

ÉCOLE POLYTECHNIQUE
Département de génie chimique
Programme de matériaux

MET 6208
ÉNERGÉTIQUE DES SOLUTIONS

CONTRÔLE II
Mercredi, le 25 novembre 2009
9h00 - 12h00

NOTES:

- *All documentation permitted*
- *There are 5 questions*

Le professeur : Arthur D. Pelton

Question 1 (4 points)

A homogeneous liquid solution at 1000°C contains 0.500 mol Mg and 0.500 mol Al. The volume of the solution is 0.0137728 litres.

When 0.01 mol of pure Mg is added to the solution, the volume increases to 0.0139341 liters. A further addition of 0.01 mol of pure Al is made. What is the final volume of the solution?

Question 2 (4 points)

(i) A liquid solution (Na^+ , K^+) (F^- , Cl^-) is prepared by mixing 1.0 mol NaCl, 2.0 mol KCl and 1.0 mol KF.
 Calculate the site fractions y_{Na} , y_{K} , y_{F} and y_{Cl} .

(ii) The standard Gibbs energies of the pure salts at 1000°C are:

$$g_{\text{NaCl}}^{\circ} = -556134 \text{ J/mol}$$

$$g_{\text{KCl}}^{\circ} = -596244 \text{ J/mol}$$

$$g_{\text{NaF}}^{\circ} = -683533 \text{ J/mol}$$

$$g_{\text{KF}}^{\circ} = -702772 \text{ J/mol}$$

The four binary common-ion solutions are approximately regular.

At 1000°C:

$$\text{NaCl-KCl} \quad g^E = X_{\text{NaCl}}X_{\text{KCl}}(-2156) \text{ J/mol}$$

$$\text{NaF-KF} \quad g^E = X_{\text{NaF}}X_{\text{KF}}(2880) \text{ J/mol}$$

$$\text{NaF-NaCl} \quad g^E = X_{\text{NaF}}X_{\text{NaCl}}(2058) \text{ J/mol}$$

$$\text{KF-KCl} \quad g^E = X_{\text{KF}}X_{\text{KCl}}(38) \text{ J/mol}$$

Calculate the Gibbs energy of the solution at 1000°C using the Compound Energy Formalism with the first-order Taylor expansion approximation for short-range-ordering. (Assume $Z=6$.)

Question 3 (4 points)

See the accompanying figure.

Calculating an expression for the limiting slope at $X_B=0$

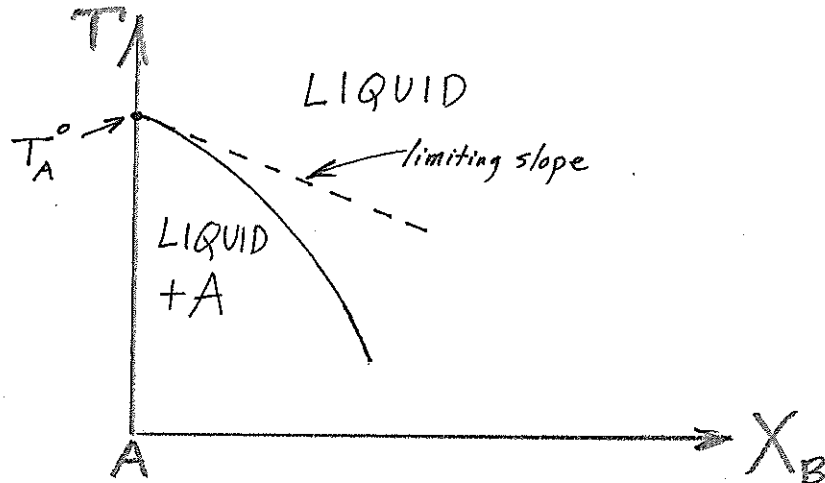
$$\lim_{X_B \rightarrow 0} (dT/dX_B)$$

of the liquidus of a binary metallic system with components A-B, with no solid solubility, as a function of the melting point of pure A, T_A° , and the molar enthalpy of fusion of A,

$$\Delta h_{f(A)}^{\circ}$$

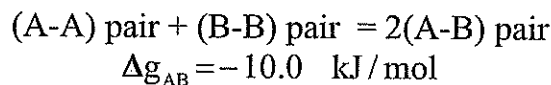
State clearly all assumptions which are required. Do not list assumptions which are not required.

Note $\lim_{y \rightarrow 0} \ln(1+y) = y$



Question 4 (4 points)

Assume a one-sublattice quasichemical model (in the pair approximation) for a liquid solution of components A-B with $Z = 2$ and a constant pair exchange energy:



Calculate the pair fractions X_{AB} , X_{AA} and X_{BB} in a solution at $X_A = X_B = 0.5$ at $T = 1000 \text{ K}$ and compare to the corresponding values for a random mixture.

Question 5 (4 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 α as the fraction of “Ag-sublattice” sites occupied by Cu atoms. (Clearly, α is also the fraction of “Cu-sublattice” sites occupied by Ag atoms.) When $T = 0$ K, $\alpha = 0$. When $T \geq T_c$, $\alpha = 1/2$.

Assume that the first-nearest-neighbour bond energies $\epsilon_{\text{Cu-Cu}}$, $\epsilon_{\text{Ag-Ag}}$ and $\epsilon_{\text{Cu-Ag}}$ are constant, and that the coordination number is Z . Let $\omega = (N_{\text{Avog}} Z/2) (2\epsilon_{\text{Ag-Cu}} - \epsilon_{\text{Ag-Ag}} - \epsilon_{\text{Cu-Cu}})$ 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. 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 α for $T < T_c$, and $T > T_c$. Show that $T_c = -\omega/4R$.