ÉCOLE POLYTECHNIQUE

Département de génie chimique

Programme de matériaux

MET 6208

ÉNERGÉTIQUE DES SOLUTIONS

CONTRÔLE I

Mercredi le 19 octobre 2011

10h00 - 13h00

NOTES:

- *Open book exam*
- *There are 6 questions and 2 figures*

Le professeur : Arthur D. Pelton

Question 1 (3 points)

$BaCO_3$ (solid) is heated under an atmosphere of CO_2. When $p_{CO_2} = 0.10$ bar, the temperature of decomposition is observed to be 1566 K, and when $p_{CO_2} = 1.00$ bar, the decomposition temperature is 1820 K.

Calculate ΔH^o and ΔS^o of the following reaction, stating any assumptions which you make:

$$BaO\,(solid) + CO_2\,(gas) = BaCO_3\,(solid)$$

Question 2 (3 points)

A metallic liquid alloy Ag-Cu with $X_{Ag} = 0.8$ is at equilibrium at 1600 K with a matte which is an ideal liquid solution of $AgS_{1/2}$ and $CuS_{1/2}$. At this temperature and composition, the activities of Ag and Cu in the metal alloy are 0.8433 and 0.3088 respectively (with respect to pure liquid Ag and Cu as standard states.) Calculate the equilibrium composition of the matte.

$$Ag\,(liq.) + \tfrac{1}{4}S_2(gas) = AgS_{1/2}\,(liq.)$$
$$\Delta G^o = -1771 \text{ J at 1600 K}$$
$$Cu\,(liq.) + \tfrac{1}{4}S_2\,(gas) = CuS_{1/2}\,(liq.)$$
$$\Delta G^o = -787 \text{ J at 1600 K}$$

Question 3 (3 points)

The integral molar enthalpy of mixing of a liquid solution with components A and B is represented by a regular solution equation:

$$\Delta h = \omega X_A X_B \text{ J/mol}$$

where ω is a constant.

Solution I consists of 2 moles of A and 8 moles of B (already mixed).
Solution II consists of 7 moles of A and 3 moles of B (already mixed).
Solution I and II are mixed isothermally. What is the enthalpy change associated with this process?

Question 4 (4 points)

The integral molar excess Gibs energy of a solution with components A and B is represented by the equation:

$$g^E = (a + bT + cT\ln T)\, X_A X_B$$

where a, b, c are constants, independent of temperature and composition, X_A and X_B are the mole fractions, and T is temperature in kelvins.

Derive equations for:

(i) the chemical activity of component A, a_A.
(ii) the partial molar enthalpy of mixing of component A, Δh_A
(iii) the partial molar entropy of mixing of component A, Δs_A.
(iv) the excess partial molar heat capacity c_p^E.

Question 5 (4 points)

An equilibrium diagram for the Pb-Sn-Cl system is shown in Fig. 1. The y-axis is the equilibrium Cl_2 pressure. The x-axis is the metallic molar ratio $\xi = n_{Pb}/(n_{Sn} + n_{Pb})$. There are two phases shown: a liquid metal solution Sn-Pb and a liquid chloride solution $SnCl_2$-$PbCl_2$. The temperature is constant at 800 K.

The solution $SnCl_2$-$PbCl_2$ is ideal. The Sn-Pb alloy is a regular solution with:

$$s^E = 0$$

$$\Delta h = 5520 X_{Pb} X_{Sn} \ \text{J/mol}$$

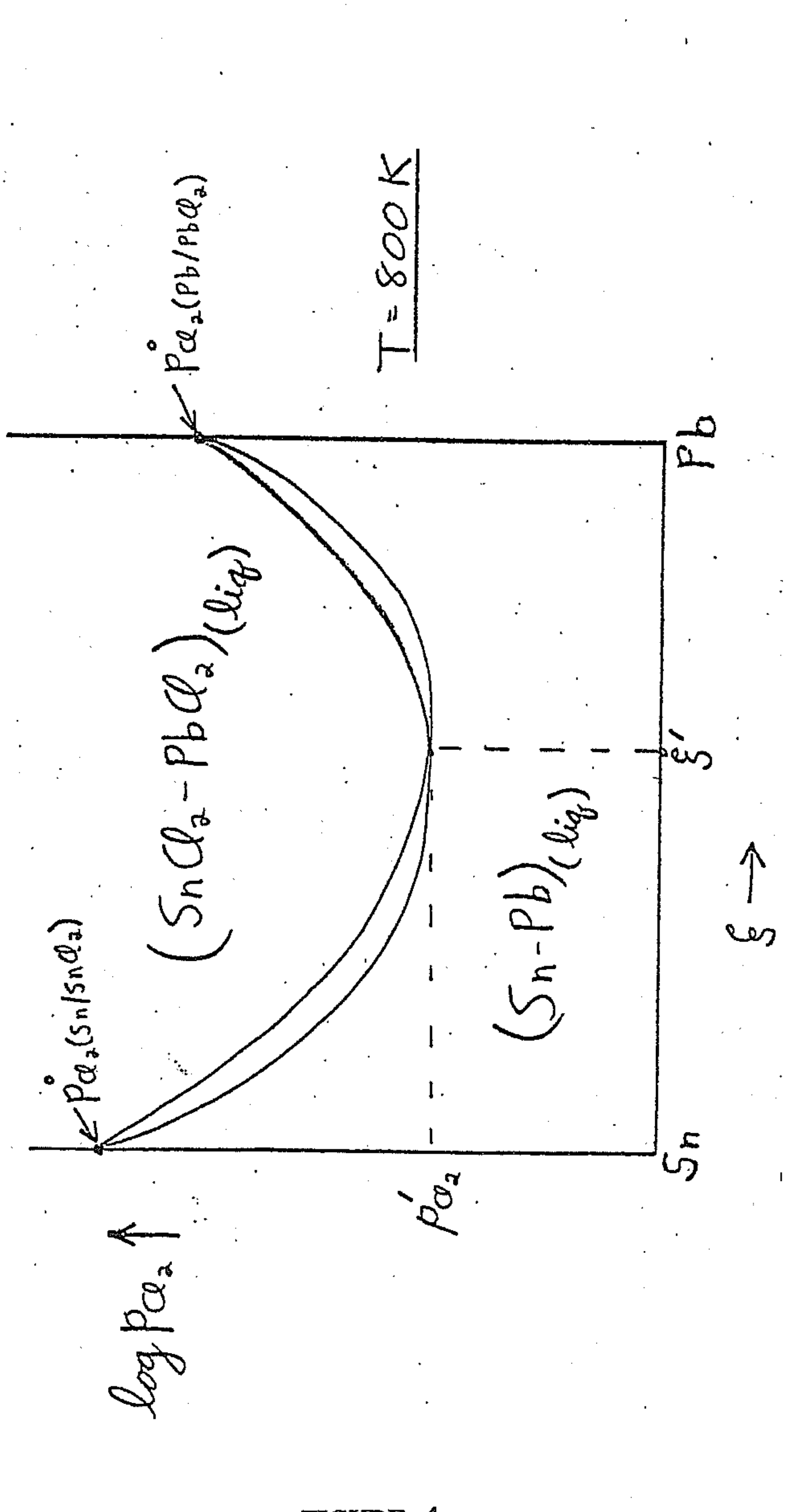
The equilibrium Cl_2 pressure when pure Sn and pure $SnCl_2$ are in equilibrium is $p^o_{Cl_2}(Sn/SnCl_2) = 2.74 \times 10^{-16}$ bar at 800 K, and for the equilibrium between pure Pb and $PbCl_2$, $p^o_{Cl_2}(Pb/PbCl_2) = 1.57 \times 10^{-16}$ bar at 800 K.

Calculate the chlorine pressure p'_{Cl_2} and the composition ξ' at the minimum point of the two-phase region (as shown on the figure.)

Question 6 (3 points)

A phase diagram for the system Fe-Cr-S_2-O_2 is shown in Figure 2. The temperature is constant at 925°C, and the overall molar ratio of the system $n_{Cr}/(n_{Fe} + n_{Cr}) = 0.5$ is also constant. The axes are the equilibrium S_2 and O_2 pressures.

(i) Some of the lines on the diagram are simple phase boundaries while others are infinetely narrow multiphase regions. Write an "X" on those lines which are infinitely narrow multiphase regions. (Write your name of the diagram and hand it in with your answer booklets).
(ii) Is point "A" an invariant point? Discuss with reference to the Phase Rule.



T = 800 K
$p^{\circ}_{Cl_2(Pb/PbCl_2)}$
$p^{\circ}_{Cl_2(Sn/SnCl_2)}$
$(SnCl_2 - PbCl_2)_{(liq)}$
$(Sn-Pb)_{(liq)}$
$\log p_{Cl_2}$ ↑
p'_{Cl_2}
Sn
Pb
ξ'
ξ →

FIGURE 1

Figure 2

Phase diagram of the Fe-Cr-S_2-O_2 system at 925° C showing equilibrium S_2 and O_2 partial pressures at constant molar ratio Cr/(Cr + Fe) = 0.5