2005 (contrôle I)

Question 6

(a) $$g^E = aX_AX_B + cX_CX_A + \left(b_0 + b_1\frac{X_C}{X_B+X_C}\right)X_BX_C$$

(b) $$n_{TOT} = (n_A + n_B + n_C)$$

$$G^E = n_{TOT}\cdot g^E = a\frac{n_An_B}{n_{TOT}} + c\frac{n_Cn_A}{n_{TOT}} + \left(b_0 + b_1\frac{n_C}{(n_B+n_C)}\right)\frac{n_Bn_C}{n_{TOT}}$$

$$g_A^E = \left(\frac{\partial G^E}{\partial n_A}\right)_{n_B,n_C}$$

$$= a\cdot n_B\left(\frac{1}{n_{TOT}} - \frac{n_A}{n_{TOT}^2}\right) + c\cdot n_C\left(\frac{1}{n_{TOT}} - \frac{n_A}{n_{TOT}^2}\right) + \left(b_0 + b_1\frac{n_C}{(n_B+n_C)}\right)\frac{n_Bn_C}{-(n_{TOT})^2}$$

$$= a\cdot n_B\left(\frac{n_B+n_C}{n_{TOT}^2}\right) + c\cdot n_C\left(\frac{n_B+n_C}{n_{TOT}^2}\right) - (b_0 + b_1X_C)X_BX_C$$

$$= a(1-X_A)X_B + c(1-X_A)X_C - X_BX_C(b_0 + b_1X_C)$$

$$= a(1-X_A)^2\frac{X_B}{X_B+X_C} + c(1-X_A)^2\frac{X_C}{X_B+X_C} - X_BX_C(b_0+b_1X_C)$$

1996 ④ $(A_x B_{1-x})_2 (B_y V_{1-y})$

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

$$= \frac{4-6x+2y}{2+y}$$

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

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

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

$$(x+y)\, g^\circ_{A_2B} + (1-x)\, g^\circ_{B_2B} - y\, g^\circ_{B_2B} + (1-y)\, g^\circ_{A_2V} - x\, g^\circ_{A_2V}$$

$$-(1-x)\, g^\circ_{B_2V} - (1-y)\, g^\circ_{B_2V}$$

$$+RT\left(\ln x^2 - \ln(1-x)^2 + \ln y - \ln(1-y)\right) = 0$$

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

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

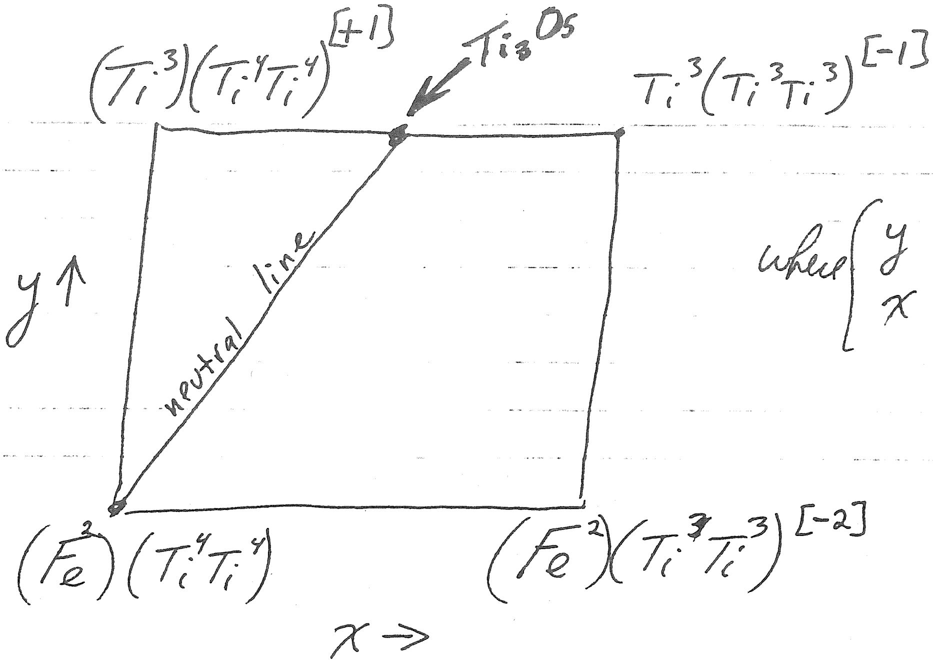
Let: $\begin{cases} \Delta g^\circ_1 \equiv g^\circ_{B_2B} - g^\circ_{A_2B} \\ \Delta g^\circ_2 \equiv g^\circ_{A_2V} - g^\circ_{A_2B} \end{cases}$

$$-(\Delta g^\circ_1 + \Delta g^\circ_2) = RT(\ln x^2 - \dots) = 0$$

$$\left(\frac{x^2 y}{(1-x)^2(1-y)}\right)^{-1} = \exp\left(\frac{-(x+y)}{2RT}(\Delta g^\circ_1 + \Delta g^\circ_2)\right)$$

1999

(5)



where $\begin{cases} y = (\text{"}x\text{"}) \\ x = \left(\dfrac{\text{"}x\text{"}}{2}\right) \end{cases}$

$\downarrow$

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

$$x = \frac{n_{Ti^{3+}_B}}{n_{Ti^{3+}_B} + n_{Ti^{4+}_B}} \qquad y = \frac{n_{Ti^{3+}_A}}{n_{Fe^{2+}_A} + n_{Ti^{3+}_A}}$$

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

$$+\underline{\underline{2}}RT\big(x\ln x + (1-x)\ln(1-x)\big) + RT\big(y\ln y + (1-y)\ln y\big)$$

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

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

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