MET6208 - Contrôle I - le 31 oct/05

Question 1

$N_2 = 2N$ (Assume: dissolves monatomically)

$$K = \frac{a_N^2}{P_{N_2}} = \frac{(X_N \cdot \gamma_N)^2}{P_{N_2}}$$

Assume: Henrian solution (γ_N = constant)

Also, in a dilute solution, $(wt\%)_N \approx C \cdot X_N$ (C = constant)

Therefore: $\frac{(wt\%)_N^2}{P_{N_2}} \approx$ constant

$$\frac{(0.045)^2}{1} = \frac{(wt\%)_N^2}{10}$$

$$(wt.\%)_N = 0.045\sqrt{10} = 0.142 \text{ wt \%}$$

Question 2

Solid solutions are Henrian (That is, Raoult's Law is obeyed for the solvents)

Ag (solid) solution: $RT\ln\gamma^{\circ}_{Cu} = 18450$ $\quad T = 1000K$

$$\gamma^{\circ}_{Cu} = 9.197$$

$$\text{and} \begin{cases} a_{Cu} = 9.197\xi_A & (\text{where } \xi_{Cu} = X_{Cu} \text{ in this solution}) \\ a_{Ag} = (1-\xi_A) & (\text{Raoultian for solvent}) \end{cases}$$

Cu (solid) solution: $RT\ln\gamma^{\circ}_{Ag} = 27780$

$$\gamma^{\circ}_{Ag} = 28.246$$

$$\begin{cases} a_{Ag} = 28.246(1-\xi_c) \\ a_{Cu} = \xi_c \end{cases}$$

These two solutions are in equilibrium
Therefore, the activities of Ag and Cu are equal
That is:

$$\begin{cases} 9.197\xi_A = \xi_c \\ (1-\xi_A) = 28.246(1-\xi_c) \end{cases}$$

Solve to get: $\xi_A = 0.1053$ $\quad \xi_c = 0.9683$

$$Ag + \tfrac{1}{2}Cl_2 = AgCl \qquad \Delta G^{\circ} = -79910 = -RT\ln K$$

$$K = \frac{a_{AgCl}}{a_{Ag}\cdot P_{Cl_2}^{1/2}} = 14918 = \frac{\xi_B \xrightarrow{\text{ideal liquid}}}{(1-\xi_A)\cdot P_{Cl_2}^{1/2}} = \frac{\xi_B}{(0.8947)\,P_{Cl_2}^{1/2}}$$

$$Cu + \tfrac{1}{2}Cl_2 = CuCl \qquad \Delta G^{\circ} = -91840 = -RT\ln K$$

$$K = \frac{a_{CuCl}}{a_{Cu}\cdot P_{Cl_2}^{1/2}} = \frac{(1-\xi_B)}{\xi_c\cdot P_{Cl_2}^{1/2}} = \frac{(1-\xi_B)}{(0.9683)\,P_{Cl_2}^{1/2}} = 62636$$

Solve 2 equations

Solve to get: $\xi_B = 0.180$

$P_{Cl_2} = 1.83 \times 10^{-10}$ atm

Question 3

$A(s) \rightarrow A(\ell)$ $\quad \Delta g^\circ_{fusion} = 5000 - 10T$

(because $\Delta S^\circ_{fusion} = \frac{\Delta H^\circ_{fusion}}{T^\circ_{fusion}} = \frac{5000}{500}$)

$2A(s) + B(s) \rightarrow A_2B(s)$ $\quad \Delta g^\circ = -35000 + 8.0T$

$2A(\ell) + B(s) \rightarrow A_2B(s)$ $\quad \Delta g^\circ = (-35000 + 8.0T) - 2(5000 - 10T)$

$\Delta g^\circ = -45000 + 28.0T$

$\Delta g^\circ_{1000K} = -17000$

$\Delta g^\circ_{700K} = -25400$

$\Delta g^\circ_{500K} = -31000$

$\Delta g^\circ = -RT \ln K$

At 1000K $\quad -17000 = -R(1000) \ln K$

$$K = 7.7253 = \frac{a_{A_2B}}{a_A^2 \cdot a_B} = \frac{1.0}{(1-X_B)^2 (X_B \cdot \gamma^\circ_B)} = \frac{1.0}{(1-0.02)^2 (0.02 \cdot \gamma^\circ_B)}$$

(At saturation, a_A (with respect to liquid standard state) $= X_A = (1 - X_B)$)

($a_B = \gamma^\circ_B \cdot X_B$ where $\gamma^\circ_B \simeq$ cst. (Henry's Law))

$\gamma^\circ_B = 6.74$ at 1000K

At 700K $\quad -25400 = -R(700) \ln K$

$$K = 78.562 = \frac{1.0}{(1-0.003)^2 (0.003 \gamma^\circ_B)}$$

$\gamma^\circ_B = 4.269$ at 700K

(ii) $RT \ln \gamma^\circ_B = A - BT$

$R(1000) \ln(6.74) = A - 1000B$

$R(700) \ln(4.269) = A - 700B$

$T_E \simeq 500K$ Solve to get: $\quad A = -8861 \quad B = -24.73$

Therefore at 500K: $\quad R(500) \ln \gamma^\circ_B = -8861 + 24.73(500) \quad \gamma^\circ_B = 2.323$

$-31000 = -R(500) \ln K$

$$K = 1731 = \frac{1}{(1-X_B)^2 (2.323) X_B} \quad X_B = 0.00025$$

(Question 3– continued)

Finally, on the A-liquidus

$$RT \ln a_A = -\Delta g^{\circ}_{fusion(A)}$$

$$R(T_E) \ln(1 - 0.00025) = -5000 + 10\,T_E$$

$$T_E = 499.9\ K$$

Question 4

AgCl liquidus:

$$RT\ln a_{AgCl}^{E} = -\Delta g^{\circ}_{fusion(AgCl)}$$

$$RT\ln X_{AgCl} + g_{AgCl} = -13200\left(1-\frac{T}{455+273}\right)$$

$$RT\ln X_{AgCl} + aX_{KCl}^{2} = -13200\left(1-\frac{T}{728}\right)$$

KCl liquidus:

$$RT\ln X_{KCl} + aX_{AgCl}^{2} = -25520\left(1-\frac{T}{1043}\right)$$

The two liquidus curves meet at $T_E = 579K$

$$\begin{cases} R(579)\ln(1-X_E) + aX_E^{2} = -13200\left(1-\frac{579}{728}\right) \\ R(579)\ln X_E + a(1-X_E)^{2} = -25520\left(1-\frac{579}{1043}\right) \end{cases}$$

(where $X_E = X_{KCl(E)}$)

Two equations with two unknowns (X_E and a).

$$4814\ln(1-X) + aX^{2} = -985$$

$$4814\ln X + a(1-X)^{2} = -11353$$

Guess values of "a" until X is same in both equations

$$X_{KCl(E)} = 0.163$$

$$a = -4000 \text{ Joules}$$