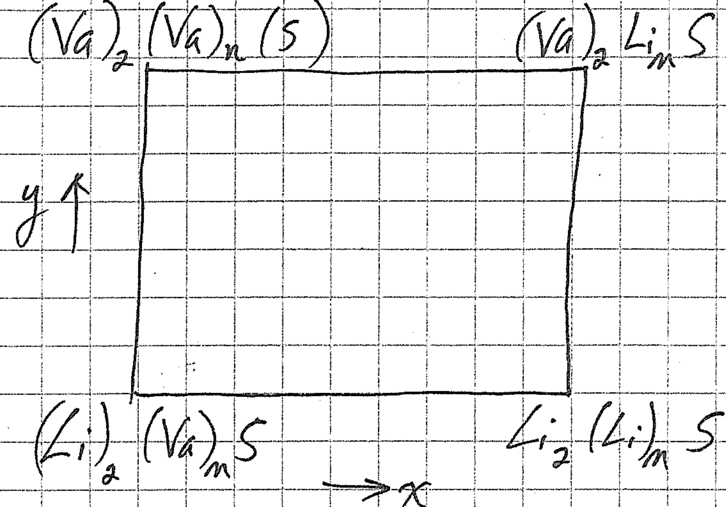
2008 Contrôle II

Question 5

(a)



$(Li, Va)_2 \, (Li, Va)_n \, (S)$ — interstitial lattice

x = site fraction of Li on interstitial lattice
y = site fraction of vacancies on Li lattice

n = mols of interstitial sites per mole Li_2S

(b)

$$g = (1-x)(1-y)\, g^o_{(Li)_2(Va)_n(S)} + x(1-y)\, g^o_{(Li)_2(Li)_n(S)} + (1-x)y\, g^o_{(Va)_2(Va)_n(S)} + xy\, g^o_{(Va)_2 Li_n S}$$
$$+ 2RT(y\ln y + (1-y)\ln(1-y)) + nRT(x\ln x + (1-x)\ln(1-x))$$

(c) $g^o_{(Li)_2(Va)_n(S)}$ = Gibbs energy of hypothetical defect-free Li_2S (close to g^o of real stoichiometric Li_2S

$$g^o_{Li_2(Li)_n(S)} = g^o_{(Li_2)(Va)_n(S)} + \Delta g^o_1$$
$$g^o_{(Va)_2(Va)_n(S)} = g^o_{(Li)_2(Va)_n(S)} + \Delta g^o_2$$
$$g^o_{(Va)_2(Li)_n S} = g^o_{(Li)_2(Va)_n(S)} + \Delta g^o_1 + \Delta g^o_2$$

where: $\Delta g^o_1 = a_1 + b_1 T > 0$ = energy to form n moles of interstitial defects

$\Delta g^o_2 = a_2 + b_2 T > 0$ = energy to form 2 moles of cation vacancies on the Li lattice.

MET 6208

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Contrôle II

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Solutionnaire

Question 2

(i)

$$\begin{cases} n_{S^{2-}} = n_{MnS} \\ n_{SiO_4^{4-}} = n_{SiO_2} \\ n_{O^{2-}} = n_{MnO} - 2n_{SiO_2} \end{cases}$$

$$a_{MO} = \frac{n_{O^{2-}}}{n_{O^{2-}} + n_{S^{2-}} + n_{SiO_4^{4-}}} = \frac{n_{MnO} - 2n_{SiO_2}}{n_{MnO} - n_{SiO_2} + n_{MS}} = \frac{X_{MO} - 2X_{SiO_2}}{X_{MO} + X_{MS} - X_{SiO_2}}$$

$$a_{MS} = \frac{n_{S^{2-}}}{n_{O^{2-}} + n_{S^{2-}} + n_{SiO_4^{4-}}} = \frac{X_{MS}}{X_{MO} + X_{MS} - X_{SiO_2}}$$

(ii) $\Delta G^{\circ} = -RT\ln K$

$$K = 5.914 \times 10^{-3} = a_{MS} \cdot P_{O_2}^{1/2} / a_{MO} P_{S_2}^{1/2}$$

$$5.914 \times 10^{-3} = \frac{X_{MnS} (10^{-4})^{1/2}}{(5 \times 10^{-4})^{1/2} (X_{MnO} - 2X_{SiO_2})}$$

$X_{MnO} \simeq 0.75$

$X_{SiO_2} \simeq 0.25$

Solve to get X_{MnS} = **0.0033**

(4) $(A_x B_{1-x})_2 (B_y V_{1-y})$

T996 Exam

$$\frac{1+\delta}{3} = \frac{n_B}{n_A+n_B} = \frac{2-2x+y}{2+y} \qquad \delta = \frac{6-6x+3y}{2+y} - 1 = \frac{4-6x+2y}{2+y}$$

$$g = \left(xy\, g^o_{A_2B} + (1-x)y\, g^o_{B_2B} + x(1-y) g^o_{A_2V} + (1-x)(1-y)\, g^o_{B_2V}\right)$$
$$+ RT\left(2x\ln x + 2(1-x)\ln(1-x) + y\ln y + (1-y)\ln(1-y)\right)$$

$$\partial g/\partial x = \partial g/\partial y = 0$$

$$(x+y) g^o_{A_2B} + (1-x)\, g^o_{B_2B} - y\, g^o_{B_2B} + (1-y)\, g^o_{A_2V} - x\, g^o_{A_2V}$$
$$-(1-x)\, g^o_{B_2V} - (1-y)\, g^o_{B_2V}$$
$$+RT\left(\ln x^2 - \ln(1-x)^2 + \ln y - \ln(1-y)\right) = 0$$

Let: $g^o_{B_2V} = g^o_{(A_2)V} + g^o_{(B_2)B} - g^o_{A_2B}$ (Energy to form both defects is sum of energies to form each individual defect)

Substitute: $\left[2g^o_{A_2B} - g^o_{B_2B} - g^o_{A_2V}\right] + RT(\ln x^2 - \dots) = 0$

Let: $\begin{cases} \Delta g^o_1 \equiv g^o_{B_2B} - g^o_{A_2B} \\ \Delta g^o_2 \equiv g^o_{A_2V} - g^o_{A_2B} \end{cases}$

$$-(\Delta g^o_1 + \Delta g^o_2) = RT(\ln x^2 - \dots) = 0$$

$$\left(\frac{x^2 y}{(1-x)^2(1-y)}\right)^{-1} = \exp\left(\frac{-(x+y)}{2RT}\left(\Delta g^o_1 + \Delta g^o_2\right)\right)$$

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Question 2

(i)
$$\begin{cases} n_{SiO_4^{4-}} = n_{SiO_2} & n_{S^=} = n_{Na_2S} \\ n_{O^{2-}} = n_{Na_2O} - 2n_{SiO_2} \end{cases}$$

$$a_{Na_2O} = \frac{n_{O^{2-}}}{n_{O^{2-}} + n_{S^{2-}} + n_{SiO_4^{4-}}} = \frac{X_{Na_2O} - 2X_{SiO_2}}{X_{Na_2O} - X_{SiO_2} + X_{Na_2S}} = \frac{0.88 - 0.20}{0.88 - 0.10 + 0.02} = \underline{\underline{0.85}}$$

$$a_{Na_2S} = \frac{n_{S^{2-}}}{n_{O^{2-}} + n_{S^{2-}} + n_{SiO_4^{4-}}} = \frac{X_{Na_2S}}{X_{Na_2O} - X_{SiO_2} + X_{Na_2S}} = \frac{0.02}{0.80} = \underline{\underline{0.025}}$$

(ii) Assume ~~that the~~ S^{2-} content is very low so that

$$a_{Na_2O} \approx \frac{X_{Na_2O} - 2X_{SiO_2}}{X_{Na_2O} - X_{SiO_2}} = \frac{0.9 - 0.20}{0.9 - 0.10} = 0.875$$

$$a_{Na_2S} \approx \frac{X_{Na_2S}}{X_{Na_2O} - X_{SiO_2}} = \frac{X_{Na_2S}}{0.8}$$

$$Na_2O + \tfrac{1}{2}S_2 = Na_2S + \tfrac{1}{2}O_2$$

$$\Delta G^\circ = -43016 = -R(1923)\ln K$$

$$K = 14.7416 = \frac{\left(\frac{X_{Na_2S}}{0.8}\right) p_{O_2}^{1/2}}{(0.875)\, p_{S_2}^{1/2}} = \frac{(X_{Na_2S}/0.8)\,(10^{-2})}{0.875\,(10^{-3})}$$

$$X_{Na_2S} = 1.032$$

Now do an iteration: $a_{Na_2O} = \frac{0.9 - 0.2}{0.9 - 0.1 + 0.01} = 0.86$

$$a_{Na_2S} = X_{Na_2S}/(0.9 - 0.1 + 0.01) = \frac{X_{Na_2S}}{0.81}$$

$$K = 14.7416 = \frac{(X_{Na_2S}/0.81)\, p_{O_2}^{1/2}}{(0.86)\, p_{S_2}^{1/2}} \qquad X_{Na_2S} = \underline{\underline{1.027}}$$