}{10 \text{ kcal}} = \frac{T}{300}$

$T = 450K$.

3. 15.3

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> mu := ln(x) + chi*(1-x)^2;
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$$\mu := \ln(x) + \chi\,(1-x)^2$$

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> mu_0 := subs(chi=0,mu);
> mu_2 := subs(chi=2,mu);
> mu_4 := subs(chi=4,mu);
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$$mu\_0 := \ln(x)$$

$$mu\_2 := \ln(x) + 2\,(1-x)^2$$

$$mu\_4 := \ln(x) + 4\,(1-x)^2$$

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> plot([mu_0,mu_2,mu_4],x=0.01..1,axes=boxed);
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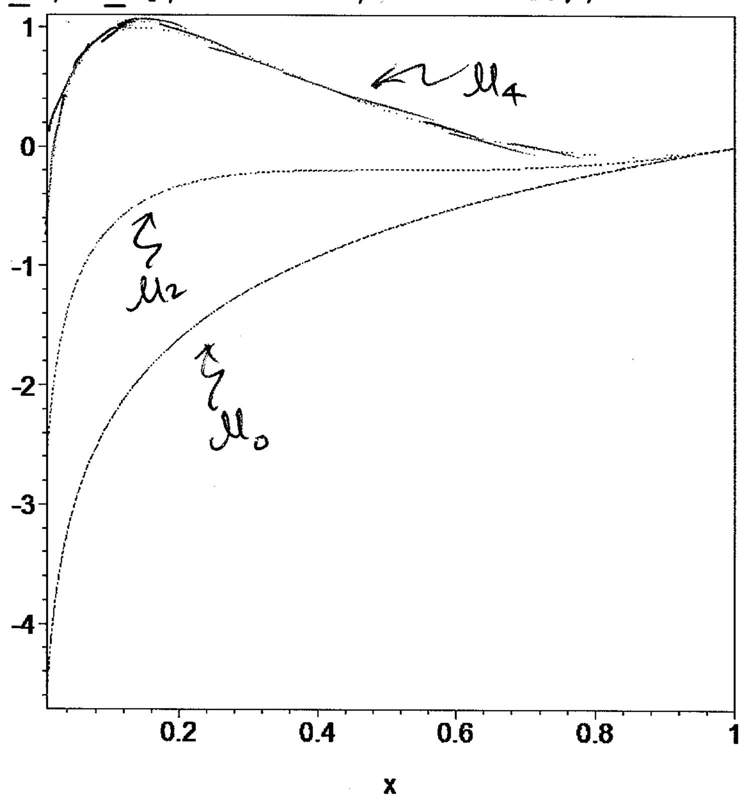


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>
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3\. 15.3 Plot $\mu(x)$,

$$\beta\mu(x) = \ln x_A + \frac{zw_{AA}}{2k_BT} + \chi_{AB}(1-x_A)^2$$

$\chi_{AB} = 0$, $\chi_{AB} = 2, 4$ (see enclosed plot).

4\. 16.2

$$P_{\text{vapor pressure of } N_2} = k_H x_{N_2}$$

k_H: 86,000 atm

As we compress water, the vapor pressure of the N_2 also increases.

$$P = 1\,\text{atm} + \frac{d(\text{feet})}{33\,\text{ft/atm}}$$

air is 78% N_2

$$x_{N_2} = \frac{0.78}{86\times10^3}\left\{1 + \frac{d(\text{ft})}{33}\right\}$$

5\. T-dependence of the Henry's law const.

$$P_B = x_B P_B^0 \exp(\chi_{AB}(1-x_B)^2)$$

$$\chi_{AB} = z\{w_{AB} - \tfrac{1}{2}(w_{AA}+w_{BB})\}/k_BT$$
$$= z\Delta w/k_BT$$

Henry's law is the limit of $x_B \to 0$

$$P_B = k_H x_B$$

$$k_H = k_H(T) + \Delta T\left(\frac{\partial k_H}{\partial T}\right) = k_H(T+\Delta T)$$

$$\frac{\partial}{\partial T} P_B^{\circ} \exp(z\Delta W / k_B T) = -\frac{z\Delta W}{k_B T^2} k_H$$

$$\therefore \left(\frac{\partial k_H}{\partial T}\right) = -\frac{z\Delta W}{k_B T^2} k_H(T)$$

6. 16.21 From the figure, $\chi \simeq 2$, so that

$$\chi_{AB} = 2 = z\,\Delta W / k_B T$$

$z \approx 6$, and $\Delta W \sim \frac{1}{3} k_B T$

a) $\Delta W/\text{mole} \sim \frac{1}{3} RT \sim \frac{300}{3} R = 100 R \cong 8.3\,\text{kJ}$

b) $\chi_{AB} \sim 2$

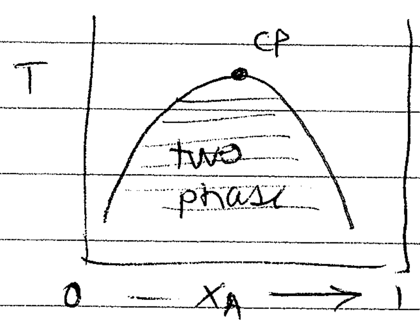
c) $P_B = x_B P_B^{\circ} \exp(\chi_{AB}(1-x_B)^2)$

as $x_B \to 1$, $P_B \to x_B P_B^{\circ}$

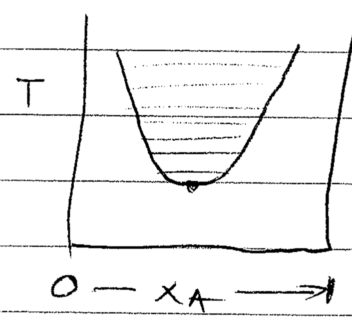
Raoult's law.

7. 25.3

Normally



when χ increases with T, phase separation occurs as $T > T_c$.



8. 25.10 At compositions near the Azeotrope, distillation will always produce the the mixture, i.e, can not be separated into pure components.