Examen final - 2003 - 4

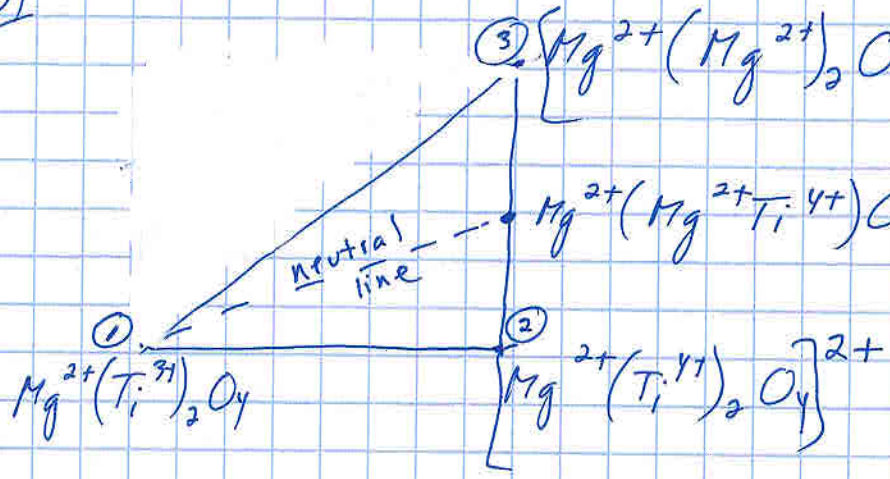
(a) $(Mg^{2+})(Mg^{2+}_{1-x}\ Ti^{4+}_{1-x}\ Ti^{3+}_{2x})O_y$

$$a_{MgTi_2O_y} = (1)\left(\frac{2x}{2}\right)^2 = x^2 = \left(x^2_{Ti^{3+}_{B}}\right)$$

$$a_{Mg_2TiO_y} = \frac{(1)\left(\frac{1-x}{2}\right)\left(\frac{1-x}{2}\right)}{\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)} = (1-x)^2 = \left(x_{Mg^{2+}_{B}}\ x_{Ti^{4+}_{B}}\right)$$

→ Value for pure Mg_2TiO_y

(b)



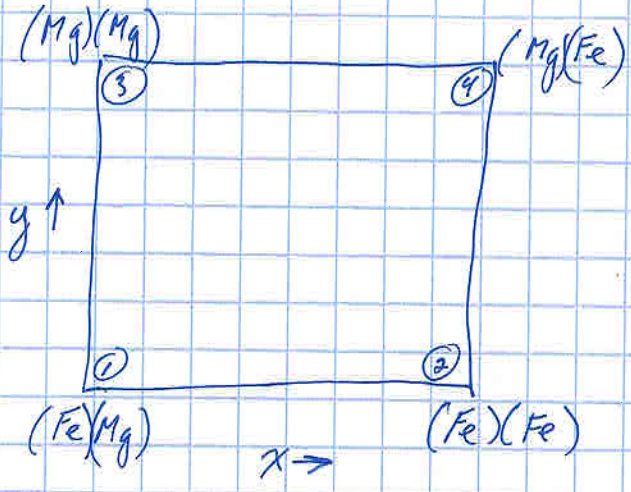
$$G = (n_1 g_1^\circ + n_2 g_2^\circ + n_3 g_3^\circ) + RT(n_1+n_2+n_3)\left(\frac{2x}{2}\ln\frac{2x}{2} + \frac{(1-x)}{2}\ln\left(\frac{1-x}{2}\right)\right)$$

where: $\frac{n_2+n_3}{2} = n_{Mg_2TiO_y}$

$$g^\circ_{Mg_2TiO_y} = \frac{1}{2}(g_2^\circ + g_1^\circ) + RT\left(\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\right)$$

2005 - Contribute II - 5

$(Fe, Mg)_{M1}(Fe, Mg)_{M2}(Si)(O_4)$



$$g = \left((1-x)(1-y)g_1^\circ + x(1-y)g_2^\circ + y(1-x)g_3^\circ + xy\,g_4^\circ\right) + RT\left(x\ln x + (1-x)\ln(1-x) + y\ln y + (1-y)\ln(1-y)\right)$$

$$\begin{cases} g_3^\circ = g^\circ_{Mg_2SiO_4} \\ g_2^\circ = g^\circ_{Fe_2SiO_4} \end{cases}$$

$$(g_4^\circ + g_1^\circ) - (g_2^\circ + g_3^\circ) = \Delta G^{Exchange} = \text{model parameter}$$

The model parameter is related to the relative preference of Fe^{2+} and Mg^{2+} for the M1 and M2 sites.

If no data on site distribution, set $\Delta G^{Exch} = 0$.

(Examen Final - 1999)

(4)(a) $(Fe^{3+})(Fe^{3+}\ Fe^{2+}_{1-3x}\ Ni^{2+}_{3x})O_4$

where: $x = X_{NiFe_2O_4}$ in the Fe_3O_4-Ni_3[illegible]O_4 system

$$a_{Fe_3O_4} = \frac{X_{Fe^{2+}(B)}\, X_{Fe^{3+}(B)}}{(X_{Fe^{2+}(B)})(X_{Fe^{3+}(B)})_{\text{when } x=0}} = \frac{\left(\frac{1-3x}{2}\right)\left(\frac{1}{2}\right)}{\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)} = (1-3x)$$

$$a_{NiFe_2O_4} = \frac{X_{Fe^{3+}(B)}\, X_{Ni^{2+}(B)}}{\left(X_{Fe^{3+}(B)}\, X_{Ni^{2+}(B)}\right)_{x=\frac{1}{3}}} = \frac{\left(\frac{3x}{2}\right)\left(\frac{1}{2}\right)}{\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)} = 3x$$

(b) $Ni + \frac{1}{2}O_2 = NiO \qquad K_1 = 9.239 \times 10^{5} = \dfrac{X_{NiO}}{X_{Ni} \cdot P_{O_2}^{1/2}}$

$Fe + \frac{1}{2}O_2 = FeO \qquad K_2 = 2.365 \times 10^{8} = \dfrac{(1-X_{NiO})\,\gamma^{\circ}_{FeO}}{(1-X_{Ni})\,P_{O_2}^{1/2}}$

$3Fe + 2O_2 = Fe_3O_4 \qquad K_3 = 3.769 \times 10^{32} = \dfrac{(1-3x)}{(1-X_{Ni})^3\, P_{O_2}^{2}}$

$Ni + 2Fe + 2O_2 = NiFe_2O_4 \qquad K_4 = 9.328 \times 10^{29} = \dfrac{3x}{X_{Ni}(1-X_{Ni})^2\, P_{O_2}^{2}}$

4 equations. 4 unknowns

$X_{NiO} = 0.815$

$P_{O_2} = 7.78 \times 10^{-13}$

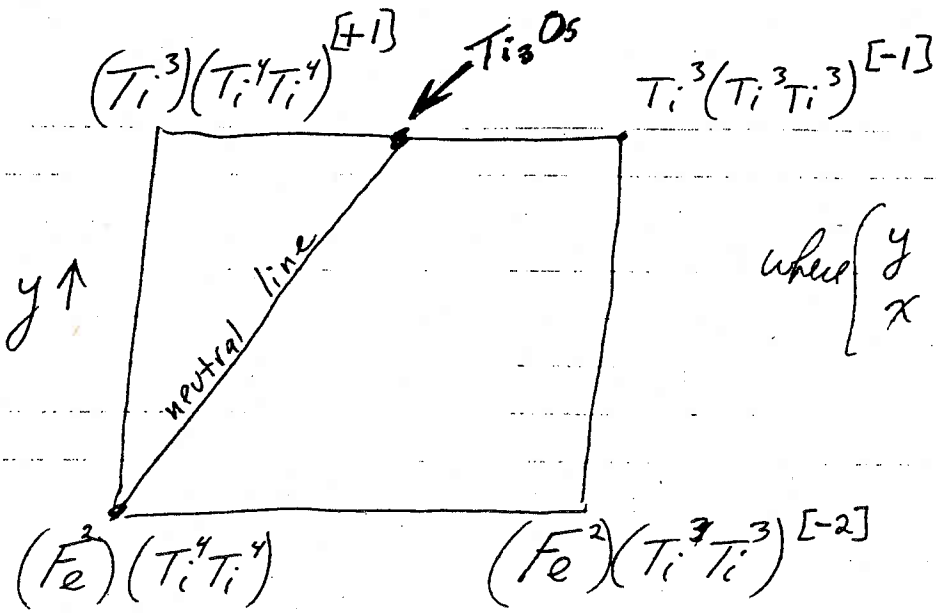
$x = 0.21$

X_{Ni} = 1.00

Example Final

1999

(5)



where $\begin{cases} y = "x" \\ x = \dfrac{"x"}{2} \end{cases}$

$m(Fe^{2+}_{1-"x"}\ Ti^{3+}_{"x"})(Ti^{3+}_{2-x}\ Ti^{3+}_{"x"})$

$$x = \frac{n_{Ti_B^{3+}}}{n_{Ti_B^{3+}} + n_{Ti_B^{4+}}} \qquad y = \frac{n_{Ti_A^{3+}}}{n_{Fe_A^{2+}} + n_{Ti_A^{3+}}}$$

$$g = \Big\{(1-x)(1-y)\,g^{\circ}_{(Fe^{2}Ti^{4})_2} + x(1-y)\,g^{\circ}_{(Fe^{2}Ti^{3})_2^{(2-)}} + y(1-x)\,g^{\circ}_{Ti^{3}(Ti^{4})_2^{(+1)}} + xy\,g^{\circ}_{Ti^{3}(Ti^{3})_2^{[-1]}}\Big\}$$

$$+2RT(x\ln x + (1-x)\ln(1-x)) + RT(y\ln y + (1-y)\ln y)$$

$$\begin{cases} g^{\circ}_{Fe^{2+}(Ti^{4})_2} = g^{\circ}_{FeTi_2O_5(real)} \\ -g^{\circ}_{Ti_3O_5(real)} = \left(\frac{1}{2}g^{\circ}_{Ti^{3}(Ti^{4})_2^{(+1)}} + \frac{1}{2}g^{\circ}_{Ti^{3}(Ti^{3})_2^{(-1)}}\right) + 2RT\left(\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\right) \\ \qquad\qquad = (\text{- - - - -}) \quad -2RT\ln 2 \end{cases}$$

This leaves 2 g°'s to fix. Can choose one arbitrarily.

Then: Model parameter $= \Delta G'^{\,EXCHANGE}$