2005(II)
Question 3

$$g^E = \omega X_A X_B X_C \qquad \omega < 0$$

$$g_A^E = \frac{\partial G}{\partial n_A} = \omega \frac{\partial}{\partial n_A}\left[\left(\frac{n_A n_B n_C}{(n_A+n_B+n_C)^3}\cdot(n_A+n_B+n_C)\right)\right]$$

$$g_A^E = \omega n_B n_C \frac{\partial}{\partial n_A}\left(\frac{n_A}{(n_A+n_B+n_C)^2}\right)$$

$$= \omega n_B n_C \left(\frac{1}{(n_A+n_B+n_C)^2} - \frac{2n_A}{(n_A+n_B+n_C)^3}\right)$$

$$= \frac{\omega n_B n_C (n_B+n_C+n_A - 2n_A)}{(n_A+n_B+n_C)^3}$$

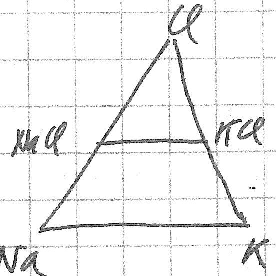
$$= \omega X_B X_C (1-2X_A)$$

$\underline{\omega < 0}$ $\quad g_A^E > 0$ when $2X_A > 1$

2005 (II) - Question 4

(i) $G = (n_{NaCl}\, g^{o}_{NaCl} + n_{KCl}\, g^{o}_{KCl}) + RT(n_{NaCl} \ln X_{NaCl} + n_{KCl} \ln X_{KCl})$

(ii) $G = (n_{Na}\, g^{o}_{Na} + n_{K}\, g^{o}_{K} + n_{Cl}\, g^{o}_{Cl})$



$$+ \left(\frac{\Delta g_{NaCl}}{2}\right) n_{Na-Cl} + \left(\frac{\Delta g_{KCl}}{2}\right)(n_{K-Cl}) + \left(\frac{\Delta g_{Na-K}}{2}\right)(n_{Na-K})$$

(number of pairs)

$$+ RT\,(n_{Na} \ln X_{Na} + n_{K} \ln X_{K} + n_{Cl} \ln X_{Cl})$$

$$+ \frac{RT}{2}\left(n_{Na-Na} \ln \frac{X_{Na-Na}}{X^2_{Na}} + n_{K-K} \ln \frac{X_{K-K}}{X_K^{2}} + n_{Cl-Cl} \ln \frac{X_{Cl-Cl}}{X_{Cl}^2}\right.$$

$$\left. + n_{Na-Cl} \ln \frac{X_{Na-Cl}}{2X_{Na}X_{Cl}} + n_{K-Cl} \ln \frac{X_{K-Cl}}{2X_K X_{Cl}} + n_{Na-K} \ln \frac{X_{Na-K}}{2X_{Na}X_K}\right)$$

(iii) Along NaCl-KCl join

$X_{Na-K} = X_{Na-Na} = X_{K-K} = X_{Cl-Cl} = 0$ $\quad n_{Na-Na} = n_{K-K} = n_{Na-K} = n_{Cl-Cl} = 0$

Note: n_{Na-Cl} = # of ~~bonds~~ moles of bonds
n_{NaCl} = # of moles of component
X_{Na-Cl} = bond fraction
X_{NaCl} = component mole fraction

$X_{NaCl} = X_{Na-Cl}$ $\quad \Delta g_{NaCl} = (g^{o}_{NaCl} - g^{o}_{Na} - g^{o}_{Cl})/Z$

$X_{KCl} = X_{K-Cl}$ $\quad \Delta g_{KCl} = (g^{o}_{KCl} - g^{o}_{K} - g^{o}_{Cl})/Z$

$n_{Na} = n_{NaCl}$

$n_K = n_{KCl}$

$(n_{Na} + n_K) = n_{Cl}$ $\quad n_{Na-Cl} = Z n_{Na} = Z n_{NaCl}$

$n_{K-Cl} = Z n_K = Z n_{KCl}$

$X_{Cl} = \frac{1}{2}$ $\quad X_{Na} = \frac{n_{Na}}{n_{Na} + n_K + n_{Cl}} = (X_{NaCl}/2)$

$X_K = (X_{KCl}/2)$

Substitute into equation (ii):

$$G = (n_{NaCl}\, g^{o}_{NaCl} + n_{KCl}\, g^{o}_{KCl})$$

$$+ RT\,(n_{NaCl} \ln X_{NaCl} + n_{KCl} \ln X_{KCl})$$

$$+ RT\,(n_{NaCl} + n_{KCl})(-2 \ln 2 + Z \ln 2)$$

This is the same as equation (i) only if $Z = 2$!!

2006(II)

Question 5 Along the diagonal: $\begin{cases} y_{Rb} = y_{Cl} = X_{RbCl} \\ y_{Li} = y_F = (1 - X_{RbCl}) \end{cases}$

$$g = \left((1-X)^2 g^o_{LiF} + X(1-X) g^o_{LiCl} + x(1-x)(g^o_{RbF}) + x^2 g^o_{RbCl}\right)$$
$$+ \underline{\underline{2}} RT\left(X \ln X + (1-X)\ln(1-X)\right) - X^2(1-X)^2\left(\frac{\Delta G^{EX^2}}{2RT}\right)$$

where $X = X_{RbCl}$

$$\frac{dg}{dX} = -2(1-X)g^o_{LiF} + 2x g^o_{RbCl} + (1-2x)(g^o_{LiCl} + g^o_{RbF})$$
$$+ 2RT\left(\ln X - \ln(1-X)\right) - \left[2X(1-X)^2 - 2X^2(1-X)\right]\left(\frac{\Delta G^2}{2RT}\right)$$

$$\frac{d^2g}{dX^2} = \overbrace{2\left(g^o_{LiF} + g^o_{RbCl} - g^o_{LiCl} - g^o_{RbF}\right)}^{\Delta G^{EXCHANGE}} + RT\left(\frac{1}{X} + \frac{1}{1-X}\right)$$
$$-\left(-2X(2)(1-X) + 2(1-X)^2 + 2X^2 - 4X(1-X)\right)\frac{\Delta G}{2RT}$$

$$= 2\Delta G^{EXCH.} + 2RT\left(\frac{1}{X} + \frac{1}{1-X}\right) - \left(12X^2 - 12X + 2\right)\frac{(\Delta G^{EXCH})^2}{2RT}$$

By symmetry T_c is at $X = 0.5$

$$2\Delta G^{EX} + 2RT_c + (\Delta G^{EX})^2/2RT_c = 0$$

(i) Ignoring final term

$$2\Delta G^{EX} + 2RT_c = 0 \qquad \underline{T_c = \frac{-\Delta G^{EX}}{2R} > 0}$$

(ii) With Final term:

$$2RT_c = -2\Delta G^{EX} - (\Delta G^{EX})^2/2RT_c$$

Hence, T_c is lowered by including the final term