MET 6208 - Final Exam - Autumn 2016 - Solutionnaire

Question 1 $\quad (X_{SiO_2} + X_{GeO_2} + X_{K_2O} + X_{CaO}) = 1.0$

$$n_{SiO_4^{=}} = X_{SiO_2}$$

$$n_{GeO_4^{=}} = X_{GeO_2}$$

$$n_{K^+} = 2X_{K_2O}$$

$$n_{Ca^{++}} = (1 - X_{SiO_2} - X_{GeO_2} - X_{K_2O})$$

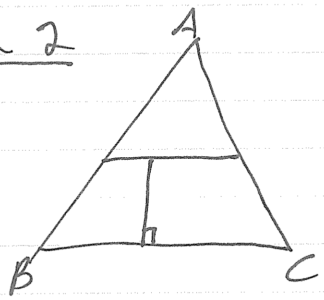
$$n_{O^{=}} = (X_{K_2O} + X_{CaO} - 2X_{SiO_2} - 2X_{GeO_2}) = (1 - 3X_{SiO_2} - 3X_{GeO_2})$$

$$\sum n_+ = (n_{K^+} + n_{Ca^{++}}) = (1 + X_{K_2O} - X_{SiO_2} - X_{GeO_2})$$

$$\sum n_- = (n_{SiO_4^{=}} + n_{GeO_4^{=}} + n_{O^{=}}) = (X_{K_2O} + X_{CaO} - X_{SiO_2} - X_{GeO_2}) = (1 - 2X_{SiO_2} - 2X_{GeO_2})$$

$$a_{CaO} = y_{Ca^{++}}\, y_{O^{=}} = \frac{(1 - X_{SiO_2} - X_{GeO_2} - X_{K_2O})}{(1 + X_{K_2O} - X_{SiO_2} - X_{GeO_2})} \cdot \left(\frac{1 - 3X_{SiO_2} - 3X_{GeO_2}}{1 - 2X_{SiO_2} - 2X_{GeO_2}}\right)$$

Question 2



$$g^E = X_A X_B (a + b(1 - X_A)) + X_C X_A (c + d X_A) + X_B X_C (e + f(X_C - X_B))$$

Question 3

(i)	1 (Ca^{2+})	(vi)	1 (SiO_4^{4-})
(ii)	2 (Ca^{2+}, Va)	(vii)	1 (O_2)
(iii)	3 (Ca^{2+}, F^-, F^-)	(viii)	2 (O, O)
(iv)	4 (Ca^{2+}, Va, F^-, F^-)	(ix)	2 (Al^{3+}, Al^{3+})
(v)	1 (Br^-)	(x)	1

O Y Al^{3+} O

O Na^+ O

Question 4

- In the liquid there ~~are~~ is <u>1</u> "new" particle formed per mole of MCl_3 $(A^+, M^{3+})(Cl^-)$
- In the solid there are <u>3</u> "new" particles per mole of MCl_3 since each M^{3+} creates 2 cation vacancies

$$(A^+, M^{3+}, Va)(Cl^-)$$

- (At higher concentrations of MCl_3, the vacancies, which have an effective negative charge, will start to associate with the M^{3+} ions. Nevertheless, the effective number of "new" particles will still be greater than 1.0)
- Hence, the <u>entropy of the solid solution is greater</u> than that of the liquid. Hence the Gibbs energy of the solid is more negative than the liquid. That is the solid is ~~more~~ <u>more stable</u> than the liquid. Hence a maximum appears.

Question 5

(a) There is a strongly negative g^E_{AB} with a minimum near the AB composition

(b) (1) Random Mixing - Largest gap. -
- A and B atoms "want" to be together as neighbours. Since mixing of A, B + C is random (no S.R.O.) this can only be accomplished by separating into an AB-rich and a C-rich phase

(3) S.R.O. - Smaller gap.
- A + B atoms can now become nearest neighbours in a single phase. Hence, the driving force to separate into 2 phases is reduced.

(2) Associates - No gap.
- A and B atoms are already "nearest-neighbours" in the AB associates. There is, therefore, no further advantage to separation into 2 phases.

Question 6

(i) SRO only (1 sublattice)

just the modified quasichemical model equations with $Z=2$ (See Handout #17)

(ii) LRO only
2 sublattices (See Handout #40 (page 1)) → copy on next page

- With SRO, the probability that a B-atom is in the n^{th} coordination shell of a given central A-atom is greater than X_B when n is small, but decreases to X_B as n increases.

- With LRO, the probability that a B atom is in the n^{th} coordination shell of a given central A-atom is constant and greater than X_B when n is even and constant and less than X_B when n is small, and these values are independent of n, even for very large values of n.

Handout (40)

3

ORDER/DISORDER

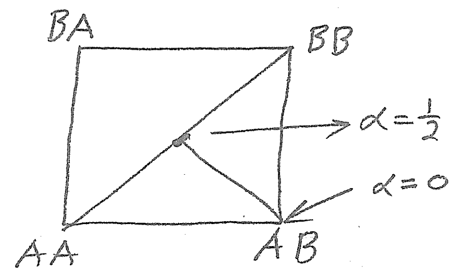
Long-Range Order (l.r.o.) 2 sublattices

$$\underset{(1-\alpha)}{A_A} + \underset{(1-\alpha)}{B_B} = \underset{\alpha}{A_B} + \underset{\alpha}{B_A}$$

$\alpha = 0 \Rightarrow 100\%$ l.r.o.
$\alpha = \frac{1}{2} \Rightarrow 0\%$ l.r.o.
$\alpha =$ l.r.o. parameter

Let: $2\omega = (2g^{\circ}_{AB} - g^{\circ}_{AA} - g^{\circ}_{BB})$
where $(g^{\circ}_{AB} = g^{\circ}_{BA})$

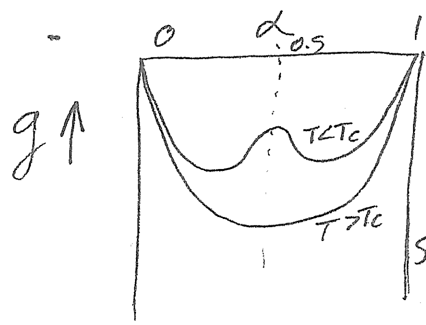
$\omega = 0 \Rightarrow \alpha = \frac{1}{2}$
$\omega = -\infty \Rightarrow \alpha = 0$



$$\Delta S = 2RT(\alpha \ln \alpha + (1-\alpha)\ln(1-\alpha))$$

Then: $G = \alpha^2 g^{\circ}_{BA} + (1-\alpha)^2 g^{\circ}_{AB} + \alpha(1-\alpha) g^{\circ}_{AA} + \alpha(1-\alpha) g^{\circ}_{BB}$
$- T\Delta S$

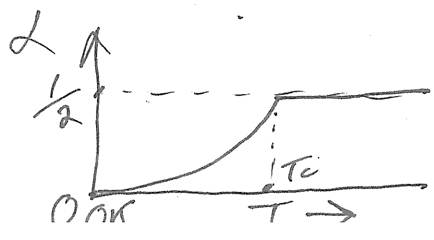
$$\left(\frac{dG}{d\alpha}\right) = 0 \Rightarrow 2\alpha g^{\circ}_{AB} - (2-2\alpha) g^{\circ}_{BA} + (1-2\alpha) g^{\circ}_{AA} + (1-2\alpha) g^{\circ}_{BB}$$
$$+ 2RT(\ln\alpha - \ln(1-\alpha))$$
$$= 2\omega(2\alpha - 1) + 2RT \ln\frac{\alpha}{1-\alpha} = 0$$
$$\ln\left(\frac{\alpha}{1-\alpha}\right) = e^{-\omega(2\alpha-1)/RT}$$



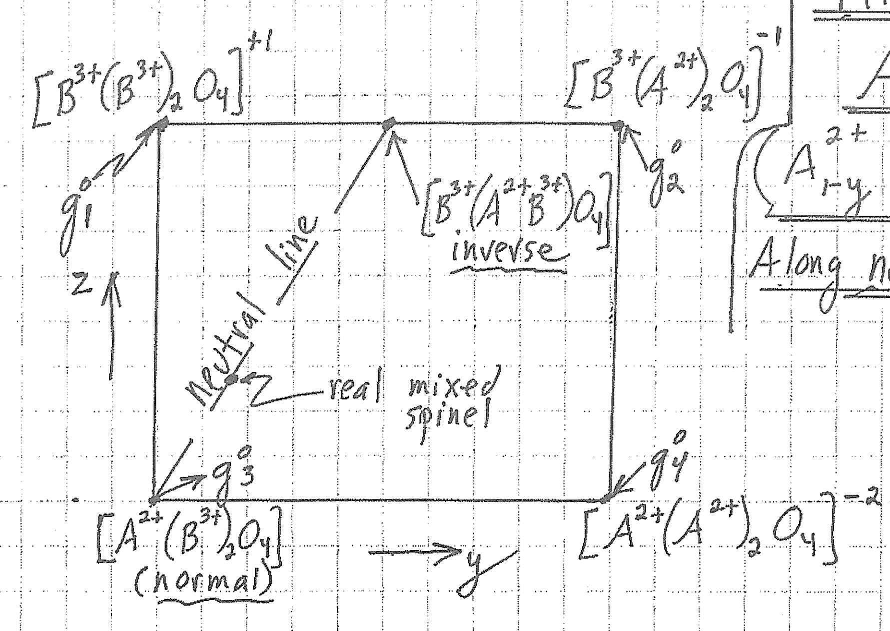
Always a solution at $\alpha = \frac{1}{2}$
For $T < T_c$ there are solutions for $\alpha \leq \frac{1}{2}$

Set $\left(\frac{d^2G}{d\alpha^2}\right)_{\alpha=\frac{1}{2}} = 0$

$$2\omega(2) + 2RT\left(\frac{1}{\alpha} + \frac{1}{1-\alpha}\right) = 0$$
$$4\omega + 2RT(2+2) = 0$$
$$T_c = \frac{-\omega}{2R}$$



Question 7 $A = Fe^{2+}$, $B = Fe^{3+}$



Mixed Spinel

AB_2O_4

$(A^{2+}_{1-y} B^{3+}_y)(A^{2+}_z B^{3+}_{1-z})_2 O_4$

Along neutral line, $z = y/2$

$$g = \left[y(1-y/2)g_1^o + y(y/2)g_2^o + (1-y)(1-y/2)g_3^o + (1-y)(y/2)g_4^o\right]$$
$$+ RT\left[y \ln y + (1-y)\ln(1-y)\right] + 2RT\left[\frac{y}{2}\ln\frac{y}{2} + (1-y/2)\ln(1-y/2)\right]$$

$$A_T^{2+} + B_O^{3+} = B_T^{3+} + A_O^{2+} \;:\; \Delta G^{(\text{site exchange})} \quad \text{(model parameter)}$$

where "T" = on a tetrahedral ~~site~~ site
"O" = on an octahedral site

$\Delta G^{\text{site exchange}}$ determines the degree of inversion

Consider: $\left(\frac{1}{2}g_1^o + \frac{1}{2}g_2^o + 2RT\left(\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\right)\right) = g^o_{\text{(inverse spinel)}}$

$$\left(g^o_{\substack{\text{inverse}\\\text{spinel}}} - g^o_{\substack{\text{normal}\\\text{spinel}}}\right) = \left(\frac{1}{2}g_1^o + \frac{1}{2}g_2^o + 2RT\left(\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\right)\right) - g_3^o$$
$$= \frac{1}{2}\left(g^o_{B_T} + 2g^o_{B_O}\right) + \frac{1}{2}\left(g^o_{B_T} + 2g^o_{A_O}\right) - \left(g^o_{A_T} + 2g^o_{B_O}\right) - RT\ln 2$$
$$= \left(g^o_{B_T} + g^o_{A_O} - g^o_{A_T} - g^o_{B_O}\right) - RT\ln 2$$
$$= \Delta G^{\text{site exchange}} - RT\ln 2$$

Therefore, the "model parameter" is $\left(\frac{1}{2}g_1^o + \frac{1}{2}g_2^o - g_3^o\right)$