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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 $MgCl_2$, 3 moles $AlCl_3$, 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 $AlCl_3$. Why not? (1 pt)

Question 2 (3 pts)

A curve of log P_{S_2} for S_2 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 α, and with negative spins $(1 - \alpha)$

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Assume that the energy of interaction between a neighboring pair of atoms is ϵ, 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 ϵ.

(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_3O_4 and $NiFe_2O_4$ are inverse spinels. Develop a model giving the activities of Fe_3O_4 and of $NiFe_2O_4$ as a function of

$X_{Fe_3O_4}$ in the Fe_3O_4-$NiFe_2O_4$ 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_{O_2}. Assume that the metal phase is ideal and that the FeO-NiO solution is Henrian with $\gamma^o_{FeO} = 1.32$.

DATA :

$Ni + \frac{1}{2}O_2 = NiO$	$\Delta G^o_{1173} = -133955$	Joules
$Fe + \frac{1}{2}O_2 = FeO$	$\Delta G^o_{1173} = -188035$	Joules
$3Fe + 2O_2 = Fe_3O_4$	$\Delta G^o_{1173} = -731485$	Joules
$Ni + 2Fe + 2O_2 = NiFe_2O_4$	$\Delta G^o_{1173} = -672955$	Joules

Question 5 (5 pts)

"Ferropseudobrookite", $FeTi_2O_5$, is a ceramic with 2 cation sublattices. The "A" sublattice is occupied by Fe^{2+} ions and the "B" sublattice by Ti^{4+} ions as: $(Fe^{2+})_A\ (Ti_2^{4+})_B\ O_5$.

The ceramic Ti_3O_5 has the same structure, and can be represented as: $(Ti^{3+})_A\ (Ti^{3+}Ti^{4+})_B O_5$. That is, the A sites are occupied only by Ti^{3+}, while Ti^{3+} and Ti^{4+} are randomly distributed on the B sites.

Solid solutions of $FeTi_2O_5$ and Ti_3O_5 are represented as: $\left(Fe^{2+}_{1-x}\ Ti^{3+}_x\right)_A \left(Ti^{4+}_{2-x}\ Ti^{3+}_x\right)_B O_5$ with the ions mixing randomly on each sublattice.

Write an expression for the Gibbs energy, G, of $FeTi_2O_5$-Ti_3O_5 solutions as a function of composition. Use the Compound Energy Model, expressing energies in terms of the "g^o" values of "pseudocomponents". Ignore excess mixing terms. Draw the "composition square" and show the path of charge neutrality. Relate the g^o values of the pseudocomponents to g^o of pure real $FeTi_2O_5$ and g^o of pure real Ti_3O_5.