Thermodynamics of Materials II Homework#6

$$1\ atm = 760\ mmHg = 1.01 \times 10^5\ N\ m^{-2}, R = 8.314\ J\ mol\ K^{-1}$$

1 The A-B solution is mixed at 600 K, which the activity coefficient of A is followed by:

$$ln\,\gamma_A = 0.8x_B^2 - 0.5x_B^3$$

Answer the below questions.

1.1 Is the A-B solution a positive deviation solution or a negative deviation solution?

1.2 Calculate γ_A and a_A at $x_A = 0.5$.

1.3 Calculate $\Delta\bar{G}_A^M$ at $x_A = 0.5$.

1.4 Derive the expression of $\ln\gamma_B$ based on the composition by Gibbs-Duhem equation.

1.1 $\ln\gamma_A = x_B^2(0.8 - 0.5x_B)$, Since $0 \le x_B \le 1 \Rightarrow 0 \le x_B^2 \le 1$, $0 < 0.8 - 0.5x_B \le 1$

So $0 \le x_B^2(0.8 - 0.5x_B) \le 1$, $0 < \ln\gamma_A \le 1$, $1 < \gamma_A \le e \longrightarrow$ Positive deviation *

1.2 $\ln\gamma_A = 0.8 \cdot 0.5^2 - 0.5 \cdot 0.5^3 = 0.1375$, $\gamma_A = e^{0.1375} = \underline{1.147}$ *, $a_A = 1.147 \cdot 0.5 = \underline{0.5735}$ *

1.3 $\Delta\overline{G_A^M} = RT\ln a_A = 8.314 \cdot 600 \cdot \ln 0.5735 = \underline{-2773.5\ J/mol}$ *

1.4 $x_A\, d\ln\gamma_A + x_B\, d\ln\gamma_B = 0$, $d\ln\gamma_B = -\frac{x_A}{x_B} d\ln\gamma_A$, $\frac{d\ln\gamma_A}{dx_B} = 1.6x_B - 1.5x_B^2$

$\Rightarrow d\ln\gamma_B = -\frac{x_A}{x_B}(1.6x_B - 1.5x_B^2)\,dx_B = -1.6x_A + 1.5x_Ax_B\,dx_B = 1.6x_A - 1.5x_A(1-x_A)\,dx_A$

$d\ln\gamma_B = 0.1x_A + 1.5x_A^2\,dx_A$, $\int_0^{\ln\gamma_B} d\ln\gamma_B = \int_0^{x_A} 0.1x_A + 1.5x_A^2\,dx_A$, $\underline{\ln\gamma_B = 0.05x_A^2 + 0.5x_A^3}$ *

2 The A-B solution is mixed at 800 K, which obeys Henry's law at specific molar fractions. The Henry's constants (Henrian activity coefficients) of k_A and k_B are 1.5 and 1.8, respectively. Answer the below questions, assuming that they obey Henry's law.

2.1 At $x_A = 0.1$, calculate $\Delta\bar{G}_A^M, \Delta\bar{G}_B^M, \Delta G^M, \Delta\bar{H}_B^M$ and $\Delta\bar{S}_B^M$

2.2 At $x_A = 0.9$, calculate $\Delta\bar{G}_A^M, \Delta\bar{G}_B^M, \Delta G^M, \Delta\bar{H}_A^M$ and $\Delta\bar{S}_A^M$

2.1 At $X_A = 0.1$, $X_B = 0.9$ $\Rightarrow$ A obey's Henry's law, B obey's Raoult's law

$a_A = k_A X_A = 1.5 \cdot 0.1 = 0.15$, $\Delta\bar{G}_A^M = 8.314 \cdot 800 \cdot \ln 0.15 = \underline{-12618\ J/mol}$ *

$\Delta\bar{G}_B^M = 8.314 \cdot 800 \cdot \ln 0.9 = \underline{-701\ J/mol}$ *, $\Delta G^M = X_A \Delta\bar{G}_A^M + X_B \Delta\bar{G}_B^M = 0.1 \cdot (-12618) + 0.9 \cdot (-701)$

$= \underline{-1892.7\ J/mol}$ *

$\Delta\bar{S}_B^M = -8.314 \cdot \ln 0.9 = \underline{0.876\ J/mol \cdot K}$ *, $\underline{\Delta\bar{H}_B^M = 0\ J/mol}$ * (Raoult solution)

2.2 At $X_A = 0.9$, $X_B = 0.1$ $\Rightarrow$ B obey's Henry's law, A obey's Raoult's law

$a_B = k_B X_B = 1.8 \cdot 0.1 = 0.18$, $\Delta\bar{G}_B^M = 8.314 \cdot 800 \cdot \ln 0.18 = \underline{-11405\ J/mol}$ *

$\Delta\bar{G}_A^M = 8.314 \cdot 800 \cdot \ln 0.9 = \underline{-701\ J/mol}$ *, $\Delta G^M = X_A \Delta\bar{G}_A^M + X_B \Delta\bar{G}_B^M = 0.9(-701) + 0.1 \cdot (-11405)$

$= \underline{-1771.4\ J/mol}$ *

$\Delta\bar{S}_A^M = -8.314 \cdot \ln 0.9 = \underline{0.876\ J/mol \cdot K}$ *, $\Delta\bar{H}_A^M = \underline{0\ J/mol}$ * (Raoult solution)