# National Exams December 2002

## 98-met-A1, Metallurgical Thermodynamics

### 3 hours duration

**NOTES:**

1. Answer only five questions. Any five questions(out of seven) constitute a complete paper. Only the first five questions as they appear in your answer book will be marked.

2. All questions are of equal value(20 marks each out of 100).

3. If doubt exists as to the interpretation of any question, the candidate is urged to submit with the answer paper a clear statement of any assumptions made.

4. Candidates may use one of two calculators, the Casio or Sharp approved models. This is a closed book exam.

5. The exam consists of six pages

Marking Scheme

| | |
|---|---|
| Question 1: | (a) 8, (b) 6, (c) 6 |
| Question 2: | (a) 4, (b) 6, (c) 4, (d) 3, (e) 3 |
| Question 3: | (a) 4, (b) 4, (c) 6, (d) 6 |
| Question 4: | (a) 4, (b) 4, (c) 4, (d) 4, (e) 4 |
| Question 5: | (a) 5, (b) 5, (c) 5, (d) 5 |
| Question 6: | (a) 3, (b) 3, (c) 2, (d) 2, (e) 2, (f) 2, (g) 2, (h) 2, (i) 2 |
| Question 7: | (a) 3, (b) 3, (c) 3, (d) 3, (e) 8 |

**Problem No. 1(20 marks):** Solid copper scrap is recycled by taking the copper scrap initially at 10 °C and heating it to 1175 °C upon which it is molten. The melting point of the copper is 1084 °C.

a) Determine the minimum amount of energy(kJ/kg copper) required to heat up and melt copper scrap to the final temperature of 1175 °C.
b) An induction furnace with a power of 700 kW is used for the heating and melting process. The furnace has an overall energy efficiency of 75%. How much copper can be treated per hour.
c) Calculate the equilibrium vapour pressure(atm) of arsenic(As) in the copper melt when the arsenic content is 0.1 mol%. The activity coefficient of arsenic in copper is $4.8 \cdot 10^{-4}$ and the vapour pressure of pure arsenic at 1175 °C is $2.5 \cdot 10^{-4}$ atm.

Data:

$M_{Cu} = 63.5$ g/mol, $\Delta H^{\circ}$(melting at 1084 ° C) = 13.01 kJ/mol

Solid Cu: $C_{p,s}$(J/K·mol) = $22.6 + 0.0063 \cdot T$; Where T is given in Kelvin

Liquid Cu: $C_{p,l}$(J/K·mol) = 31.38

**Problem 2(20 marks):** One method to remove oxygen from nitrogen is to pass the impure nitrogen gas through a fine copper mesh at about 500 °C. The following reaction takes place

$$2Cu(s) + 0.5O_2(g) = Cu_2O(s)$$

a) Calculate $\Delta G^{\circ}$ for this reaction at 25 °C
b) Calculate $\Delta G^{\circ}$ for this reaction at 500 °C
c) Assuming that equilibrium is reached and that the total gas pressure is 1 atm, calculated the vol.% $O_2$ present in the purified nitrogen.
d) What would be the effect of raising the temperature to 800 °C? Or lowering it to 300 °C? What is the reason for using 500 °C?
e) What would be the effect of increasing the total gas pressure to 10 atm?

Data: Gas Constant R = 8.314 J/mol·K = 0.082 l·atm/(mol·K); T(K) = 273 + T(°C)

| Species | $\Delta H^{\circ}_{f,298}$(kJ/mol) | $S^{\circ}_{298}$(J/mol·K) | $C_p$(J/mol·K) |
|---|---|---|---|
| Cu(s) | 0 | 33.2 | $22.6 + 6.3 \cdot 10^{-3}T$ |
| $O_2$(g) | 0 | 205 | $29.96 + 3.9 \cdot 10^{-3}T$ |
| $Cu_2O$(s) | -167.4 | 93.1 | $63.34 + 23.8 \cdot 10^{-3}T$ |

**Problem 3(20 marks):** Liquid FeO is reduced to liquid metallic iron at 1600 °C with CO(gas) according to the following reaction:

$$FeO(liquid) + CO(g) = Fe(liquid) + CO_2$$

a) Calculate $\Delta G^\circ$ at 1600 °C for this reaction

b) Determine the minimum $CO/CO_2$ ratio required to reduce pure liquid FeO to pure metallic iron at 1600 °C.

c) Determine the minimum $CO/CO_2$ ratio required to reduce FeO dissolved in a liquid slag to metallic iron at 1600 °C. The metallic iron formed has a purity of 96 mole % iron. The liquid slag contains 45 mol% FeO and the activity coefficient of FeO in the liquid slag is 0.7.

d) In the production of a $TiO_2$ slag from a $TiO_2$-FeO feed material by reduction of FeO to metallic iron, the final slag contains 93 mol% $TiO_2$ and 7 mol% FeO. The activity of iron in the Fe-C-Ti alloy is 0.96. Calculate the mol% Ti in the iron phase when the activity coefficient of Ti in iron is 0.037. Assume that the slag forms an ideal solution.

Data: At 1600 °C: CO(g): $\Delta G^\circ = -274.9$ kJ/mol; $CO_2(g)$: $\Delta G^\circ = -396.3$ kJ/mol

FeO: $\Delta G^\circ = -144.6$ kJ/mol; $TiO_2$: $\Delta G^\circ = -590$ kJ/mol

$R = 8.314$ J/mol·K $= 1.987$ cal/mol·K

**Problem 4(20 marks):** Aluminum is produced by electrolysis(DC current) of $Al_2O_3$ dissolved in a molten salt electrolyte at 960 °C. The electrolyte is based on cryolite($Na_3AlF_6$), $AlF_3$, $CaF_2$ and $Al_2O_3$. Carbon is used as a consumable anode forming $CO_2$ gas that leaves the cell. At the cathode a pool of liquid aluminium is formed. On a daily basis an amount of liquid aluminium corresponding to one days production, is removed from the cell. For a particular cell, the current is 330,000 Amp and the cell voltage is 4.4V. The corresponding cathodic current density is 6,500 $A/m^2$, where the surface area refers to the horizontal area of the liquid aluminium pool. The principal reaction is:

$$Al_2O_3 + 1.5C \rightarrow 2Al(cathode) + 1.5CO_2(anode)$$

For a 100% efficient process calculate

a) How much(kg) $Al_2O_3$ is consumed and how much(kg) $CO_2$ is produced per kg of Al produced
b) For a period of 24 hours, how much(kg) liquid aluminium is formed
c) How much(cm) will the level of liquid aluminium raise during this 24 hour period between tapping
d) How many kWh of energy is consumed during the 24 hour period and what is the specific energy consumption(kWhr/kg Al)
e) Why is cryolite used as electrolyte and what are the required properties for such an electrolyte

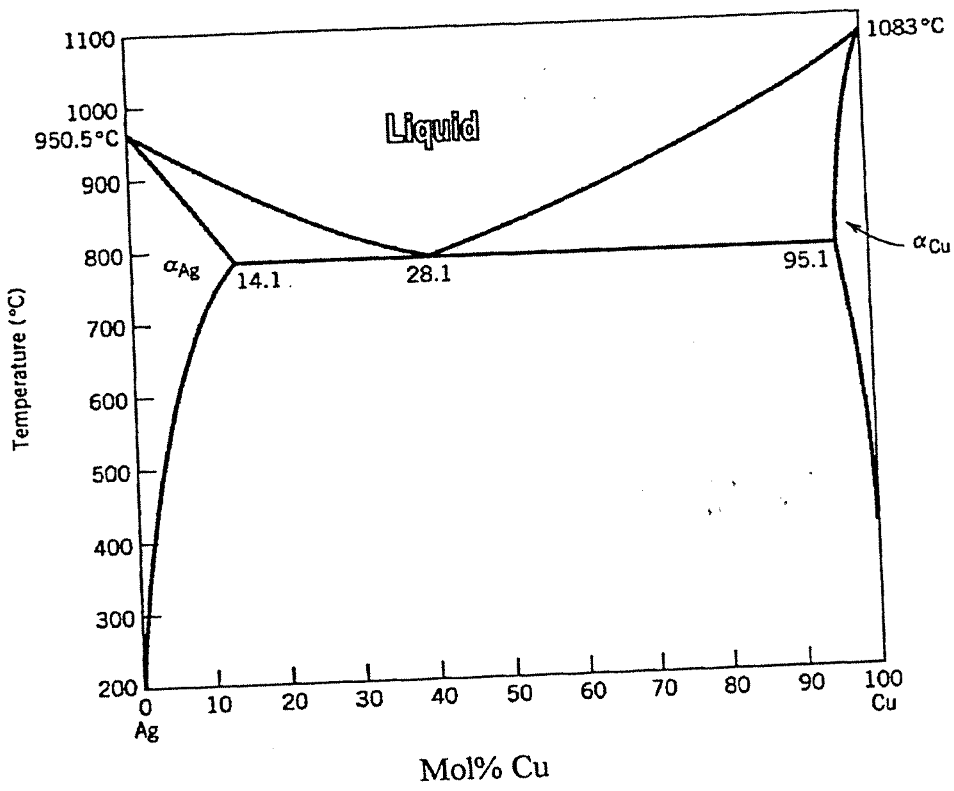
Data: Molecular mass: $M_{Al} = 26.98$ kg/kmol; Density of liquid aluminium = 2,280 $kg/m^3$;
$M_C = 12$ kg/kmol; $M_O = 16$ kg/kmol; Faraday's Constant: $F = 96500$ C/mol

Problem 5(20 marks): Consider an alloy with 80 atom% Cu as seen in the Ag-Cu phase diagram.

a) At 850 °C, determine the relative amounts of the three possible phases($\alpha_{Cu}$, $\alpha_{Ag}$, and liquid).
b) At 700 °C, determine the relative amounts of the three possible phases($\alpha_{Cu}$, $\alpha_{Ag}$, and liquid).
c) At 700 °C, estimate the activity of copper and silver for this alloy.
d) At 700 °C, determine whether copper or silver in this alloy, will oxidize in air

Data:

$$4Ag + O_2 = 2Ag_2O,\ \Delta G^\circ(J/mol) = -58{,}600 + 122.2T(K)$$
$$4Cu + O_2 = 2Cu_2O,\ \Delta G^\circ(J/mol) = -334{,}700 + 144.8T(K)$$




**Ag – Cu Phase Diagram**

**Problem 6(20 marks):**

With respect to the Ellingham diagram on the following page, answer the following questions:

a) Discuss the fundamentals behind the construction of the Ellingham diagram.
b) Explain the y-axis(why is $\Delta G^\circ$ equal to $RT \times \ln p_{O_2}$?)
c) Explain the slope changes for the reaction $2Mg + O_2 = 2MgO$
d) You want to heat up and melt a piece of aluminium metal to 1000 °C, decide on a suitable crucible material.
e) What is the value of $\Delta H^\circ$ of formation of $Cr_2O_3$?
f) Find $\Delta G^\circ$ for the reaction $Fe + 0.5O_2 = FeO$ at 1200 °C
g) Find $\Delta G^\circ$ for the reaction $3Mg + Al_2O_3 = 3MgO + 2Al$ at 1500 °C
h) What is the equilibrium oxygen pressure when metallic nickel is in equilibrium with NiO at 1000 °C?
i) If you want to reduce pure $TiO_2$ to pure metallic titanium at 1000 °C using a $CO/CO_2$ gas mixture, what is the minimum $CO/CO_2$ ratio that can achieve such a reduction.

**Problem 7(20 marks):** From vapour pressure measurements, the following values have been determined for the activity of mercury in liquid mercury-bismuth alloys at 593 K as a function of mole fraction.

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $X_{Hg}$ | 0.949 | 0.893 | 0.851 | 0.753 | 0.653 | 0.537 | 0.437 | 0.330 | 0.207 | 0.063 |
| $a_{Hg}$ | 0.961 | 0.929 | 0.908 | 0.840 | 0.765 | 0.650 | 0.542 | 0.432 | 0.278 | 0.092 |

a) Plot the activity of mercury as a function of composition
b) Determine the activity coefficient of mercury as a function of composition
c) Is the solution ideal, or does it show positive or negative deviation from ideality
d) What is the vapour pressure(atm) of mercury in an alloy with 43.7 atom% mercury
e) Use Gibbs Duhem integration to determine the activity coefficient of bismuth for the same alloy

Data: Gas Constant R = 8.314 J/mol·K = 0.082 l·atm/(mol·K); 1 atm = 760 Torr

$$\log[p_{Hg}(Torr)] = 10.355 - \frac{3,305}{T(K)} - 0.795 \times \log(T(K))$$

# Ellingham Diagram