ÉCOLE POLYTECHNIQUE

Programme de métallurgie et génie des matériaux

MET 6208
ÉNERGÉTIQUE DES SOLUTIONS
CONTRÔLE II
jeudi, le 27 novembre 2003
9 :30 - 12 :30

NOTES :
- Toute documentation premise (open book exam)
- Tous moyens de calcul permis (all calculators permitted)
- Il y a 6 questions (there are 6 questions)

Le professeur : Arthur D. Pelton
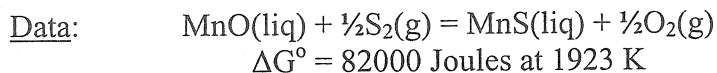
Question 1   (5 points)

For each of the following solutions, propose a structural model in one or two sentences.

   (a)   10% $HfCl_4$, 90% RbCl (liquid)

   (b) $Ag_{0.501}Br_{0.499}$ (solid)

   (c)   45% Fe, 50% Mn, 5% C (solid)

   (d)   10% GeO_2 + 90% CaO (liquid)

   (e)   90% B_2O_3 + 10% CaO (glass)

   (f)   1% $PbCl_2$ in NaCl (solid)

   (g)   1% $PbCl_2$ in NaCl (liquid)

   (h)   A liquid solution with X_{Fe} = 0.75, X_S = 0.25

   (i)   Oxygen dissolved in liquid Fe

   (j)   80% $MgCl_2$, 20% KCl (liquid)

Question 2   (4 points)

   (i.)   A basic liquid slag contains SiO_2, MnO and MnS. Assuming that the species in solution are Mn^{2+}, O^{2-}, S^{2-} and SiO_4^{4-} , calculate expressions for the activities of MnO and MnS. State your assumptions.

   (ii.)   A slag with X_{SiO_2} = 0.25 and X_{MnO} = 0.75 is placed in an atmosphere where P_{O_2} = 10^{-4} bar and P_{S_2} = 5 x 10^{-4} bar at 1923 K. Calculate the equilibrium sulfur content of the slag.

   <div align="center">Data: $MnO(liq) + \frac{1}{2}S_2(g) = MnS(liq) + \frac{1}{2}O_2(g)$

   ΔG° = 82000 Joules at 1923 K</div>

Question 3   (2 points)

AgBr is slightly soluble in water. Addition of a soluble salt with a common ion (such as $AgNO_3$ or NaBr) to the solution decreases the solubility of AgBr. However, addition of a soluble salt with no common ion (such as $NaNO_3$) generally increases the solubility of AgBr. Give reasonable explanations for each of these observed effects.

Question 4   (4 points)

For a "regular" solution with several components, the excess molar Gibbs energy is given by:

$$g^E = \omega_{12}X_1X_2 + \omega_{13}X_1X_3 + \omega_{23}X_2X_3 + \omega_{14}X_1X_4 + \ldots$$
$$= \sum_{j > i} \omega_{ij}X_iX_j$$

where the ω_{ij} are constants and X_i are the mole fractions. Calculate an expression for the partial property of component 1: $g_1^E = RT \ln \gamma_1$

Question 5   (2 points)

The binary solution A-B is regular:

$$g^E = \alpha_{AB}^o X_A X_B$$

The binary solution A-C is also regular:

$$g^E = \alpha_{AC}^o X_A X_C$$

The binary solution B-C is sub-regular:

$$g^E = X_B X_C \left(\alpha_{BC}^o + \alpha_{BC}^1 \left(X_C - X_B\right)\right)$$

where α_{AB}^o , α_{AC}^o , α_{BC}^o and α_{BC}^1 are constants.

Write an expression for the integral molar excess Gibbs energy (g^E) of the ternary A-B-C solution as a function of X_A , X_B and X_C using the Kohler (symmetric) approximation.

Question 6   (3 points)

At room temperature the solid alloys $Ag_{0.5}Cu_{0.5}$ (that is, at $X_{Ag}=X_{Cu}=0.5$) are ordered. Almost all the Cu atoms are surrounded by Ag atoms and almost all the Ag atoms are surrounded by Cu atoms. That is, there is long-range order and one can define two sublattices: a Cu-sublatice and a Ag-sublattice. An atom on its own sublattice is indicated by the symbol Cu_{Cu} or Ag_{Ag} . At higher temperatures, a fraction of the Cu atoms can occupy the Ag sublattice and vice-versa. A Cu atom on the Ag-sublattice and a Ag atom on the Cu-sublattice are designated as Cu_{Ag} and Ag_{Cu} respectively. Above the critical temperature, T_C = 600 K, the alloy becomes completely disordered. Above this temperature the Cu and Ag atoms are randomly distributed on both sub-lattices and the long-range order disappears (that is, there is no longer a distinction between the two sublattices.) The order/disorder transformation at T_C is a second-order transformation (Cp is discontinuous, but there is no discontinuity in H.)

Let α be the fraction of Ag-sublattice sites occupied by Cu. Clearly, α is also equal to the fraction of Cu-sublattice sites occupied by Ag. At T = 0 K, α = 0, and when $T > T_C$, α = 1/2 .

The energies of the nearest-neighbour pair bonds between an atom on one sublattice and an atom on the other sublattice are designated:

ε_{CuCu} , ε_{AgAg} , and $\varepsilon_{AgCu} = \varepsilon_{CuAg}$.

The coordination number is Z.

(i.)   Give equations for the entropy and enthalpy of mixing, Δs and Δh, as functions of α (at $X_{Ag} = X_{Cu} = 0.5$), assuming random mixing on each sublattice.

(ii.)   By setting $(\partial \Delta g / \partial \alpha) = 0$, derive the following equation:

$$\ln\left(\frac{\alpha}{1-\alpha}\right) = \frac{\omega(1-2\alpha)}{RT} \quad \text{where } \omega = \text{constant.}$$

(iii.)   Sketch the curve of α as a function of (RT/ω). Show that $T_C = \omega/2R$.

ÉCOLE POLYTECHNIQUE

Programme de métallurgie et génie des matériaux

MET 6208
ÉNERGÉTIQUE DES SOLUTIONS
Examen Final
mercredi, le 17 décembre 2003

9 :30 - 12 :30

NOTES :
- Toute documentation premise (open book exam)
- Tous moyens de calcul permis (all calculators permitted)
- Il y a 5 questions (there are 5 questions)

Le professeur : Arthur D. Pelton

Question 1   (4 points)

The system $LaCl_3$-LaF_3 is a simple eutectic system with no solubility in the solid phases. The eutectic temperature is 654°C. Assume a regular term for the enthalpy of mixing:
$\Delta h = \omega X_{LaCl_3} X_{LaF_3}$ and assume that the entropy of mixing is given by an ideal Temkin ionic model.

Calculate the regular solution parameter ω as well as the composition of the eutectic point.

Data:
$$\Delta g^o_{fusion\,(LaCl_3)} = 54392 - 48.092\,T \; J/mol$$
$$\Delta g^o_{fusion\,(LaF_3)} = 50208 - 28.430\,T \; J/mol$$

Question 2   (4 points)

An isopleth of the C-Fe-W system is shown in the following figure. This is a diagram of T versus weight % C at constant weight percent W = 5.0%.

a) Five phase fields (indicated by "?") are not labeled. Put these labels on the diagram.
b) Draw the "Zero Phase Fraction Line" of the bcc phase on the diagram.

(Be sure to put your name on the diagram and hand it in with your answer booklet.)

Question 3   (4 points)

A client asks you to "estimate the temperature and composition of the eutectic point in the ternary system $MgCl_2$-MgF_2-$LaCl_3$". He gives you the phase diagrams of the three systems $MgCl_2$-MgF_2, $MgCl_2$-$LaCl_3$, MgF_2-$LaCl_3$. All three of these are simple eutectic phase diagrams with no solubility in the solid phases.

What model would you use to perform the calculation? What additional data (other than the three phase diagrams) would you require in order to perform the calculations using this model?

Question 4   (4 points)

The "2-3 spinel" $MgTi_2O_4$ is normal: $\left(Mg^{2+}\right)\left(Ti^{3+}_2\right)O_4$. The spinel Mg_2TiO_4 is a "2-4" spinel in which all the Ti^{4+} ions are found on the octahedral sites:
$$\left(Mg^{2+}\right)\left(Mg^{2+}Ti^{4+}\right)O_4$$
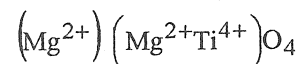
a) Propose a model for the spinel solution $MgTi_2O_4$-Mg_2TiO_4 and give equations for the activities of $MgTi_2O_4$ and Mg_2TiO_4 as functions of x, where x is the overall mole fraction of $MgTi_2O_4$ and (1-x) is the overall mole fraction of Mg_2TiO_4.
b) Write an expression for the Gibbs energy G of the solution as a function of composition using the "Compound Energy Formalism".

Question 5   (4 points)

Experimental liquidus temperatures for dilute solutions of KCl in liquid PbS are given in the following table:

X_{KCl}	$T(°C)$
0.0019	1112.1
0.0031	1111.3
0.0088	1108.2
0.0243	1100.3
0.0333	1095.8

KCl is insoluble in solid PbS. The melting point of PbS is 1113.4°C and its enthalpy of fusion is 36400 Joules/mol.

(i) For each of the experimental points, calculate ν, the number of "new" particles introduced per mole of KCl.

(ii) For very dilute solutions ($X_{PbS} \approx 1.0$), KCl dissolves as K^+ and Cl^- ions. However, in liquid $Pb^{2+}S^{2-}$, the relative charge of a K ion is (-1) and the relative charge of a Cl ion is (+1). Therefore, there is a tendency to form pairs (association):

$$K^+ + Cl^- = (K^+Cl^-) \text{ pairs}$$
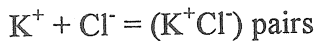
Write an expression for the equilibrium constant K of this reaction as a function of ν and of X_{KCl}. Calculate K for each experimental point in order to verify the model.

(MET 6208) - ÉNERGÉNITQUE DES SOLUTIONS

C - Fe - W System at 5 wt% W

Your Name:
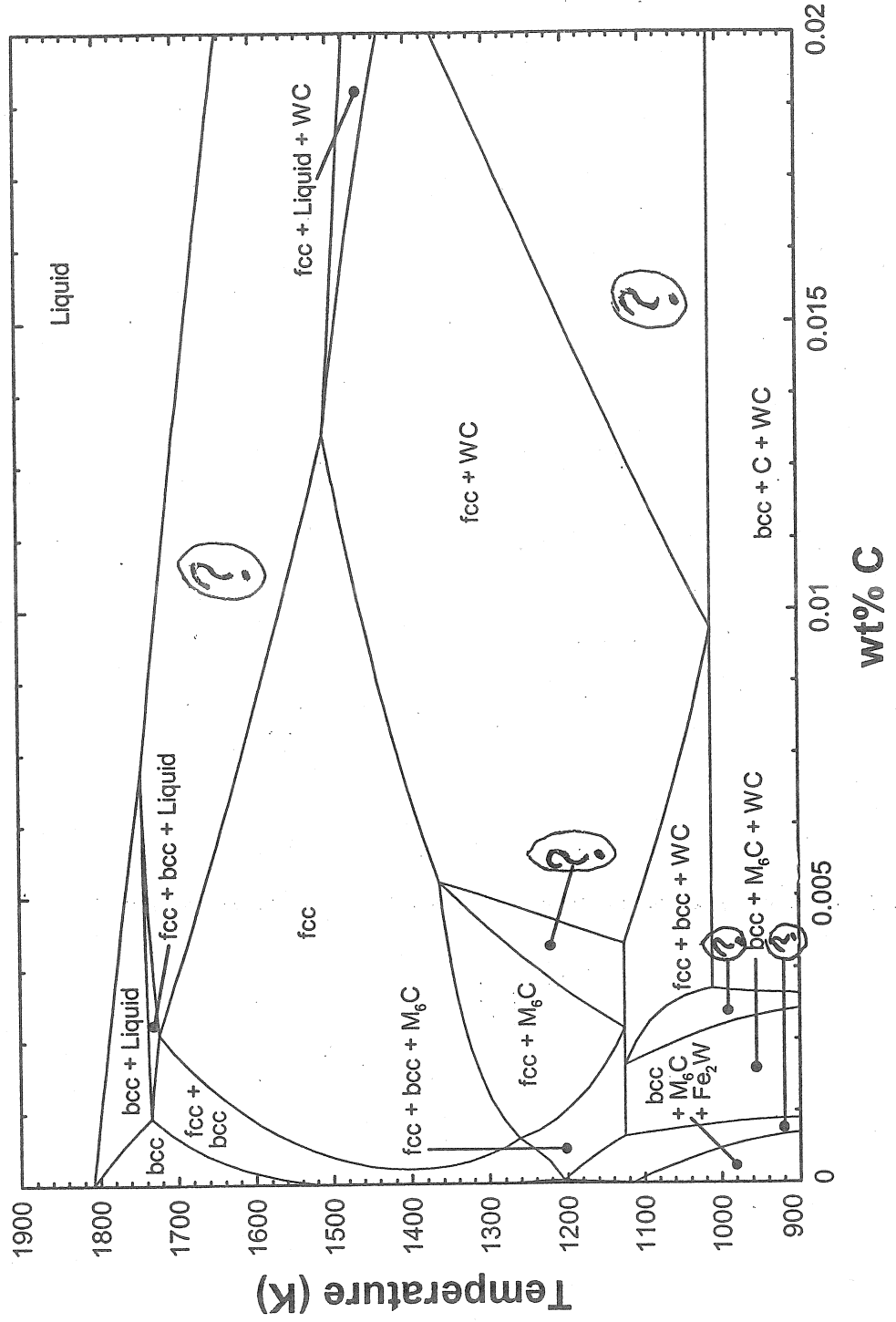
ÉCOLE POLYTECHNIQUE

Département de génie chimique

Programme de matériaux

MET 6208

ÉNERGÉTIQUE DES SOLUTIONS

CONTRÔLE I

Lundi, le 31 octobre 2005

9:30 - 12:30

NOTES :
- *All documentation permitted*
- *There are 6 questions*

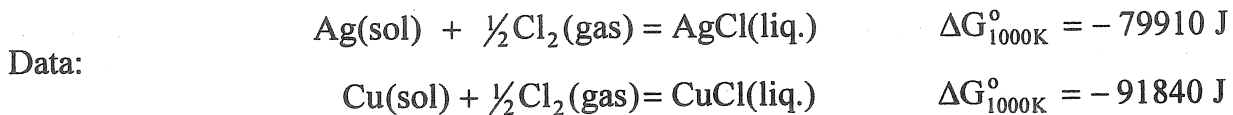Le professeur : Arthur D. Pelton

Question 1 (2 points)

The nitrogen content of liquid Fe in equilibrium at 1600°C with a gas phase in which $P_{N_2} = 1.0$ bar is 0.045 weight %.

Calculate the nitrogen content of liquid Fe in equilibrium at 1600°C with a gas phase in which $P_{N_2} = 10.0$ bar, assuming that nitrogen dissolves in the liquid as monatomic N atoms. State your assumptions.

Question 2 (3 points)

A phase diagram is sketched in Fig. 1. This is an isothermal diagram at 1000 K. The vertical axis in the partial pressure of Cl_2 at equilibrium. The horizontal axis is the molar ratio $\xi = n_{Cu}/(n_{Cu} + n_{Ag})$. That is, for the metallic phases $\xi = X_{Cu}$, the mole fraction of Cu, while for the molten AgCl-CuCl solution, $\xi = X_{CuCl}$, the mole fraction of CuCl. The phase labeled "Ag solid" is a Henrian solution where $RT \ln \gamma_{Cu}^0 = 18450$ J. The phase labeled "Cu solid" is a Henrian solution where $RT \ln \gamma_{Ag}^0 = 27780$ J. The liquid AgCl-CuCl solution is ideal. Calculate the partial pressure of Cl_2, $P_{Cl_2}^{'}$, when all 3 phases are simultaneously in equilibrium at 1000 K, and also calculate the values of ξ at the three equilibrium points A, B and C shown in the figure.

Data:

$$Ag(sol) \; + \; \tfrac{1}{2}Cl_2(gas) = AgCl(liq.) \qquad \Delta G_{1000K}^{o} = -79910 \text{ J}$$

$$Cu(sol) + \tfrac{1}{2}Cl_2(gas) = CuCl(liq.) \qquad \Delta G_{1000K}^{o} = -91840 \text{ J}$$

Question 3 (4 points)

The phase diagram of a binary system A-B is sketched in Fig. 2 (not to scale). The compound A_2B is stoichiometric. The solubility of B in liquid A has been measured as $X_B = 0.02$ at 1000 K and $X_B = 0.003$ at 700 K as shown in the figure (where X_B = mole fraction). The melting point of pure A is 500 K (as in the figure). The enthalpy of fusion of pure A is 5000 J/mol at 500 K. Finally, the Gibbs energy of formation of the compound A_2B has been measured independently:

$$2A(solid) \; + \; B(solid) = A_2B(solid) \qquad \Delta G_{formation}^{o} = -35000 + 8.0T \; J/(\text{mole of } A_2B)$$

(i) Assume that the liquid solution is Henrian in the dilute region. Calculate the Henrian activity coefficient of B, γ_B^0, relative to pure solid B as standard state, at 1000 K and at 700 K.

(ii) Calculate the eutectic temperature, T_E, and the composition of the eutectic liquid, $X_{B(E)}$ (see figure), stating your assumptions.

Question 4   (3 points)

The phase diagram of the AgCl-KCl system is sketched in Fig. 3. The solubilities in the terminal solid solutions are negligible. The eutectic temperature has been measured by thermal analysis as 306°C. The melting points of the pure components have also been measured and are shown on Fig. 3. Finally, the enthalpies of fusion of AgCl and KCl at their melting points have been measured and are equal, respectively, to 13 200 J/mol (for AgCl) and 25 520 J/mol (for KCl).

Assume that the liquid is a strictly regular solution with $g^E = aX_{AgCl}X_{KCl}$, where a is a constant.

Calculate the value of the constant a, as well as the composition, $X_{KCl(E)}$, of the liquid at the eutectic temperature.

Question 5   (4 points)

Consider a dilute solution of carbon in fcc γ-Fe(austenite). The carbon dissolves in the octahedral interstitial sites. (Note that in an fcc lattice, the number of interstitial sites is equal to the number of lattice sites.) Assume that the distribution of carbon atoms on the interstitial sites is random. Assume that the enthalpy of mixing of the dilute solution varies linearly with the number of carbon atoms in solution. That is:

$$\Delta h^{mix} = h^{solution} - \left(X_C h_C^o + X_{Fe} h_{Fe}^o\right) = aX_C$$

where X_C and X_{Fe} are the mole fractions, a is a constant, and $h^{solution}$, h_C^o and h_{Fe}^o. are the molar enthalpies of the solution, pure graphite, and pure γ - Fe respectively. Assume that the excess non-configurational entropy is zero.

(i)   Write an expression for the molar Gibbs energy of the solution, g, as a function of X_C , X_{Fe} , a, T, g_{Fe}^o and g_C^o (where g_{Fe}^o and g_C^o are the molar Gibbs energies of pure γ-Fe and C)

(ii)   Using the expression from part (i), derive expressions for the chemical activities of Fe and C, a_{Fe} and a_C.

Question 6   (4 points)

Consider a ternary solution with components A, B, C. The binary molar integral excess Gibbs energies of the binary sub-systems are well represented by the following equations:

$$g^E_{(AB)} = aX_A X_B$$

$$g^E_{(BC)} = (b_o + b_1 X_C) X_B X_C$$

$$g^E_{(CA)} = cX_C X_A$$

where X_A, X_B, X_C are the mole fractions and a, b_o, b_1 and c are constants. That is, the A-B and C-A binary solutions are regular and the B-C binary solution is sub-regular.

(a) Using the Toop/Kohler model with A as the "asymmetric component", write an expression for g^E in the ternary A-B-C solution.

(b) Using the same Toop/Kohler model, derive an expression for the partial molar excess Gibbs energy of A, g^E_A, as a function of composition in the ternary solution.
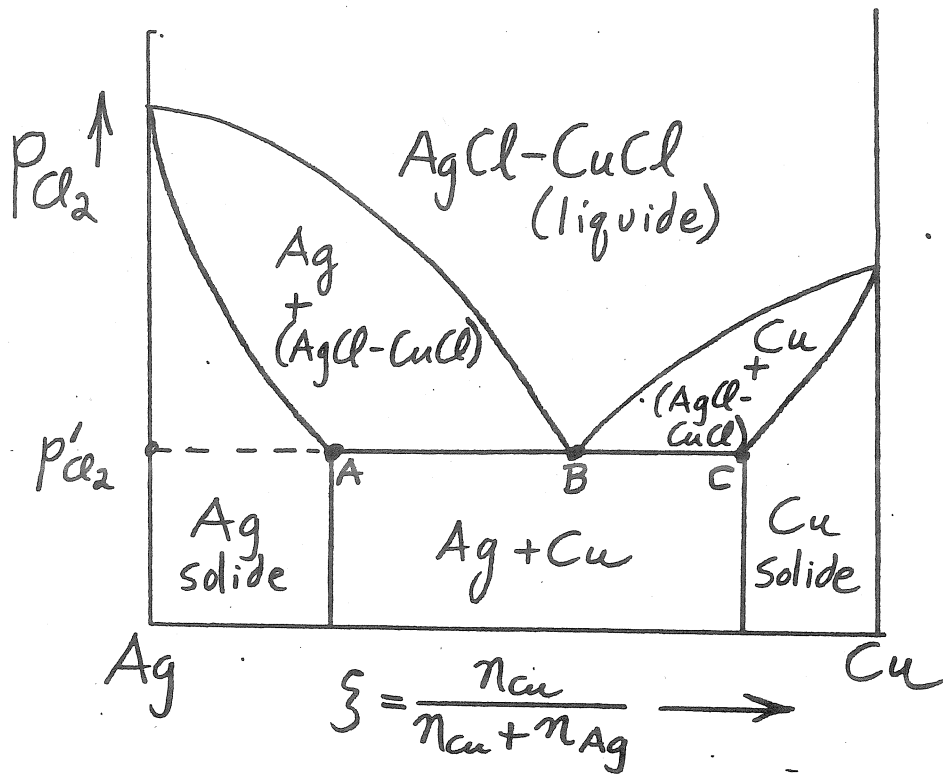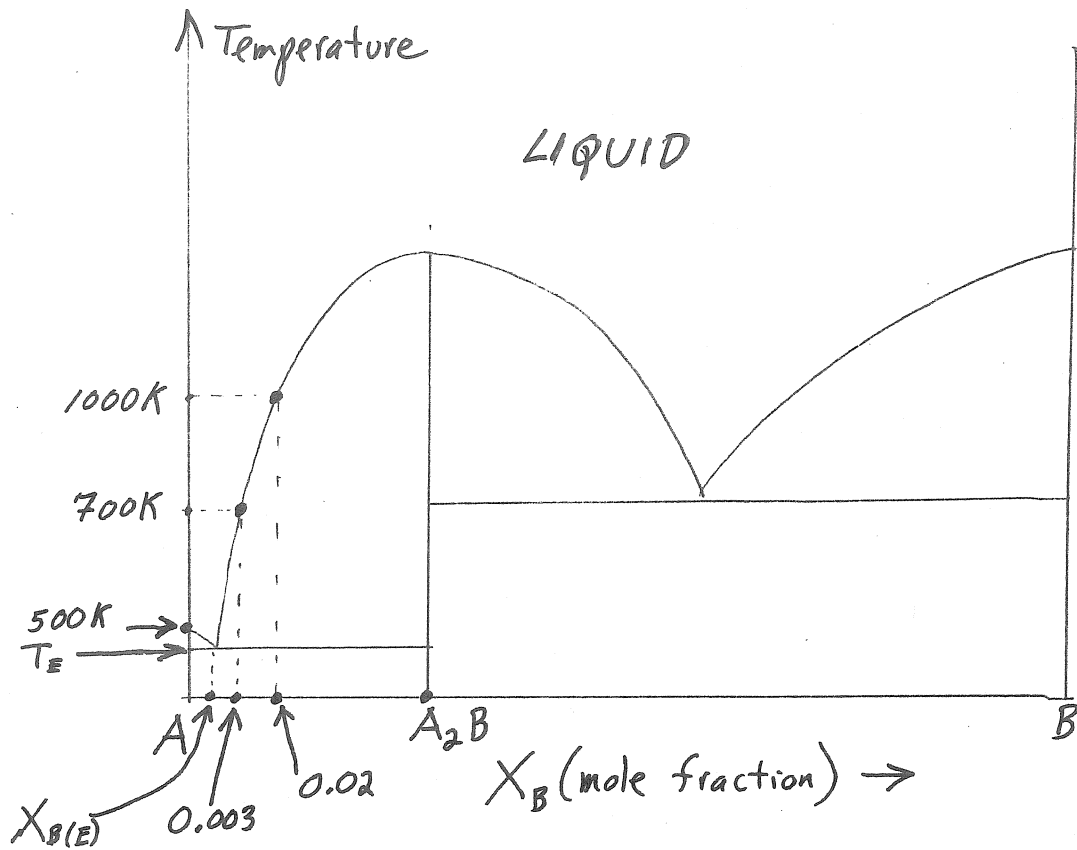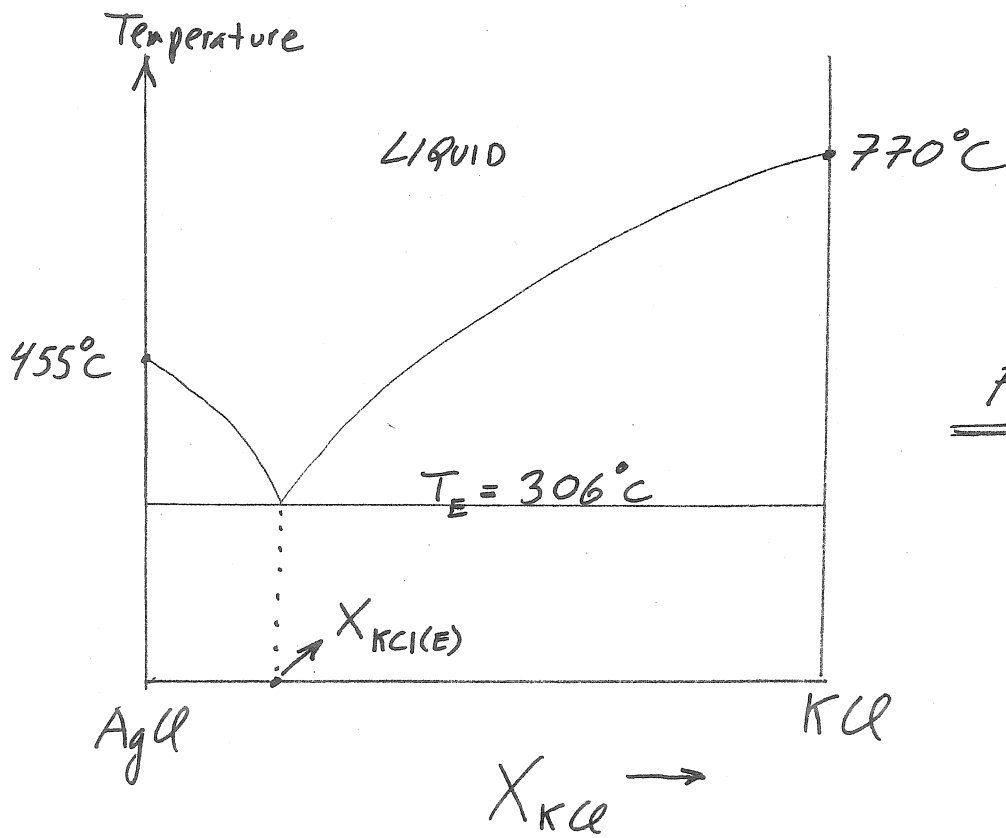
P_{Cl_2}

$AgCl-CuCl$
(liquide)

Ag
$+$
$(AgCl-CuCl)$

Cu
$+$
$(AgCl-CuCl)$

P'_{Cl_2}

A   B   C

Ag
solide

$Ag + Cu$

Cu
solide

Ag Cu

$$\xi = \frac{n_{Cu}}{n_{Cu} + n_{Ag}} \longrightarrow$$

Figure 1

Figure 2

Figure 3

6

ÉCOLE POLYTECHNIQUE

Département de génie chimique

Programme de matériaux

MET 6208

ÉNERGÉTIQUE DES SOLUTIONS

CONTRÔLE II

Jeudi, le 15 décembre 2005

9:30 - 12:30

NOTES :
- *All documentation permitted*
- *There are 6 questions*

Le professeur : Arthur D. Pelton

Question 1   (4 points)

For each of the following solutions, propose a structural model in one or two sentences.

(i)   Liquid with 80% MgO, 10% Na_2O, 10% SiO_2 .

(ii) A liquid solution of $AlCl_3$ and $FeCl_3$.

(iii) A solution of oxygen in liquid iron.

(iv) A solution of oxygen in water.

(v)   Liquid with 90% SiO_2 , 5% CaO, 5% MgO

(vi) Liquid with 80 mol % SiO_2, 20 mol % $NaAlO_2$.

(vii) Solid solution of $FeTi_2O_5$ and Ti_3O_5.

(viii) Solid dilute solution of $CaCl_2$ in NaCl ($X_{CaCl_2} < 0.01$).

(ix) Liquid solution $X_{Fe} = 0.9$, $X_S = 0.1$.

Question 2   (3 points)

The ability of a liquid oxide slag to dissolve sulfur (its "sulfide capacity") is an important property in the iron and steel industry.

Consider a liquid slag solution CaO-SiO_2 in the basic region (high CaO content, $X_{CaO} > 2/3$) which contains a small amount of sulfur in solution. The dissolved sulfur is in the form of S^{2-} ions. Treat the solution as a ternary solution with components CaO-SiO_2-CaS (where X_{CaS} is small and $X_{CaO} > 2/3$). Using a simple "complex ion" model, and stating all your assumptions, write expressions for the activities of CaO and CaS (a_{CaO} and a_{CaS}) as functions of X_{CaO} , X_{SiO_2} and X_{CaS} .

Write an expression giving the sulfur content X_{CaS} as a function of the ratio (X_{CaO}/X_{SiO_2}), P_{O_2} , P_{S_2} and the Gibbs energies of pure CaO, CaS, O_2 and S_2.

Question 3   (3 points)

You have obtained optimized binary parameters for binary solutions in the A-B, B-C and C-A systems using the Bragg-Williams approximation. You then use a geometric technique (Kohler, Toop or Muggianu) to estimate the Gibbs energy of the A-B-C ternary solution from these binary parameters. You then compare your calculated (i.e. estimated) values of the partial excess Gibbs energy of component $A\left(g_A^E = RT \ln \gamma_A\right)$ with experimental values at several compositions in the ternary solution. You find that the calculated values are slightly less negative than the experimental values. Therefore you add a negative empirical "ternary parameter" $\omega X_A X_B X_C$ (with $\omega < 0$) to your expression for g^E in the ternary solution in order to stabilize the solution and decrease g_A^E. At ternary compositions where X_A is small, you get the desired effect. However, when X_A is relatively large you discover, to your horror and dismay, that g_A^E has become __less__ negative. That is, including the __negative__ excess term has caused g_A^E to __increase__.

Explain this result clearly by means of a calculation.

Question 4   (3points)

Liquid salt solutions are usually modeled with a two-sublattice model. Strictly speaking, this is an approximation because a liquid, lacking long-range-ordering, cannot be said to consist of more than one sublattice.

(i)   Write an equation for the extensive Gibbs energy of a molten salt solution of NaCl and KCl, in the Bragg-Williams approximation using a two-sublattice model, as a function of the numbers of moles and mole fractions of NaCl and KCl (n_{NaCl}, n_{KCl}, X_{NaCl}, X_{KCl}) and of the molar Gibbs energies of the pure salts, g^o_{NaCl} and g^o_{KCl}. Ignore excess Gibbs energy terms.

(ii)   Write an equation, using the quasichemical model, for the extensive Gibbs energy of a solution of Na, K and Cl atoms on one sublattice as a function of the numbers of moles of the atoms (n_{Na}, n_K, n_{Cl}), the numbers of moles and mole fractions of the nearest-neighbour pairs ($n_{Na\text{-}Na}$, $n_{Na\text{-}Cl}$, $n_{K\text{-}K}$, $n_{K\text{-}Cl}$, $n_{Cl\text{-}Cl}$, $n_{Na\text{-}K}$; $X_{Na\text{-}Na}$, $X_{Na\text{-}Cl}$, $X_{K\text{-}K}$, $X_{K\text{-}Cl}$, $X_{Cl\text{-}Cl}$, $X_{Na\text{-}K}$), the molar Gibbs energies g^o_{Na}, g^o_K and g^o_{Cl}, and the Gibbs energy changes $\Delta g_{Na\text{-}Cl}$ and $\Delta g_{K\text{-}Cl}$ of the pair-exchange reactions:
$$(Na - Na) + (Cl - Cl) = 2\,(Na - Cl); \quad \Delta g_{Na\text{-}Cl}$$
$$(K - K) + (Cl - Cl) = 2\,(K - Cl); \quad \Delta g_{K\text{-}Cl}$$
(For the pair exchange reaction (Na-Na) + (K-K) = 2 (Na-K), assume that $\Delta g_{Na\text{-}K} = 0$.)

(iii)   In the limit where $\Delta g_{Na\text{-}Cl}$ and $\Delta g_{K\text{-}Cl}$ are extremely negative, and along the stoichiometric join between NaCl and KCl (that is, where ($n_{Na} + n_K) = n_{Cl}$) show, by making the appropriate substitutions, that the quasichemical equation of part (ii) reduces exactly to the two-sublattice Bragg-Williams approximation of part (i).

Question 5   (3points)

The compounds Fe_2SiO_4 and Mg_2SiO_4 with the olivine crystal structure are miscible at all compositions. There are two distinct crystallographic sites, the "M1" and "M2" sites, which can be occupied by the Fe^{2+} and Mg^{2+} ions. The sublattice structure of the solution can thus be written as:
$$(Fe^{2+}Mg^{2+})^{M1}\ (Fe^{2+}Mg^{2+})^{M2}\ (Si)\ (O_4)$$
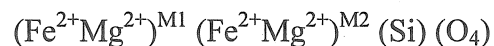
Note that the M1 and M2 sites have different crystallographic environments. Hence, the energies of $(Mg)^{M1}\,(Fe)^{M2}(Si)\,(O_4)$ and $(Fe)^{M1}(Mg)^{M2}\,(Si)\,(O_4)$ are in general not equal.

Write an expression for the molar Gibbs energy of the Fe_2SiO_4-Mg_2O_4 solutions using the Compound Energy Formalism. (The g^E excess terms can be ignored.) Define all variables clearly. The "formalism parameters" are the Gibbs energies, g^o_i, of the end-members.

Propose a set of "model parameters" which have physical significance. Explain this physical significance. Relate the formalism parameters to these model parameters and to the Gibbs energies of the pure real components. If the only available experimental information were the Gibbs energies of pure Fe_2SiO_4 and Mg_2SiO_4, how would you estimate the formalism parameters?

Question 6 (3points)

Write an expression for the molar Gibbs energy of a ternary liquid solution A-B-C using the Bragg-Williams and Kohler approximations when the excess Gibbs energies of the binary liquid solutions are given by: $g_{A-C}^{E} = g_{B-C}^{E} = 0$ and $g_{A-B}^{E} = \omega X_A X_B$

Show clearly by a calculation that, if ω is sufficiently negative, a miscibility gap will appear, centered on the join between the equimolar "$A_{1/2}B_{1/2}$" composition and pure C as shown in the figure.
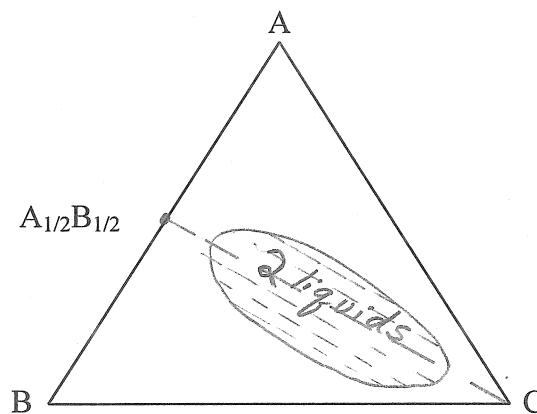
ÉCOLE POLYTECHNIQUE

Département de génie chimique

Programme de matériaux

MET 6208

ÉNERGÉTIQUE DES SOLUTIONS

CONTRÔLE II

Mardi, le 28 novembre 2006

13:45 - 16:45

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

Le professeur : Arthur D. Pelton

Question 1 (4 points)
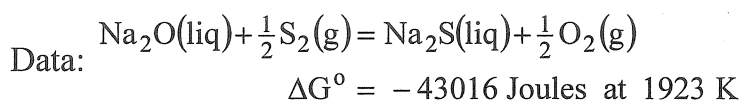
The system $LaCl_3$-LaF_3 is a simple eutectic system with no solubility in the solid phases. The eutectic temperature is $654°C$. Assume a regular term for the enthalpy of mixing: $\Delta h = \omega X_{LaCl_3} X_{LaF_3}$ and assume that the entropy of mixing is given by an ideal Temkin ionic model.

Calculate the regular solution parameter ω as well as the composition of the eutectic point.

Data:
$$\Delta g^o_{fusion(LaCl_3)} = 54392 - 48.092\ T\ J/mol$$
$$\Delta g^o_{fusion(LaF_3)} = 50208 - 28.430\ T\ J/mol$$

Question 2 (4 points)

(i)   A liquid slag contains 10 mol % SiO_2, 88 mol % Na_2O and 2 mol % Na_2S. Calculate approximate expressions for the activities of Na_2O and Na_2S. State all your assumptions clearly.

(ii) A slag of composition 10 mol % SiO_2, 90 mol % Na_2O is equilibrated at 1923 K with an atmosphere in which $P_{O_2} = 10^{-4}$ bar and $P_{S_2} = 10^{-6}$ bar. Calculate the sulfur content of the slag.

Data:
$$Na_2O(liq) + \tfrac{1}{2}S_2(g) = Na_2S(liq) + \tfrac{1}{2}O_2(g)$$
$$\Delta G^o = -43016\ Joules\ at\ 1923\ K$$

Question 3 (4 points)

For each of the following solutions, propose a structural model in one or two sentences.

(a)   10% $HfCl_4$, 90% $RbCl$ (liquid)

(b) $Ag_{0.501}Br_{0.499}$ (solid)

(c)   45% Fe, 50% Mn, 5% C (solid)

(d)   10% GeO_2 + 90% CaO (liquid)

(e)   90% B_2O_3 + 10% CaO (glass)

(f)   1% $PbCl_2$ in NaCl (solid)

(g)   1% $PbCl_2$ in NaCl (liquid)

(h)   A liquid solution with $X_{Fe} = 0.75$, $X_S = 0.25$

(i)   Oxygen dissolved in liquid Fe

(j)   80% $MgCl_2$, 20% KCl (liquid)

Question 4 (4 points)

For a solution of components A-B, a one-sublattice quasichemical model is written as follows:

$$g = X_A g_A^o + X_B g_B^o$$
$$- R\left(X_A \ln X_A + X_B \ln X_B\right) - \frac{RZ}{2}\left(X_{AA} \ln \frac{X_{AA}}{X_A^2} + X_{BB} \ln \frac{X_{BB}}{X_B^2} + X_{AB} \ln \frac{X_{AB}}{2X_A X_B}\right)$$
$$+ ZX_{AB}\,\omega/4$$

That is, $Z_A = Z_B = Z$ = constant, and ω is a constant independent of T and composition.

(i)   If $\omega \ll 0$, show that the enthalpy of mixing has a "V-shape" consisting of two nearly straight lines, and that the entropy of mixing has an "m-shape" with a minimum at $X_A = X_B = \frac{1}{2}$.

(ii) For what value of Z will the entropy of mixing be equal to zero at $X_A = X_B = \frac{1}{2}$ when $\omega = -\infty$? Explain why this is not the case for other values of Z.

Question 5 (4 points)

The molten salt solution (Li, Rb)(F, Cl) is modelled by the equation:

$$g = \left(y_{Li}y_F\,g_{LiF}^o + y_{Li}y_{Cl}\,g_{LiCl}^o + y_{Rb}y_F\,g_{RbF}^o + y_{Rb}y_{Cl}\,g_{RbCl}^o\right)$$
$$+ RT\left(y_{Li} \ln y_{Li} + y_{Rb} \ln y_{Rb} + y_F \ln y_F + y_{Cl} \ln y_{Cl}\right) \qquad\qquad [1]$$
$$- y_{Li}y_{Rb}\,y_F y_{Cl}\,\left(\Delta G^{exchange}\right)^2/ZRT$$

where the y_i are site fractions. That is, second-nearest-neighbour (binary) terms are assumed to be negligible, and short-range-ordering is approximated by the final term. The phase diagram along the LiF-RbCl stable diagonal is sketched in the accompanying figure.

Derive an equation giving the critical temperature T_C as a function of $\Delta G^{exchange}$, Z, and X_{RbCl}, where $X_{RbCl} = n_{RbCl} / (n_{RbCl} + n_{LiF})$ is the mole fraction of RbCl in the LiF-RbCl pseudobinary system. Firstly, derive this equation ignoring the final term in Equation [1]. Then derive the equation including this final term.

Show that including the final term always lowers T_C. Explain in words why this is so.
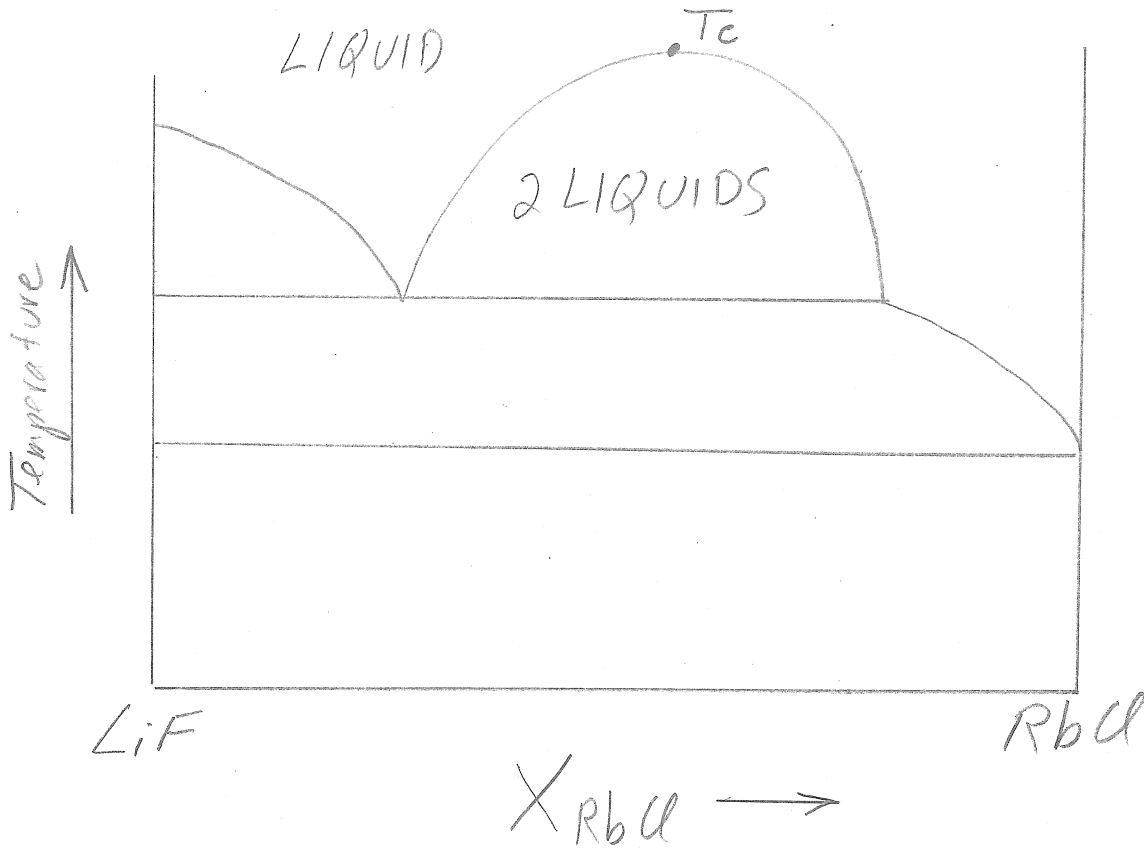
Phase Diagram along the pseudobinary
LiF-RbCl join

ÉCOLE POLYTECHNIQUE

Programme de métallurgie et génie des matériaux

MET 6208

ÉNERGÉTIQUE DES SOLUTIONS

Examen Final

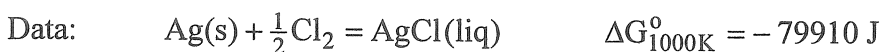mercredi, le 20 décembre 2006

13 :45 - 16 :45

NOTES :
- **Toute documentation premise (open book exam)**
- **Tous moyens de calcul permis (all calculators permitted)**
- **Il y a 5 questions (there are 5 questions)**

Le professeur : Arthur D. Pelton

Question 1 (4 points)

An equilibrium diagram is sketched in the accompanying figure. The diagram is isothermal at T=1000 K. The vertical axis is the equilibrium chlorine pressure while the horizontal axis is the molar metal ratio:

$\xi = n_{Cu}/(n_{Au} + n_{Cu})$. That is, for the metallic phases, $\xi = X_{Cu}$, and for the AgCl-CuCl phase, $\xi = X_{CuCl}$. The metallic phases are Henrian solutions with $RT \ln \gamma^o_{Ag} = 18450$ J/mol in the "Ag solid" phase and $RT \ln \gamma^o_{Ag} = 27780$ J/mol in the "Cu solid" phase. The liquid salt solution is ideal. Calculate the pressure P'_{Cl_2} when the three phases are at equilibrium at 1000 K. Calculate also the three equilibrium compositions ξ of the three phases at points A, B and C.

Data: $Ag(s) + \frac{1}{2}Cl_2 = AgCl(liq)$ $\Delta G^o_{1000K} = -79910$ J

$Cu(s) + \frac{1}{2}Cl_2 = CuCl(liq)$ $\Delta G^o_{1000K} = -91840$ J

Question 2 (4 points)

In a binary system A-B, the excess Gibbs energy is observed to pass through a minimum value g^E_{min} at a composition $X_{B(min)}$ where $X_{B(min)} \neq 0.5$. In order to reproduce the observed values of g^E_{min} and $X_{B(min)}$, a two-parameter model is required. Two possible models are:

(i) A sub-regular solution model; (ii) a regular solution model with equivalent fractions (that is, with $Z_A \neq Z_B$).

(a)   Write out fully the equations for the molar Gibbs energy for both models (i) and (ii).

(b)   Suppose that, in each model, parameters are chosen so as to reproduce the experimental point at g^E_{min} at $X_{B(min)}$. Although both models reproduce this one point, the curves of g^E versus $X_B (0 \leq X_B \leq 1)$ at other compositions will be different in the two models. Discuss this difference with the aid of a sketch, particularly as regards the resultant partial Gibbs energies. How might you decide which model to use for a given system?

Question 3 (4 points)

For a solution of components A-B, the following equation is proposed for the molar Gibbs energy:

$$g = \left(X_A g^o_A + X_B g^o_B\right)$$
$$+RT\left(X_A \ln X_A + X_B \ln X_B\right) + RT\left(X_{AA} \ln \frac{X_{AA}}{X_A^2} + X_{BB} \ln \frac{X_{BB}}{X_B^2} + X_{AB} \ln \frac{X_{AB}}{2X_A X_B}\right)$$
$$+ X_{AB}\omega_1/2 + X_A X_B \omega_2$$

If $\omega_2 = 0$ (and $\omega_1 \neq 0$), then this is just the modified quasichemical model (with $Z = 2$). If $\omega_1 = 0$ (and $\omega_2 \neq 0$), then this is just a regular solution (Bragg-Williams) model. The physical interpretation of this equation is that ω_1 represents the nearest-neighbour interactions, while ω_2 represents the longer-range interactions.

(a) Calculate the numerical value of g at $X_A=X_B=0.5$ at $T = 1000$ K for the following three cases:

   (i) $\omega_1 = 0$, $\omega_2 = -20\,\text{kJ}/\text{mol}$

   (ii) $\omega_2 = 0$, $\omega_1 = -20\,\text{kJ}/\text{mol}$

   (iii) $\omega_1 = -10\,\text{kJ}/\text{mol}$, $\omega_2 = -10\,\text{kJ}/\text{mol}$

(b) Desscribe in words and/or with a sketch how the <u>shapes</u> of the curves of g versus $X_B \left(0 \leq X_B \leq 1\right)$ differ in these three cases. (A calculation is not required.)

Question 4   (4 points: 0.4 point for each correct reply and - 0.2 point for each incorrect reply)

The limiting slope of the liquidus curve at $X_A = 1$ when a solute B is dissolved in a solvent A is given by the equation:

$$\left(\frac{dX_B}{dT}\right)_{X_A=1} = -\,\Delta h^o_{fusion(A)}\Big/\!\left(T^o_{fusion(A)}\right)^2 \nu$$

(assuming no solubility of B in solid A), where ν is the number of "foreign" independent "particles" introduced per mole of B.

What values of ν will be observed for the following (liquid) solvent/solute pairs:

	solvent	solute
(a)	Fe	N_2
(b)	H_2O	N_2
(c)	NaCl	$CaBr_2$
(d)	NaCl	$CaCl_2$
(e)	CaO	SiO_2
(f)	SiO_2	CaO
(g)	SiO_2	Na_2O
(h)	SiO_2	$NaAlO_2$
(i)	FeS	S_2
(j)	Ca_2SiO_4	Na_2O

Question 5 (4 points)

In ordered Cu_3Au alloys, the Au atoms occupy the corners of the cubic unit cell while the Cu atoms occupy the centers of the faces. As the temperature is increased, substitutional disordering occurs progressively, with Cu atoms occupying Au positions and vice-versa until, above a critical temperature T_c, the alloy becomes completely disordered with Au and Cu atoms distributed randomly over the sites of a face-centered-cubic lattice.

Write an equation for the molar Gibbs energy of stoichiometric Cu_3Au using the Compound Energy Formalism. Ignore short-range-ordering and second-nearest-neighbour interactions. Your equation should contain an ordering parameter α, and end-member Gibbs energies. Show the relationship between the end-member Gibbs energies (the "formalism parameters") and "model parameters" which have physical significance. Show how to calculate α as a function of temperature, and show how to calculate T_c.