HW1.

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∘ 정규 용액 모델에서 두 용액의 mixing에 해당하는 Gibbs energy.

$$G_m = x_A {}^\circ G_A + x_B {}^\circ G_B + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L_{A,B}$$

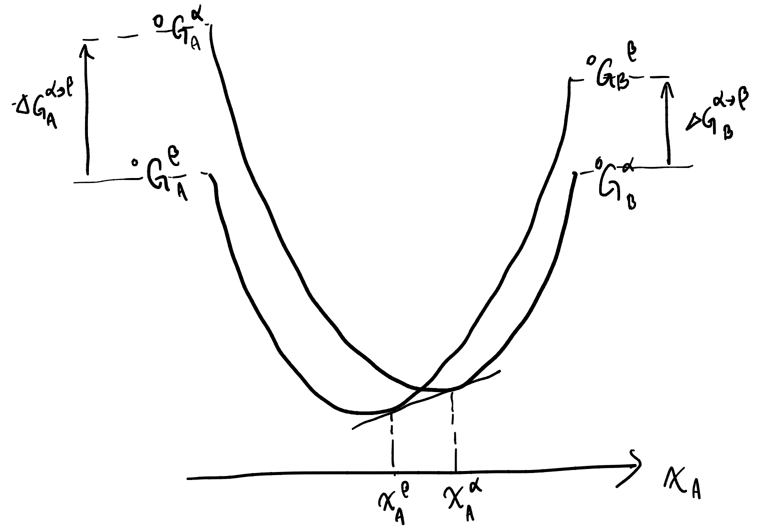
α phase에서 mixing에 대한 Gibbs energy.

$$G_m^\alpha = x_A({}^\circ G_A^{ref} + \Delta^\circ G_A^{ref\to\alpha}) + x_B({}^\circ G_B^{ref} + \Delta^\circ G_B^{ref\to\alpha}) + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L_{A.B}^\alpha$$

β phase에서 mixing에 대한 Gibbs energy.

$$G_m^\beta = x_A({}^\circ G_A^{ref} + \Delta^\circ G_A^{ref\to\beta}) + x_B({}^\circ G_B^{ref} + \Delta^\circ G_B^{ref\to\beta}) + RT(x_A \ln x_A + x_B \ln x_B) + x_A x_B L_{A.B}^\beta$$

상평형은 두 상 간의 gibbs energy curve의 공통 접선에서 이루어진다.



$$\left.\frac{\partial G_m^\alpha}{\partial x_A}\right|_{x_A = x_A^\alpha} = \left.\frac{\partial G_m^\beta}{\partial x_A}\right|_{x_A = x_A^\beta}$$

이때 $x_A + x_B = 1$을 이용하면 아래처럼 계산할 수 있다.

$$\frac{\partial G_m^\alpha}{\partial x_A} = {}^\circ G_A^{ref} + \Delta^\circ G_A^{ref\to\alpha} - {}^\circ G_B^{ref} - \Delta^\circ G_B^{ref\to\alpha} + RT\left[\ln x_A + 1 - \ln(1-x_A) - 1\right] + (1-2x_A) L_{A.B}^\alpha$$

$$= {}^\circ G_A^{ref} + \Delta^\circ G_A^{ref\to\alpha} - {}^\circ G_B^{ref} - \Delta^\circ G_B^{ref\to\alpha} + RT \ln\frac{x_A}{1-x_A} + (1-2x_A) L_{A.B}^\alpha$$

$$\frac{\partial G_m^\beta}{\partial x_A} = {}^\circ G_A^{ref} + \Delta^\circ G_A^{ref\to\beta} - {}^\circ G_B^{ref} - \Delta^\circ G_B^{ref\to\beta} + RT \ln\frac{x_A}{1-x_A} + (1-2x_A) L_{A.B}^\beta$$

$$\left.\frac{\partial G_m^{\alpha}}{\partial x_A}\right|_{x_A=x_A^{\alpha}} - \left.\frac{\partial G_m^{\beta}}{\partial x_A}\right|_{x_A=x_A^{\beta}}$$

$$= \left[{}^{\circ}G_A^{ref} + \Delta^{\circ}G_A^{ref\to\alpha} - {}^{\circ}G_B^{ref} - \Delta^{\circ}G_B^{ref\to\alpha} + RT\ln\frac{x_A^{\alpha}}{1-x_A^{\alpha}} + (1-2x_A^{\alpha})L_{A.B}^{\alpha} \right]$$

$$- \left[{}^{\circ}G_A^{ref} + \Delta^{\circ}G_A^{ref\to\beta} - {}^{\circ}G_B^{ref} - \Delta^{\circ}G_B^{ref\to\beta} + RT\ln\frac{x_A^{\beta}}{1-x_A^{\beta}} + (1-2x_A^{\beta})L_{A.B}^{\beta} \right]$$

$$= \Delta^{\circ}G_A^{ref\to\alpha} - \Delta^{\circ}G_A^{ref\to\beta} - \Delta^{\circ}G_B^{ref\to\alpha} + \Delta^{\circ}G_B^{ref\to\beta} + RT\ln\frac{x_A^{\alpha}(1-x_A^{\beta})}{x_A^{\beta}(1-x_A^{\alpha})} + (1-2x_A^{\alpha})L_{A.B}^{\alpha} - (1-2x_A^{\beta})L_{A.B}^{\beta}$$

$$= -\Delta^{\circ}G_A^{\alpha\to\beta} + \Delta^{\circ}G_B^{\alpha\to\beta} + RT\ln\frac{x_A^{\alpha}(1-x_A^{\beta})}{x_A^{\beta}(1-x_A^{\alpha})} + (1-2x_A^{\alpha})L_{A.B}^{\alpha} - (1-2x_A^{\beta})L_{A.B}^{\beta}$$

$$= 0$$

$$(\because \Delta^{\circ}G_A^{ref\to\alpha} - \Delta^{\circ}G_A^{ref\to\beta} = \Delta^{\circ}G_A^{ref\to\alpha} + \Delta^{\circ}G_A^{\beta\to ref} = \Delta^{\circ}G_A^{\beta\to\alpha})$$

위 식에서 x_A^{α}, x_A^{β}는 reference state에 의존하지 않는다.

따라서 각 원소에 대해 일관된 reference state를 사용할 때,

상평형 조성은 reference state에 관계 없이 unique하게 결정된다.