ÉCOLE POLYTECHNIQUE

Département de génie chimique
Programme de métallurgie

MET 6208
ÉNERGÉTIQUE DES SOLUTION

Contrôle II
Lundi, le 30 novembre, 2015
10:30 – 13:30

NOTES:
- All documentation permitted (open book exam)
- There are 6 questions and 4 figures
- **All questions are of equal value**

Le professeur: Arthur D. Pelton

Question 1

The phase diagram of a system A-B-C at constant T and P is sketched in Fig. 1.
Sketch the corresponding phase diagram with the chemical potential, μ_A, of component A as the y-axis and the molar ratio $n_C/(n_B + n_C)$ as the x-axis (at the same constant T and P.)

Question 2

In a solution with component A-B-C, the integral molar excess Gibbs energies in the three binary sub-systems are given by:

$$g^E_{AB} = X_A X_B (a_1 + b_1 (X_B - X_A))$$
$$g^E_{BC} = X_B X_C (a_2 + b_2 (X_C - X_B))$$
$$g^E_{CA} = X_C X_A (a_3 + b_3 (X_A - X_C))$$

where the X_i are the mole fractions and the a_i and b_i are constants.

Using a Toop-Muggianu model with A as the asymmetric component (see Fig. 2), write an expression for g^E in the ternary solution as a function of composition.

Question 3

$LaCl_3$ dissolves in dilute solution in solid KCl with the formation of La^{3+} cations and cationic vacancies.

(a) Write an expression for the activity of KCl in solid solution, as a function of the overall mole fraction of $LaCl_3$, X_{LaCl3}, at very low concentrations of $LaCl_3$ when the La^{3+} cations and the vacancies are randomly distributed.

(b) Write an expression for the activity of KCl in solid solution, as a function of the overall mole fraction of $LaCl_3$, X_{LaCl3}, at less dilute concentrations of $LaCl_3$ when the La^{3+} cations and the vacancies are highly associated (due to coulombic attraction) to form associates consisting of a lanthanum cation and two vacancies.

(c) Write an expression for the activity of KCl in a liquid solution, as a function of the overall mole fraction of $LaCl_3$, X_{LaCl3}, at low concentrations of $LaCl_3$.

Question 4

In a binary liquid solution with components A-B, it is observed that a plot of the excess Gibbs energy, g^E, versus composition has a maximum at a mole fraction $X_B = 0.2$ and is convex at all compositions (that is, the second derivative d^2g^E/dX_B^2 is everywhere negative) as shown in Fig. 3.

A regular solution model gives a convex curve, but with a maximum at $X_B = 0.5$. In order to shift the maximum to $X_B = 0.2$ it is proposed to add a second "sub-regular" term to the expression for

g^E. That is:

$$g^E = X_A X_B (a + bX_B)$$

(a) Show that it is not possible to shift the maximum in this way while still maintaining a curve which is everywhere convex.
(b) Show how it is possible to shift the maximum while still maintaining a convex curve through the use of "equivalent fractions".

Question 5

Consider a one-dimensional crystal with components A-B at the equimolar composition, $X_A = X_B = 0.5$.

(a) The crystal is described by a single-sublattice model with short-range-ordering (SRO). At a given temperature, the pair fraction of A-B pairs is $X_{AB} = 0.6$. A given lattice site is occupied by an A atom. What is the probability that a lattice site 1000 interatomic distances from this site is also occupied by an A atom.
(b) The crystal is described by a two-sublattice model (that is, by long-range-ordering (LRO)) with substitutional disorder. That is, some A-lattice sites are occupied by B atoms, and vice versa. At a given temperature the fraction of A-lattice site occupied by B atoms is 0.2. A given lattice site is occupied by an A atom. What is the probability that a lattice site 1000 interatomic distances from this site is also occupied by an A atom?
(c) In the case of SRO (as in part (a)) show that the solution becomes more disordered as the temperature increases, but that complete disorder is only approached asymptotically at $T = \infty$. (You may assume a simplified model taking account only of nearest-neighbour pair-bond energies.)
(d) In the case of LRO (as in part (b)) show that the solution becomes more disordered as the temperature increases, and that the solution becomes completely disordered above a finite transition temperature. (You may assume a simplified model taking account only of nearest-neighbour pair-bond energies.)

Question 6

The liquid phase in the $AlCl_3$-LiCl-KCl system exhibits an immiscibility gap centered approximately on a line passing from the LiCl-corner of the Gibbs triangle to the equimolar ($X_{KCl} = X_{AlCl_3} = 0.5$) composition in the KCl-$AlCl_3$ binary system, with tie-lines approximately parallel to this line, as sketched in Fig. 4.

(a) What does this tell you about the probable structure of the solution?
(b) What model would you propose to describe the liquid solution at all compositions? (Write an expression for g^E showing the most important terms and model parameters.)
(c) If you only need to describe the solution at relatively low concentrations of $AlCl_3$, can you propose a simplified model? (Write an expression for g^E showing the most important terms and model parameters.)

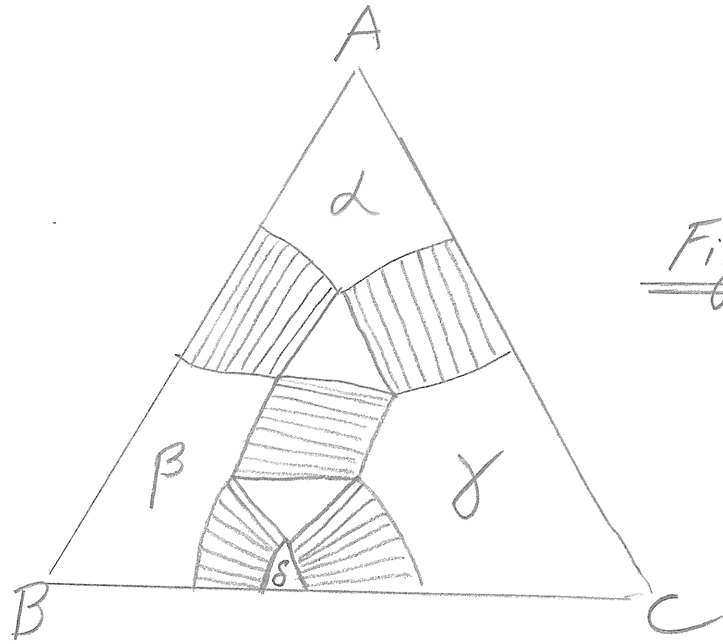

Fig. 1 (Question 1)

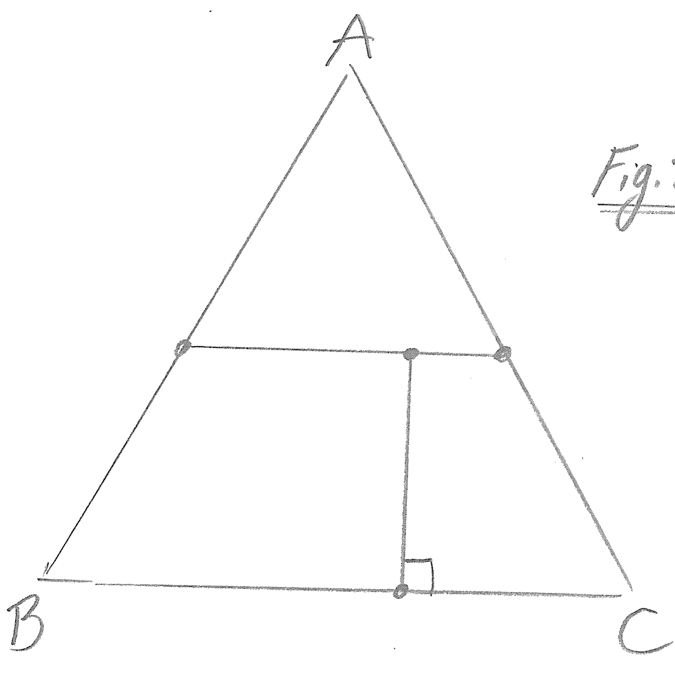

Fig. 2 (Question 2)

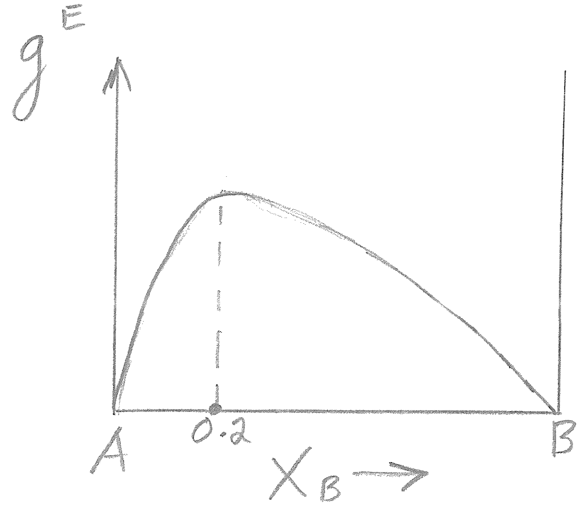

Fig. 3 (Question 4)

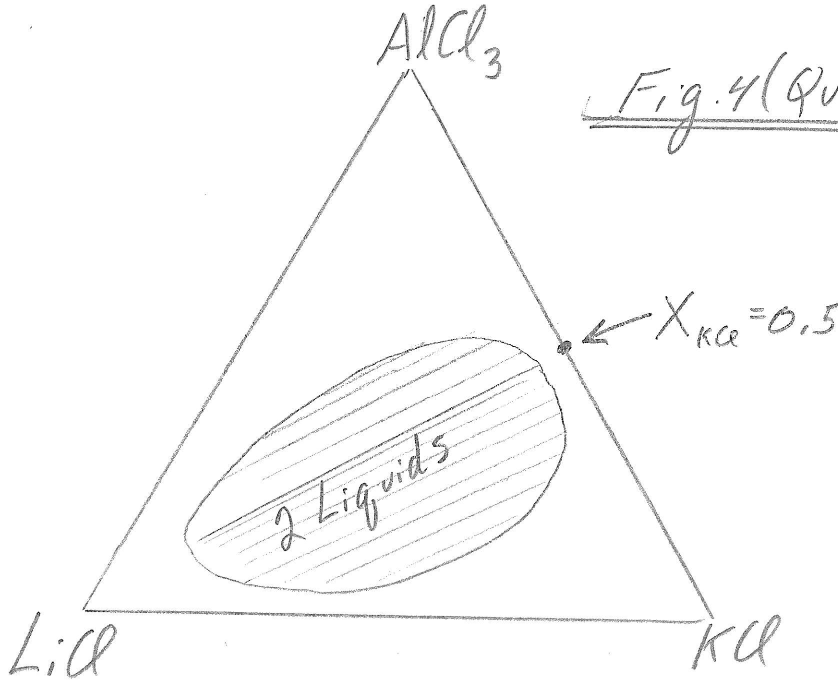

Fig. 4 (Question 6)

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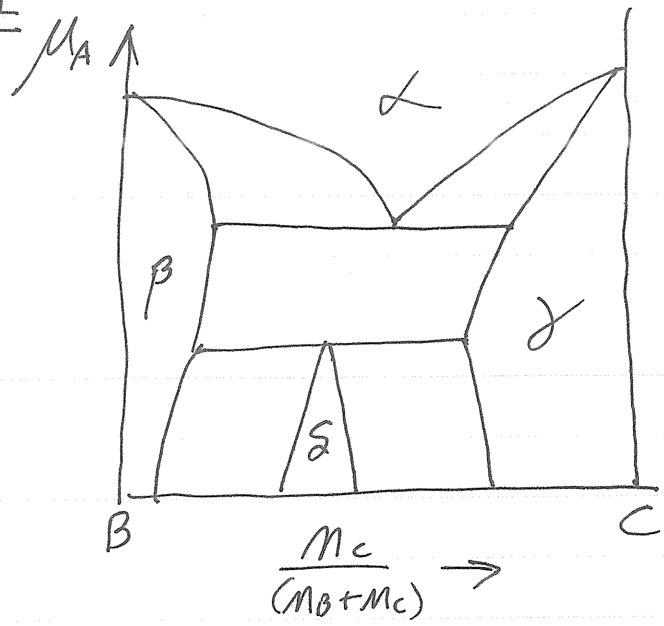
Question 1



Question 2

$$g^E = X_A X_B \left(a_1 + b_1(1-2X_A)\right) + X_C X_A \left(a_3 + b_3(2X_A - 1)\right) + X_B X_C \left(a_2 + b_2(X_C - X_B)\right)$$

Question 3

(a) Moles of cation sites $= (X_{KCl} + 3X_{LaCl_3})$

$$a_{KCl} = X_{K^+} = \frac{X_{KCl}}{X_{KCl} + 3X_{LaCl_3}} = 1 - \frac{3X_{LaCl_3}}{X_{KCl} + 3X_{LaCl_3}} \approx \underline{(1 - 3X_{LaCl_3})}$$

(since $X_{KCl} \gg X_{LaCl_3}$)

(b) Total moles of mixing species is $(X_{KCl} + X_{associates}) = (X_{KCl} + X_{LaCl_3})$

Hence $a_{KCl} = \underline{(1 - X_{LaCl_3})}$

(c) Temkin model. $a_{KCl} = \underline{(1 - X_{LaCl_3})}$

Question 4

(a) $y = X_A X_B (a + bX_B)$ (where $y = g^E$)

$= aX_B + (b-a)X_B^2 - bX_B^3$ (since $X_A = 1 - X_B$)

$(dy/dX_B) = a + 2(b-a)X_B - 3bX_B^2$

Set $(dy/dX_B) = 0$ when $X_B = 0.2$

$a + 2(b-a)(0.2) - 3b(0.2)^2 = 0$

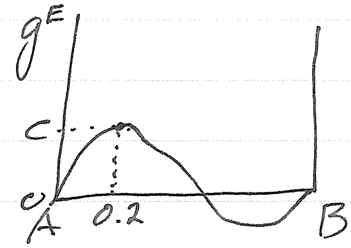
$a = -0.467b$

Let $g^E = C$ (max. value) at $X_B = 0.2$

$C = 0.2(0.8)(a + 0.2b) = 0.16(0.2 - 0.467)b \Rightarrow b = -23.40C$

Therefore: $a = 10.93C$

$$g^E = \underline{X_A X_B (10.93 - 23.40X_B)C}$$



(b) $g^E = a Y_A Y_B$

where $Y_A = \left(\frac{X_A}{X_A + 4X_B}\right)$ $Y_B = \left(\frac{4X_B}{X_A + 4X_B}\right)$

$Y_A = Y_B = 0.5$ when $X_B = 0.2$

Maximum is at $Y_B = 0.5$, i.e. at $X_B = 0.2$

$$\frac{dg^E}{dX_B} = \left(\frac{dg^E}{dY_B}\right)\left(\frac{dY_B}{dX_B}\right)$$ Clearly, $(dg^E/dY_B) < 0$ everywhere

$$\frac{dY_B}{dX_B} = \left(\frac{4}{X_A + X_B} - \frac{4(4X_B)}{(X_A + 4X_B)^2}\right)$$

$$= \frac{4X_A + 16X_B - 16X_B}{(X_A + 4X_B)^2} > 1$$ at all compositions

Therefore $(dg^E/dX_B) < 0$ everywhere.

Question 5

(a) Probability $= 0.5$

(b) Probability $= 0.8$

(c) Set $Z_A = Z_B = 2$

$$(A-A) + (B-B) = 2(A-B); \quad \Delta g_{AB} < 0$$

Using one-dimensional MQM

$$K = X_{AB}^2 / (X_{AA} \cdot X_{BB}) = 4 \exp(-\Delta g_{AB}/RT)$$

When $K = 4$; $X_{AB} = 2X_A X_B$, $X_{AA} = X_A^2$, $X_{BB} = X_B^2$

that is, the solution is completely disordered

This occurs only when $T = \infty$

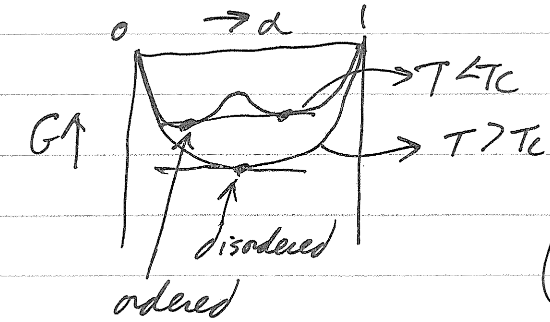
(d)
$$\underset{(1-\alpha)}{A_A} + \underset{(1-\alpha)}{B_B} = \underset{\alpha}{A_B} + \underset{\alpha}{B_A} \; ; \; 2\omega = (2g^\circ_{AB} - g^\circ_{AA} - g^\circ_{BB}) < 0$$

Continue as in handout #40 on website

$$\Delta S = 2RT(\alpha \ln \alpha + (1-\alpha)\ln(1-\alpha))$$

$$G = \alpha^2 g^\circ_{BA} + (1-\alpha)^2 g^\circ_{AB} + \alpha(1-\alpha)(g^\circ_{AA} + g^\circ_{BB}) - T\Delta S$$

Set $(\partial G/\partial \alpha) = 0 \Rightarrow \ln\left(\frac{\alpha}{1-\alpha}\right) = \exp(-\omega(2\alpha - 1)/RT)$



$$\left(\frac{d^2G}{d\alpha^2}\right)_{\alpha=\frac{1}{2}} = 4\omega + 2RT\left(\frac{1}{\alpha} + \frac{1}{1-\alpha}\right) = 4\omega + 8RT$$

$$\left(\frac{d^2G}{d\alpha^2}\right)_{\alpha=\frac{1}{2}} = 0 \text{ at } T_c \qquad \underline{T_c = -\omega/2R}$$

Since $\omega < 0$, $T_c > 0$

$$T < T_c \Rightarrow \left(\frac{d^2G}{d\alpha^2}\right)_{\alpha=\frac{1}{2}} < 0 \text{ (ordered)}$$

$$T > T_c \Rightarrow \left(\frac{d^2G}{d\alpha^2}\right)_{\alpha=\frac{1}{2}} > 0 \text{ (disordered)}$$

S. [illegible]

Question 6

(a) Structure is probably highly ordered at the $KAlCl_4$ composition and less so at the $KLiCl_4$ composition

(b) MQM one-sublattice (other sublattice occupied only by Cl^-)

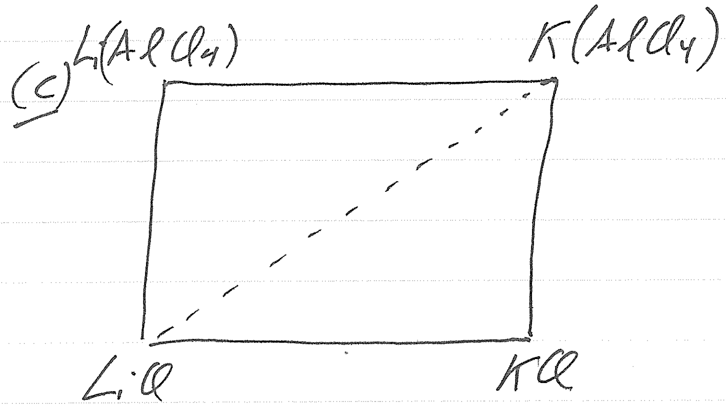
$$(Al^{3+}, K^+, Li^+)(Cl^-)$$

$$(Al\text{-}Al) + (Li\text{-}Li) = 2(Al\text{-}Li) \quad \Delta g_{AlLi} < 0$$

$$(Al\text{-}Al) + (K\text{-}K) = 2(Al\text{-}K) \quad \Delta g_{AlK} \ll 0$$

$$Z_{Al} = Z_{Li} = Z_K$$

$$G = \sum n_m g_m^\circ - T\Delta S^{config} + \sum_{n>m}\sum n_{mn}(\Delta g_{mn}/2)$$

(c) 

$$(Li^+, K^+)(Cl^-, AlCl_4^-)$$

$$G = \left((y_{Li} \cdot y_{Cl}) g^\circ_{LiCl} + \cdots\cdots\right)$$
$$+ RT(y_{Li} \ln y_{Li} + y_K \ln y_K) + RT(y_{Cl} \ln y_{Cl} + y_{AlCl_4} \ln y_{AlCl_4})$$
$$- y_{Li} y_K y_{Cl} y_{AlCl_4} (\Delta g^{EXCH})^2 / ZRT$$

Most important parameter is Δg^{EXCH} which is < 0 for the reaction:

$$KCl + Li(AlCl_4) = K(AlCl_4) + LiCl \; ; \; \Delta G^{EXCH} < 0$$