May 2016 Session

Open book examination

Non-programmable calculators: Authorized models only

Duration: 3 hours

14-MT-A1

Metallurgical Thermodynamics

Question 1 (3 points)

800 kg of pure liquid aluminum (Al) at 900°C must be cooled to 720°C by the addition of solid Al ingots (pure) initially at 15°C. Calculate the mass of Al ingots to be added if the total heat losses during the entire mixing process are equal to 122 MJ.

Data: M_{Al} : 27.0 g/mol

C_p(liquid Al): 31.7 J/mol-K C_p(solid Al): 20.8 + 0.0121 T(K) J/mol-K

T^o(fusion,Al): 660 °C

Δh^o_{fusion} (Al): 10,711.0 J/mol

Question 2 (3 points)

For the vaporization of pure Zn:

$Zn_{(liquid)} = Zn_{(gas)}$ ΔG^o = 115,295.0 – 97.586 T(K) J/mol

a) Calculate the temperature at which pure liquid Zn is boiling under a total pressure ($P_{tot} = P_{Zn}$) of 2.5 bars;
b) Calculate the boiling point (at $P_{tot} = P_{Zn}$ = 1.0 bar) of a (Zn+Al) binary liquid alloy with a mole fraction of Al (x_{Al}) of 0.978. You can assume that Al does not volatilize and that the activity coefficient of Zn (γ_{Zn}) is given by: $RT \ln \gamma_{Zn} = 6000X_{Al}^2$

Data: R (gas constant) = 8.31451 J/mol-K

1 bar = 10^5 Pa

1 J = 1 Pa·m^3

Question 3 (4 points)

In steelmaking, pure oxygen is injected into liquid Fe at 1800K in order to remove the dissolved C according to:

$C_{(dissolved\ in\ Fe)} + ½\, O_{2(g)} = CO_{(g)}$ ΔG^o = -270.5 kJ/mol at 1800K

Bubbles of $CO_{(g)}$ are formed at $P_{CO} \approx 1$ bar.

At the beginning of the blow, when the mole fraction of carbon, X_C, is relatively high, the only product of the reaction is CO. That is, FeO is not formed. However, there is a minimum carbon content at which FeO also starts to form. Calculate this minimum mole fraction of carbon, X_C, which can be attained by this refining process.

$Fe_{(liquid)} + ½\, O_{2(g)} = FeO_{(liquid)}$ ΔG^o = -145.4 kJ/mol at 1800K

Question 4 (3 points)

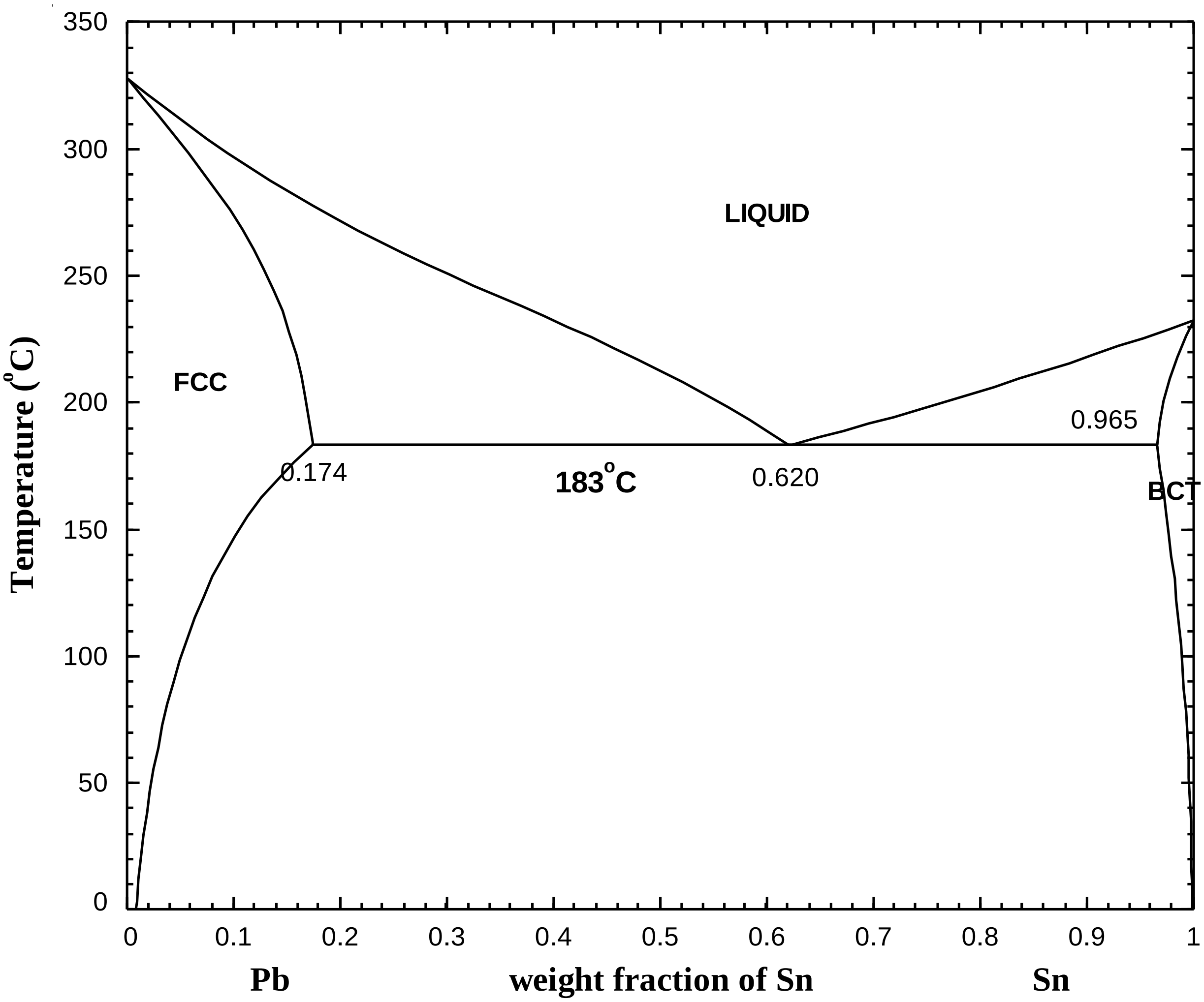

Figure 1: The Pb – Sn Phase Diagram

The Pb-Sn phase diagram (in mass fractions) is given in Figure 1. Apart from the liquid solution, two terminal solid solutions are shown: FCC-Pb and BCT-Sn.

For 180 grams of a 78 wt.% Pb – 22 wt.% Sn alloy, under equilibrium conditions:

a) Give the mass and composition (wt. fraction Sn) of the phases at equilibrium at 183.1°C (i.e. just above the eutectic temperature);
b) Give the mass and composition of the phases at equilibrium at 182.9°C (i.e. just below the eutectic temperature), and also give the mass of $FCC_{pro\text{-}eutectic}$, $FCC_{eutectic}$ and $BCT_{eutectic}$.

Question 5 (4 points)

An empty rigid closed container of a total volume of 1.00 m^3 is filled with 10 moles of pure MgO, 0.50 mole of pure Si and 0.10 mole of Ar. The container is then heated to 1200°C and equilibrium is achieved for the following 2 reactions:

$$4\ MgO_{(s)} + Si_{(s)} \leftrightarrow Mg_2SiO_{4(s)} + 2\ Mg_{(g)} \qquad \Delta G^o(1200^oC) = 149.3\ \text{kJ/mol}$$

$$MgO_{(s)} + Si_{(s)} \leftrightarrow SiO_{(g)} + Mg_{(g)} \qquad K_{equ}\ (1200^oC) = 5.41 \times 10^{-8}$$

The equilibrium products in the container are pure solid MgO, pure solid Si, pure solid Mg_2SiO_4 and a gaseous phase containing $Ar_{(g)}$, $Mg_{(g)}$ and $SiO_{(g)}$.

a) Explain in a few words or with a simple equation why the reaction of formation of Mg_2SiO_4 can proceed in the container under the above equilibrium conditions even though ΔG^o is positive.
b) Calculate the values of the partial pressures (in bar) of $Mg_{(g)}$ (P(Mg)), $Ar_{(g)}$ (P(Ar)) and $SiO_{(g)}$ (P(SiO)) and the total pressure (P(total)) at equilibrium at 1200°C (assume an ideal gas behavior and that the solids occupy a negligible volume);
c) Calculate the number of moles of solid Mg_2SiO_4 generated in the container under the same equilibrium conditions.

Data: R (gas constant) = 8.31451 J/mol-K

1 bar = 10^5 Pa

1 J = 1 Pa·m^3

Question 6 (3 points)

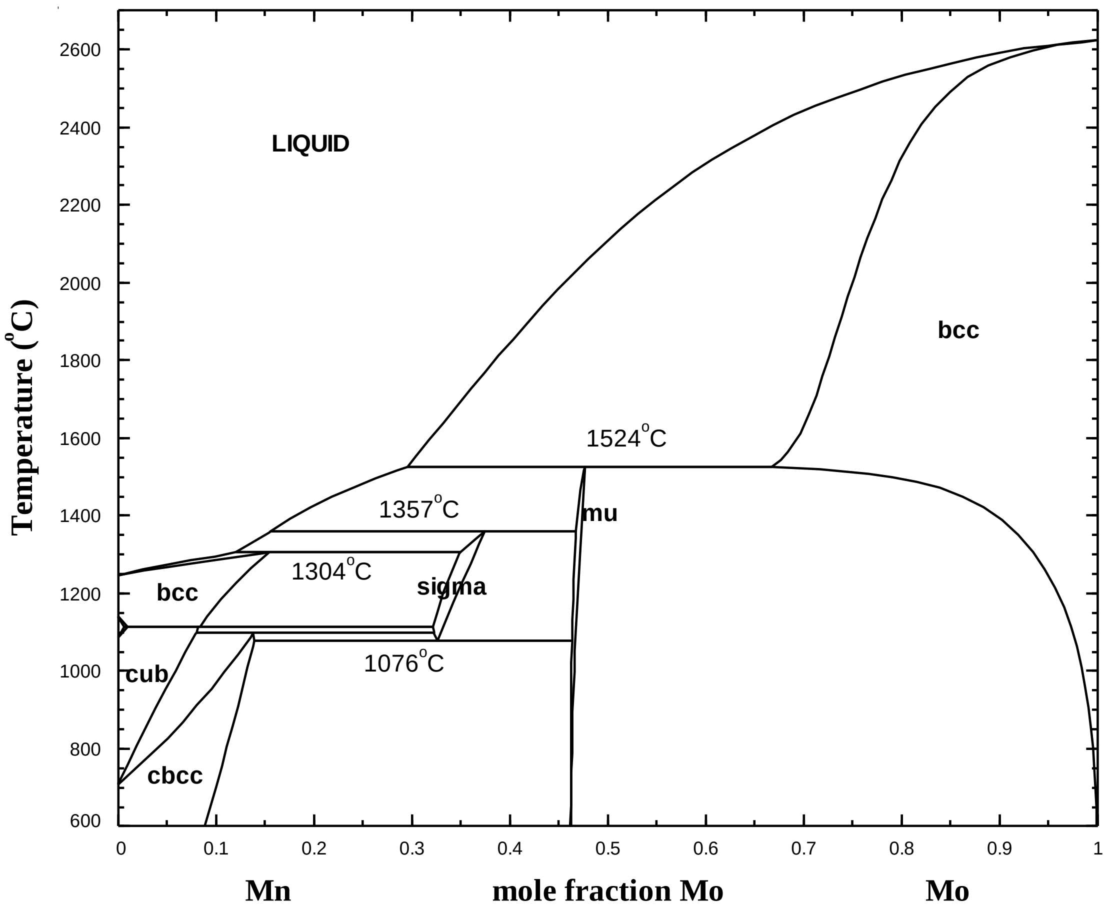

Figure 2: The Mn-Mo Phase Diagram

The manganese (Mn) – molybdenum (Mo) phase diagram is given in Figure 2.

a) What is the first melting temperature (in °C) of the following alloys when heated very slowly (i.e. near equilibrium conditions)?
   i. 70 mol.% Mn + 30 mol.% Mo;
   ii. 40 mol.% Mo;
   iii. 20 mol.% Mn;

b) What is the usual name of the invariant reaction at 1076°C, and write its reactant(s) and product(s) upon cooling?