2011 - Contrôle II - Solutionnaire

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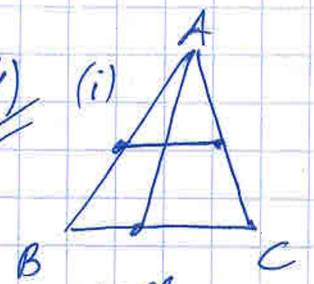
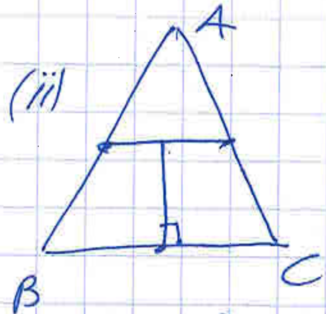
(1) (i)



Kohler-Toop

or (ii)



Muggianu-Toop

(i) $g^E = X_A X_B \left(a + b(1-X_A)\right) + X_C X_A \left(e + f X_A\right) + X_B X_C \left(c + d\left(\frac{X_C - X_B}{X_B + X_C}\right)^2\right)$

or (ii) $g^E = X_A X_B \left(a + b(1-X_A)\right) + X_C X_A \left(e + f X_A\right) + X_B X_C \left(c + d\left(X_C - X_B\right)^2\right)$

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(2) $n_{Na^+} = 6$ $\quad n_{AlCl_4^-} = 5$

$n_{Ca^+} = 90$ $\quad n_{Cl^-} = 2(90) + (6) - 5 = 181$

$\Sigma n_+ = 96$ $\quad \Sigma n_- = 186$

$$a_{CaCl_2} = y_{Ca^+} \cdot y_{Cl^-}^2 = \left(\frac{90}{96}\right)\left(\frac{181}{186}\right)^2 = 0.8878$$

Assume: (Ideal Raoultian solution
Temkin model

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(3) $RT \ln a_{LiCl} = RT \ln(y_{Li} \cdot y_{Cl}) + y_{Na} \cdot y_{Br} \Delta g^{EXCH}$

$n_{Li} = 3$ $\quad n_{Cl} = 1$ $\quad y_{Li} = 3/6 \quad y_{Cl} = 1/6$

$n_{Na} = 2+1 = 3$ $\quad n_{Br} = 2+3 = 5$ $\quad y_{Na} = 3/6 \quad y_{Br} = \frac{5}{6}$

$\Sigma n_+ = 6$ $\quad \Sigma n_- = 6$

$\Delta G^{EXCH} = \pm 8086$ joules (LiCl is member of stable pair)

$$R(1273) \ln a_{LiCl} = R(1273) \ln \left(3/6\right)\left(\frac{1}{6}\right) - \left(3/6\right)\left(5/6\right)(-8086) \Rightarrow a_{LiCl} = 0.1146$$

- The correction for short-range ordering will decrease the positive deviations along the stable diagonal, ~~thereby~~ thereby decreasing the activity of LiCl.

3 (4) $2\,\underline{Al} + 3\,\underline{O} = Al_2O_3\,(sol)$

$$K = \frac{a_{Al_2O_3}}{X_{\underline{Al}}^{2} \cdot X_{\underline{O}}^{3}} = \frac{1}{X_{\underline{Al}}^{2} \cdot X_{\underline{O}}^{3}}$$

As $X_{\underline{Al}}$ increases, $X_{\underline{O}}$ decreases.

$\cancel{2\,\underline{AlO} + \underline{O} = Al_2O_3}$

$$\cancel{K = \frac{a_{Al_2O_3}}{X_{AlO}^{2} \cdot X_{O}}}$$

$\underline{Al} + Al_2O_3 = 3\,\underline{AlO}$

$$K = \frac{X_{\underline{AlO}}^{3}}{X_{\underline{Al}}}$$

As $X_{\underline{Al}}$ increases, $X_{\underline{AlO}}$ increases

(5) 3

$$2n_A = 2n_{AA} + n_{AB}$$
$$2n_B = 2n_{BB} + n_{AB}$$

$Z=2$

$$\left\{\begin{array}{l} X_A = X_{AA} + (X_{AB}/2) \\ X_B = X_{BB} + (X_{AB}/2) \end{array}\right.$$

$$\cancel{\Delta S^{config}} \quad (n_A + n_B) = (n_{AA} + n_{BB} + n_{AB}) \qquad (X_A + X_B) = (X_{AA} + X_{BB} + X_{AB})$$

$$\Delta G = -T\Delta S^{config} + (n_{AB}/2)\,\Delta g_{AB}$$

$$\Delta g = +RT(X_A \ln X_A + X_B \ln X_B) + RT\left(X_{AA} \ln \frac{X_{AA}}{X_A^2} + X_{BB} \ln \frac{X_{BB}}{X_B^2} + X_{AB} \ln \frac{X_{AB}}{2X_A X_B}\right) + (X_{AB}/2)\,\Delta g_{AB}$$

At internal equilibrium:

$$\frac{X_{AB}^2}{X_{AA} X_{BB}} = 4\exp(-\Delta g_{AB}/RT)$$

$X_A = X_B = 0.5$

Clearly, $X_{AA} = X_{BB}$

$$X_{AB} = 2X_A - 2X_{AA} = 1 - 2X_{AA}$$

$$\frac{(1-2X_{AA})^2}{X_{AA}^2} = 4\exp\left(\frac{10\,000}{8.315(1000)}\right) = 13.3157$$

$$1 - 4X_{AA} + 4X_{AA}^2 = 13.3157\,X_{AA}^2$$

$$9.3157\,X_{AA}^2 + 4X_{AA} - 1 = 0$$

$$X_{AA} = \frac{-4 \pm \sqrt{16 + 4(9.3157)}}{2(9.3157)} = 0.1770$$

$$X_{BB} = 0.1770$$
$$X_{AB} = 1 - 2(0.1770) = 0.6460$$

$$\Delta g = RT\left(\tfrac{1}{2}\ln\tfrac{1}{2} + \cdots\right) + RT\left(0.1770 \ln \frac{0.1770}{(\frac{1}{2})(\frac{1}{2})} + \cdots\right) + \frac{0.6460}{2}(-10{,}000)$$

$$= \underline{-8634 \text{ Joules}} \quad \text{at } T = 1000K$$

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5 $(Cu_{1-\alpha} Ag_{\alpha})(Ag_{1-\alpha} Cu_{\alpha})$

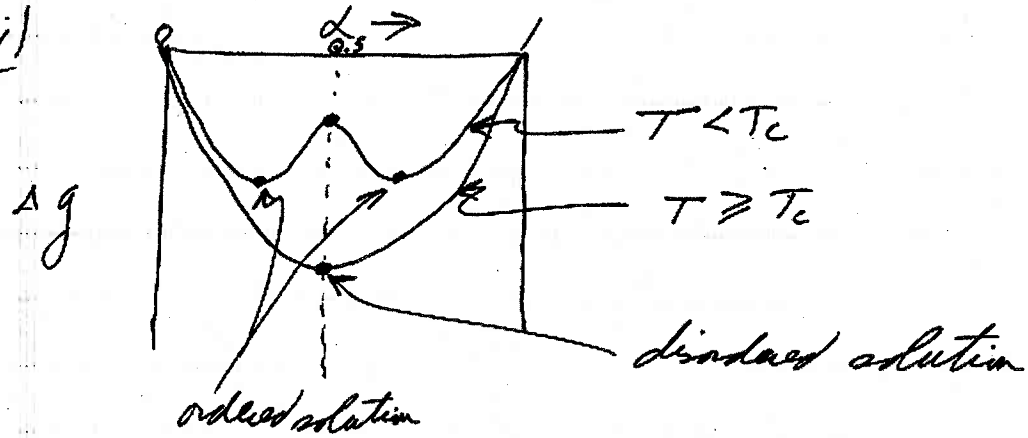
(i) $$g = \frac{N_{Av} Z}{2}\left[(1-\alpha)(1-\alpha)\epsilon_{AgCu} + \alpha^2 \epsilon_{AgCu} + (1-\alpha)\alpha\,\epsilon_{CuCu} + (1-\alpha)\alpha\,\epsilon_{AgAg}\right.$$
$$+ 2RT\left(\alpha \ln \alpha + (1-\alpha)\ln(1-\alpha)\right)$$

$$\frac{dG}{d\alpha} = \left[(2\alpha-2)\epsilon_{AgCu} + 2\alpha\,\epsilon_{AgCu} + (1-2\alpha)(\epsilon_{CuCu} + \epsilon_{AgAg})\right]\frac{ZN}{2}$$
$$+ 2RT\left(\ln\alpha - \ln(1-\alpha)\right)$$
$$= -\frac{N_{Av}Z}{2}(1-2\alpha)(2\epsilon_{AgCu} - \epsilon_{AgAg} - \epsilon_{CuCu}) + 2RT(\ln\alpha - \ln(1-\alpha))$$
$$= 0$$

$$\boxed{\ln\frac{\alpha}{1-\alpha} = \frac{w(1-2\alpha)}{2RT}}$$ where: $w = \frac{N_{Av}Z}{2}(2\epsilon_{AgCu} - \epsilon_{AgAg} - \epsilon_{CuCu})$

There is always a solution at $\alpha = \frac{1}{2}$ (disordered)
Below T_c there are two other solutions (ordered)

(ii)



$(d^2g/d\alpha^2) = 0$ at $T = T_c$ at $\alpha = 1/2$

$$(d^2g/d\alpha^2) = 2w + 2RT\left(\frac{1}{\alpha} + \frac{1}{\alpha}\right) = 2w + \frac{4RT}{\alpha}$$

At $\left.\begin{matrix} T = T_c \\ \alpha = \frac{1}{2} \end{matrix}\right)$ $2w + 8RT_c = 0$

$$\boxed{T_c = -w/4R}$$ $(w < 0)$