

Question 1

$$N_2 = 2N \quad (\text{Assume: dissolves monatomically})$$

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

Assume: Hensian solution ($\gamma_N = \text{constant}$)

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

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

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

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

Question 2

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

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

$$\gamma_{Cu}^{\circ} = 9.197$$

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: $RT \ln \gamma_{Ag}^{\circ} = 27780$

$$\gamma_{Ag}^{\circ} = 28.246$$

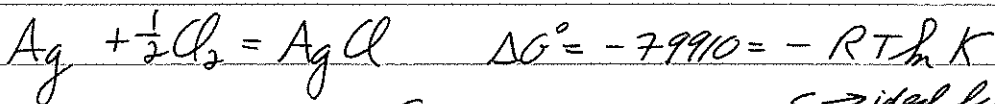
$$\begin{cases} a_{Ag} = 28.246(1 - \xi_C) \\ a_{Cu} = \xi_C \end{cases}$$

These two solutions are in equilibrium

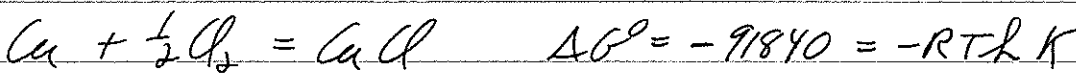
Therefore, the activities of Ag and Cu are equal

That is: $\begin{cases} 9.197 \xi_A = \xi_C \\ (1 - \xi_A) = 28.246(1 - \xi_C) \end{cases}$

Solve to get: $\xi_A = 0.1053$ $\xi_C = 0.9683$



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



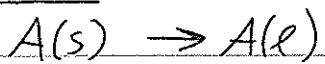
$$K = \frac{a_{CuCl}}{a_{Cu} \cdot P_{Cl_2}^{1/2}} = \frac{(1 - \xi_B)}{\xi_C \cdot P_{Cl_2}^{1/2}} = \frac{(1 - \xi_B)}{(0.9683) P_{Cl_2}^{1/2}} = 62636$$

Solve 2 equations

Solve to get: $\xi_B = 0.180$

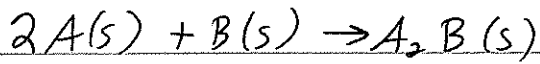
$P_{Cl_2} = 1.83 \times 10^{-10} \text{ atm}$

Question 3

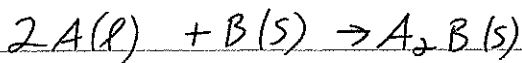


$$\Delta g_{\text{fusion}}^{\circ} = 5000 - 10T$$

$$\left(\text{because } \Delta S_{\text{fusion}}^{\circ} = \frac{\Delta H_{\text{fusion}}^{\circ} - \frac{5000}{500}}{T_{\text{fusion}}^{\circ}} \right)$$



$$\Delta g^{\circ} = -35000 + 8.0T$$



$$\Delta g^{\circ} = (-35000 + 8.0T) - 2(5000 - 10T)$$

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

$$\Delta g_{1000K}^{\circ} = -17000$$

$$\Delta g_{700K}^{\circ} = -25400$$

$$\Delta g_{500K}^{\circ} = -31000$$

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

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

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

$$\left(A \text{ at saturation, } a_A \text{ (with respect to liquid standard state)} = X_A = (1-X_B) \right)$$

$$(a_B = \gamma_B^{\circ} X_B \text{ where } \gamma_B^{\circ} \approx \text{const. (Henry's Law)})$$

$$\gamma_B^{\circ} = 6.74 \text{ at } 1000K$$

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

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

$$\gamma_B^{\circ} = 4.269 \text{ at } 700K$$

$$(ii) \quad RT \ln \gamma_B^{\circ} = A - BT$$

$$\left[R(1000) \ln(6.74) = A - 1000B \right.$$

$$\left. \left[R(700) \ln(4.269) = A - 700B \right. \right.$$

$$T_E \approx 500K \quad \text{Solve to get:} \quad A = -8861 \quad B = -24.73$$

$$\text{Therefore at } 500K: \quad R(500) \ln \gamma_B^{\circ} = -8861 + 24.73(500) \quad \gamma_B^{\circ} = 2.323$$

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

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

(Question 3 - continued)

Finally, on the A-liquidus

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

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

$$\underline{T_E = 499.9 \text{ K}}$$

Question 4

AgCl liquidus:

$$RT \ln a_{\text{AgCl}} = -\Delta G_{\text{fusion}}^{\circ}(\text{AgCl})$$
$$RT \ln X_{\text{AgCl}} + g_{\text{AgCl}} = -13200 \left(1 - \frac{T}{455+273}\right)$$

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

KCl liquidus:

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

The two liquidus curves meet at $T_E = 579\text{K}$

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

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

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

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

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