

**ÉCOLE POLYTECHNIQUE**  
**Département de génie chimique**  
**Programme de matériaux**

**MET 6208**  
**ÉNERGÉTIQUE DES SOLUTIONS**

**CONTRÔLE II**  
**Jeudi le 17 novembre 2011**  
**10h00 - 13h00**

***NOTES:***

- *Open book exam*
- *There are 6 questions*

Le professeur : Arthur D. Pelton

### **Question 1 (4 points)**

The integral molar excess Gibbs energies of the binary solutions A-B, B-C and C-A are given by the following expressions:

$$g_{AB}^E = X_A X_B (a + bX_B)$$

$$g_{BC}^E = X_B X_C (c + d(X_C - X_B)^2)$$

$$g_{CA}^E = X_C X_A (e + fX_A)$$

where an ideal (Bragg-Williams) configurational entropy is assumed.

Components B and C are chemically similar, while A is chemically different from B and C.

Write a reasonable expression for the excess integral molar Gibbs energy of the ternary solution A-B-C as a function of composition.

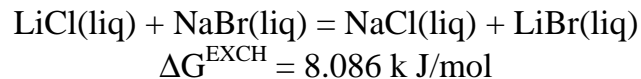
### **Question 2 (3 points)**

A liquid salt solution contains 90 moles  $\text{CaCl}_2$ , 6 moles  $\text{NaCl}$  and 5 moles  $\text{AlCl}_3$ . The  $\text{AlCl}_3$  forms “complex anions”  $\text{AlCl}_4^-$ . No other complex ions are formed.

Calculate an expression for the activity of  $\text{CaCl}_2$ , stating all assumptions.

### **Question 3 (4 points)**

In the liquid salt solution  $(\text{Li}^+, \text{Na}^+)(\text{Cl}^-, \text{Br}^-)$ , the exchange Gibbs energy at  $1000^\circ\text{C}$  is given by:



Assume that the liquid solutions in all four common-ion binary subsystems are ideal.

A solution is prepared by mixing 1.0 mol  $\text{NaCl}$ , 2.0 mol  $\text{NaBr}$  and 3.0 mol  $\text{LiBr}$ .

Using the Compound Energy Formalism (Bragg-Williams), calculate the activity of  $\text{LiCl}$ , ignoring the correction term for short-range-ordering.

Will inclusion of the short-range-ordering correction term increase or decrease the activity of  $\text{LiCl}$ ? Explain.

### **Question 4 (3 points)**

After oxygen refining, molten Fe contains dissolved oxygen in dilute solution as monatomic O. In order to remove the oxygen, Al is added, again in dilute solution, as a deoxidizer. The dissolved Al reacts with the O to form solid  $\text{Al}_2\text{O}_3$  which precipitates out as inclusions.

If only a very small amount of Al is added, the Al and O are in solution as independent dissolved Al and O atoms, and it is observed that the dissolved oxygen content decreases as Al is added. As a larger amount of Al is added, however, the

dissolved Al and O atoms associate to form dissolved AlO associates (or molecules), and now it is observed that the total amount of dissolved oxygen (as AlO molecules) increases as Al is added. By writing appropriate reaction constants, explain this phenomenon of an “oxidation minimum”.

**Question 5 (3 points)**

A binary solution A-B is modeled with the quasichemical model with  $Z = 2$  and with a constant parameter  $\Delta g_{AB} = -10 \text{ k J/mol}$  at 1000 K for the formation of A-B pairs:



At an overall composition  $X_A = X_B = 0.5$ , and at  $T=1000 \text{ K}$ , calculate the integral molar Gibbs energy of mixing of pure A and B to form one mole of solution at  $T = 1000 \text{ K}$ .

**Question 6 (3 points)**

At ambient temperature, alloys AgCu (at  $X_{Ag} = X_{Cu} = 0.5$ ) are solid solutions exhibiting long-range ordering. Virtually all Ag atoms occupy one sub-lattice and virtually all Cu atoms occupy another sub-lattice (such that virtually all first-nearest-neighbour pairs are Ag-Cu pairs). As the temperature increases, the system becomes progressively disordered, with Cu atoms occupying sites on the “Ag-sublattice” and vice-versa. The system may be modeled as (Cu,Ag) (Ag,Cu) using the Compound Energy Formalism. As the temperature increases, the system becomes progressively more disordered until, above a critical temperature  $T_c = 600 \text{ K}$  it becomes completely disordered, with Cu and Ag atoms distributed randomly and equally on both sublattices. The order/disorder transformation at 600 K is a second-order transformation (no discontinuity in H).

Define  $\alpha$  as the fraction of “Ag-sublattice” sites occupied by Cu atoms. (Clearly,  $\alpha$  is also the fraction of “Cu-sublattice” sites occupied by Ag atoms.) When  $T = 0 \text{ K}$ ,  $\alpha = 0$ . When  $T \geq T_c$ ,  $\alpha = 1/2$ .

Assume that the first-nearest-neighbour bond energies  $\epsilon_{Cu-Cu}$ ,  $\epsilon_{Ag-Ag}$  and  $\epsilon_{Cu-Ag}$  are constant, and that the coordination number  $Z$  is also constant. Let  $\omega = (N_{Avog} Z/2) (2\epsilon_{Ag-Cu} - \epsilon_{Ag-Ag} - \epsilon_{Cu-Cu})$  where  $N_{Avog}$  is Avogadro’s number. (In order for ordering to occur, it is necessary that  $\omega < 0$ .)

- (i) Using the Compound Energy Formalism write an equation for the molar Gibbs energy,  $g$ , of the solution considering only first-nearest-neighbour energies. By setting  $(dg/d\alpha) = 0$ , derive the following equation :

$$\ln\left(\frac{\alpha}{1-\alpha}\right) = \frac{\omega(1-2\alpha)}{2RT}$$

- (ii) Sketch curves of  $g$  versus  $\alpha$  for  $T < T_c$ , and  $T > T_c$ . Show that  $T_c = -\omega/4R$ .