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**ÉCOLE POLYTECHNIQUE**

**Département de génie physique et de génie des matériaux**

**MET 6208 ENERGÉTIQUE DES SOLUTIONS**

**Examen final**

**Vendredi, le 23 avril 1999**

**9 : 00 - 12 : 30**

**NOTES :**

- **Toute documentation permise**
- **Tous moyens de calcul permis**

Question 1 (3 pts)

- (a) A liquid solution consists of 90 moles NaCl, 3 moles MgCl<sub>2</sub>, 3 moles AlCl<sub>3</sub>, and 5 moles LiCl. Stating your assumptions, derive an equation for the activity of NaCl in the solution. (2 pts)
- (b) Given only the composition of this solution, you can make a reasonable estimate of the activity of NaCl, but not of the activity of AlCl<sub>3</sub>. Why not? (1 pt)

Question 2 (3 pts)

A curve of  $\log P_{S_2}$  for S<sub>2</sub> gas in equilibrium with liquid Ni-S solutions, as a function of the sulfur mole fraction of the liquid, is shown in the accompanying figure.

- (a) Sketch the corresponding curve of molar Gibbs energy,  $g$ , of the liquid solution as a function of  $X_S$ .
- (b) Describe in words, so that your grandmother can understand, the structure of liquid Ni-S solutions and why this structure gives rise to such a curve of  $g$  versus  $X_S$ .

Question 3 (5 pts)

Assume a magnetic metal with a one-dimensional lattice. Let the fraction of atoms with positive spins be  $\alpha$ , and with negative spins  $(1 - \alpha)$



Assume that the energy of interaction between a neighboring pair of atoms is  $\epsilon$ , where  $\epsilon < 0$ , when their spins are parallel (in the same direction), and that the energy of interaction is zero when their spins are opposed (in opposite directions).

- (a) Assuming an ideal (Bragg Williams) configurational entropy, calculate an expression for the Curie temperature as a function of  $\epsilon$ .
- (b) Show how this model can be improved by using the Ising model (quasichemical model). It is not necessary to solve the equations in this case.

Question 4 (4 pts)

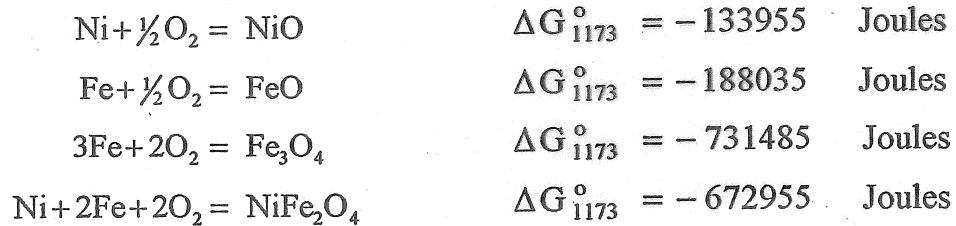
The  $\log P_{O_2}$  -composition diagram of the Fe-Ni-O system at 1173 K is sketched in the accompanying figure.

- (a) In the spinel phase, the two components Fe<sub>3</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> are inverse spinels. Develop a model giving the activities of Fe<sub>3</sub>O<sub>4</sub> and of NiFe<sub>2</sub>O<sub>4</sub> as a function of

$X_{\text{Fe}_3\text{O}_4}$  in the  $\text{Fe}_3\text{O}_4$ - $\text{NiFe}_2\text{O}_4$  solution. It is not necessary to use the Compound Energy Model.

- (b) When the 3 phases [spinel + (FeO-NiO) + (metal alloy) ] are at equilibrium, calculate the compositions of the three phases (at points A, B, and C of the figure) as well as the equilibrium  $P_{\text{O}_2}$ . Assume that the metal phase is ideal and that the FeO-NiO solution is Henrian with  $\gamma_{\text{FeO}}^\circ = 1.32$ .

DATA :



Question 5 (5 pts)

"Ferropseudobrookite",  $\text{FeTi}_2\text{O}_5$ , is a ceramic with 2 cation sublattices. The "A" sublattice is occupied by  $\text{Fe}^{2+}$  ions and the "B" sublattice by  $\text{Ti}^{4+}$  ions as:  $(\text{Fe}^{2+})_A (\text{Ti}_2^{4+})_B \text{O}_5$ .

The ceramic  $\text{Ti}_3\text{O}_5$  has the same structure, and can be represented as:  $(\text{Ti}^{3+})_A (\text{Ti}^{3+}\text{Ti}^{4+})_B \text{O}_5$ . That is, the A sites are occupied only by  $\text{Ti}^{3+}$ , while  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  are randomly distributed on the B sites.

Solid solutions of  $\text{FeTi}_2\text{O}_5$  and  $\text{Ti}_3\text{O}_5$  are represented as:  $(\text{Fe}_{1-x}^{2+} \text{Ti}_x^{3+})_A (\text{Ti}_{2-x}^{4+} \text{Ti}_x^{3+})_B \text{O}_5$  with the ions mixing randomly on each sublattice.

Write an expression for the Gibbs energy, G, of  $\text{FeTi}_2\text{O}_5$ - $\text{Ti}_3\text{O}_5$  solutions as a function of composition. Use the Compound Energy Model, expressing energies in terms of the "g°" values of "pseudocomponents". Ignore excess mixing terms. Draw the "composition square" and show the path of charge neutrality. Relate the g° values of the pseudocomponents to g° of pure real  $\text{FeTi}_2\text{O}_5$  and g° of pure real  $\text{Ti}_3\text{O}_5$ .