ÉCOLE POLYTECHNIQUE

Département de génie chimique

Programme de métallurgie

MET 6208

ÉNERGÉTIQUE DES SOLUTION

Final Exam

Wednesday, Dec. 14, 2016

14:00 – 17:00

NOTES:
- All documentation permitted (open book exam)
- There are 7 questions and 2 figures

Le professeur: Arthur D. Pelton

Question 1 (2 points)

In a dilute solution of SiO_2, GeO_2 and K_2O in liquid CaO solvent, write an approximate expression for the activity of CaO as a function of the mole fractions of SiO_2, GeO_2 and K_2O.

Question 2 (3 points)

In a solution with components A, B and C, components B and C are chemically similar while component A is dissimilar.
The binary excess Gibbs energies are represented by the following equations:

$$g^E(A\text{-}B) = X_A X_B (a + b\, X_B)$$

$$g^E(C\text{-}A) = X_C X_A (c + d\, X_A)$$

$$g^E(B\text{-}C) = (e + f(X_C - X_B))$$

Write an expression for g^E of the ternary solution using a "Toop-Muggianu formalism".

Question 3 (3 points)

For each of the following solvent/solute pairs, for dilute solutions, what is the value of ν, the number of moles of "foreign particles" introduced per mole of solute ?

Solvent	Solute
KCl (liquid)	$CaCl_2$
KCl(solid)	$CaCl_2$
KCl(liquid)	CaF_2
KCl(solid)	CaF_2
KCl(liquid)	KBr
CaO(liquid)	SiO_2
H_2O(liquid)	O_2
Ni(liquid)	O_2
SiO_2	Al_2O_3
SiO_2	$NaAlO_2$

Question 4 (3 points)

In dilute solutions of a rare earth chloride MCl_3 in a liquid alkali chloride ACl, the MCl_3 dissolves following the Temkin model, whereas in dilute solutions in a solid alkali chloride the MCl_3 dissolves with the formation of cation vacancies.
The phase diagram of an ACl-MCl_3 system in the ACl-rich composition region is sketched in Figure 1. A maximum is observed in the solidus/liquidus at low concentrations of MCl_3 (typically around 1 mole percent MCl_3).

Explain clearly, either in words or with the aid of equations, why this maximum occurs.

Question 5 (3 points)

The phase diagram of a system A-B-C is sketched in Figure 2. A liquid-liquid miscibility gap is observed, centered approximately along the join from pure C to the AB composition.

Assume that the A-C and B-C liquid solutions are approximately ideal.

(a) What does this miscibility gap tell you about the thermodynamic properties of the A-B liquid solution ?
(b) You model the liquid A-B solution using three different models:
   (1) random mixing of A and B
   (2) AB "molecular associates"
   (3) short-range ordering (modified quasichemical model)
and then approximate the properties of the ternary liquid.
With one of the models a relatively large calculated miscibility gap results.
With another model a relatively smaller calculated miscibility gap results.
With a third model the calculation yields no miscibility gap.

Which model gives which result ? Explain in words. (Equations not required.)

Question 6 (3 points)

Consider a one-dimensional crystal of A and B atoms in which A-B nearest-neighbour pairs are favoured over A-A and B-B pairs. Considering only terms involving end-member Gibbs energies and the configurational entropy, write an expression for the Gibbs energy of the solution

(i) assuming only short-range-ordering
(ii) assuming only long-range-ordering

Using this example, explain the difference between short-range and long-range ordering in terms your grandmother could understand.

Question 7 (3 points)

Fe_3O_4 is a mixed spinel.
Using the Compound Energy Formalism, write an expression for the Gibbs energy of Fe_3O_4 considering only the terms involving the end-member Gibbs energies and the configurational entropy. (That is, you may neglect the excess terms as well as short-range-ordering.)

What linear combination of the end-member Gibbs energies (that is, which "model parameter") determines the degree of inversion of the spinel ?

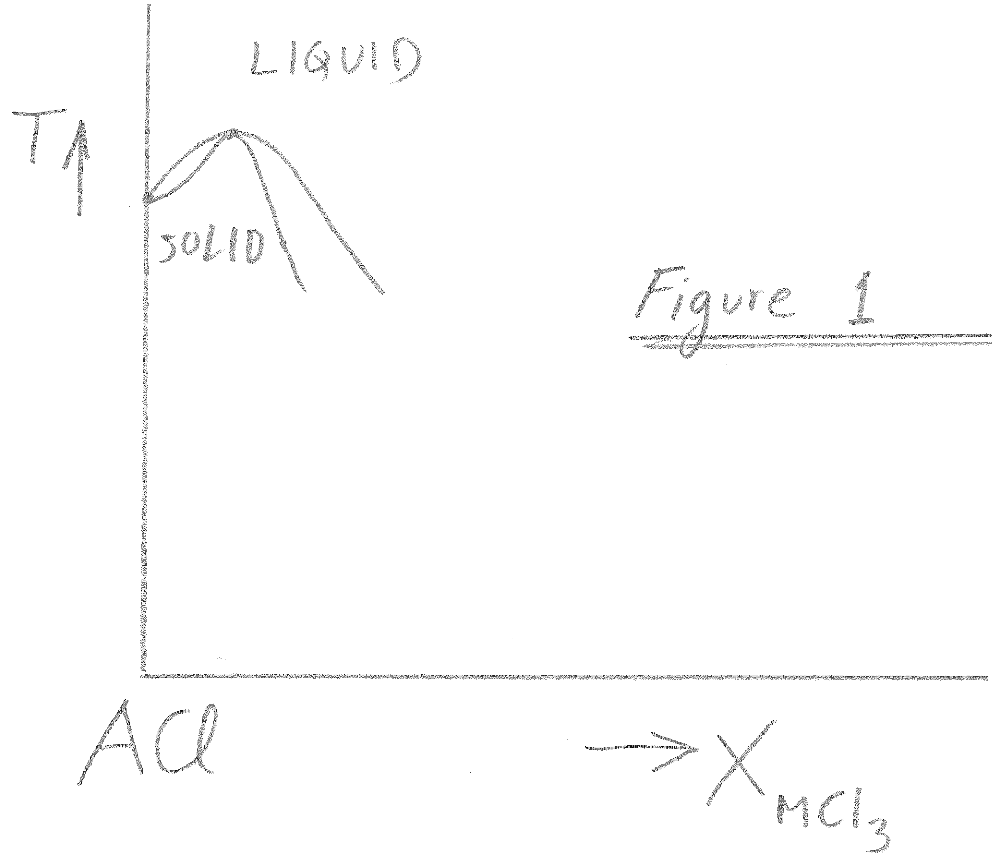

Figure 1

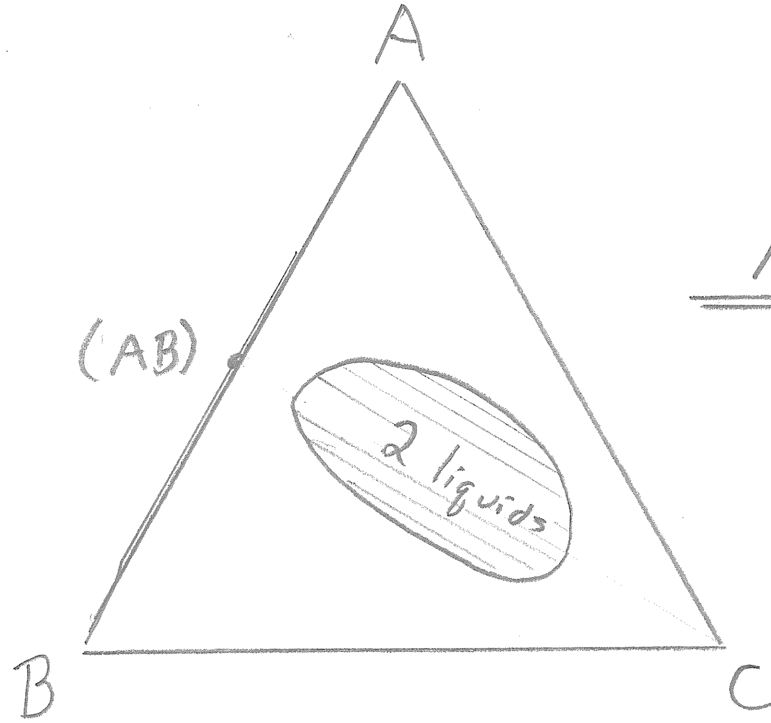

Figure 2