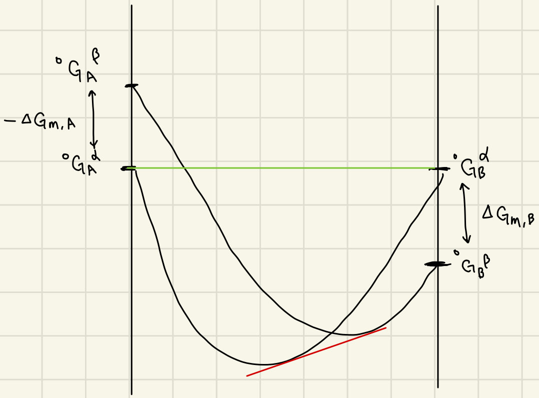
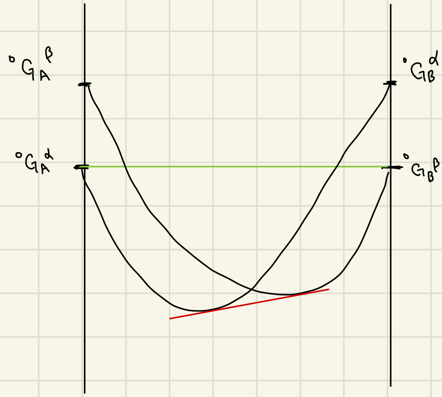
HW 1

20202942 김윤아





$-\Delta G_{m,A} = {}^\circ G_A^\beta - {}^\circ G_A^\alpha$ .. eq. 1

$\Delta G_{m,B} = {}^\circ G_B^\alpha - {}^\circ G_B^\beta$ .. eq. 2

In the regular solution model, Gibbs free energy of a binary A-B solution with two different solution phase α, β is given as,

$$G_m^\alpha = X_A^\alpha\,{}^\circ G_A^\alpha + X_B^\alpha\,{}^\circ G_B^\alpha + RT\left(X_A^\alpha \ln X_A^\alpha + X_B^\alpha \ln X_B^\alpha\right) + X_A^\alpha X_B^\alpha L_{A,B}^\alpha \quad \cdots \text{eq. 3}$$

$$G_m^\beta = X_B^\beta\,{}^\circ G_A^\beta + X_B^\beta\,{}^\circ G_B^\beta + RT\left(X_A^\beta \ln X_A^\beta + X_B^\beta \ln X_B^\beta\right) + X_A^\beta X_B^\beta L_{A,B}^\beta \quad \cdots \text{eq. 4}$$

The phase equilibrium between the two phases satisfies the condition in which both curves share a common tangent line.

$$\left.\frac{dG_m^\alpha}{dX_B}\right|_{X_B=X_B^\alpha} = \left.\frac{dG_m^\beta}{dx_B}\right|_{X_B=X_B^\beta} \quad \cdots \text{eq. 5}$$

$$X_A^\alpha + X_B^\alpha = 1 \quad \text{and} \quad X_A^\beta + X_B^\beta = 1 \quad \cdots \text{eq. 6}$$

Substitution of eq. 6 into eq. 3 & 4 gives,

$$G_m^\alpha = (1-X_B^\alpha)\,{}^\circ G_A^\alpha + X_B^\alpha\,{}^\circ G_B^\alpha + RT\left((1-X_B^\alpha)\ln(1-X_B^\alpha) + X_B^\alpha \ln X_B^\alpha\right) + (1-X_B^\alpha)X_B^\alpha L_{A,B}^\alpha$$

$$G_m^\beta = (1-X_B^\beta)\,{}^\circ G_A^\beta + X_B^\beta\,{}^\circ G_B^\beta + RT\left((1-X_B^\beta)\ln(1-X_B^\beta) + X_B^\beta \ln X_B^\beta\right) + (1-X_B^\beta)X_B^\beta L_{A,B}^\beta$$

$$\left.\frac{dG_m^\alpha}{dX_B}\right|_{X_B=X_B^\alpha} = -{}^\circ G_A^\alpha + {}^\circ G_B^\alpha + RT\left(-\ln(1-X_B^\alpha) - \cancel{1} + \ln X_B^\alpha + \cancel{1}\right) + \overbrace{\left(-X_B^\alpha + (1-X_B^\alpha)\right)}^{-2X_B^\alpha+1} L_{A,B}^\alpha$$

$$= -{}^\circ G_A^\alpha + {}^\circ G_B^\alpha + RT\left(-\ln(1-X_B^\alpha) + \ln X_B^\alpha\right) + (1-2X_B^\alpha)L_{A,B}^\alpha \quad \cdots \text{eq. 7}$$

$$\left.\frac{dG_m^\beta}{dX_B}\right|_{X_B=X_B^\beta} = -{}^\circ G_A^\beta + {}^\circ G_\beta^\beta + RT\left(-\ln(1-X_B^\beta) + \ln x_B^\beta\right) + (1-2X_B^\beta)L_{A,B}^\beta \quad \cdots \text{eq. 8}$$

Substitution of eq. 7 & 8 into eq. 5 gives

$$-{}^{\circ}G_A^{\alpha} + {}^{\circ}G_B^{\alpha} + RT\left(-\ln(1-x_B^{\alpha}) + \ln x_B^{\alpha}\right) + (1-2x_B^{\alpha})L_{A,B}^{\alpha}$$

$$= -{}^{\circ}G_A^{\beta} + {}^{\circ}G_B^{\beta} + RT\left(-\ln(1-x_B^{\beta}) + \ln x_B^{\beta}\right) + (1-2x_B^{\beta})L_{A,B}^{\beta} \quad \cdots \text{eq. 9}$$

$${}^{\circ}G_A^{\beta} - {}^{\circ}G_A^{\alpha} + {}^{\circ}G_B^{\alpha} - {}^{\circ}G_B^{\beta} + RT\ln\left(\frac{x_B^{\alpha}}{x_B^{\beta}} \cdot \frac{1-x_B^{\beta}}{1-x_B^{\alpha}}\right) + (1-2x_B^{\alpha})L_{A,B}^{\alpha} - (1-2x_B^{\beta})L_{A,B}^{\beta} = 0$$

Applying equation 1 & 2 in gibbs free E of mixing curves,

$$-\Delta G_{m,A} + \Delta G_{m,B} + RT\ln\left(\frac{x_B^{\alpha}}{x_B^{\beta}} \cdot \frac{1-x_B^{\beta}}{1-x_B^{\alpha}}\right) + (1-2x_B^{\alpha})L_{A,B}^{\alpha} - (1-2x_B^{\beta})L_{A,B}^{\beta} = 0$$

Thus, the equilibrium composition is not influenced by the reference state. It depends on the temperature and the difference between ${}^{\circ}G$ for each phase.