

National Exams May 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.
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 five pages

Problem No. 1(20 marks): Solid scrap aluminium is recycled by taking the scrap aluminium at 20 °C and heating it to 750 °C upon which it is a liquid. The melting point of aluminum is 660 °C.

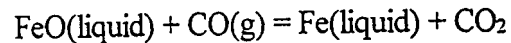
- Determine the minimum amount of energy(kJ/mol aluminum) required to heat up and melt scrap aluminum.
- Calculate the equilibrium vapour pressure(atm) of sodium for an aluminum melt containing 0.005 mol% sodium(Na). The activity coefficient of sodium in aluminum is 320 and the vapour pressure of pure sodium at 750 °C is 0.23 atm.

$$M_{Al} = 27 \text{ g/mol}, \Delta H(\text{melting}, 660^\circ \text{C}) = 10.7 \text{ kJ/mol}$$

$$\text{Solid Al: } C_{p,s}(\text{J}^\circ\text{C}\cdot\text{mol}) = 28 + 0.0033\cdot T; \text{ Where T is given in Degrees Celsius}$$

$$\text{Liquid Al: } C_{p,l}(\text{J}^\circ\text{C}\cdot\text{mol}) = 31.76$$

Problem 2(20 marks): Liquid FeO is reduced to metallic iron at 1600 °C with CO(gas) according to the following reaction:



- Calculate ΔG° at 1600 °C for this reaction
- Determine the minimum CO/CO₂ ratio required to reduce pure liquid FeO to pure metallic iron at 1600 °C.
- Determine the minimum CO/CO₂ 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 activity of FeO in the liquid slag is 0.3.

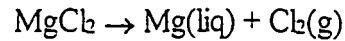
$$\text{CO(g)} \text{ at } 1600^\circ \text{C: } \Delta G^\circ = -274.9 \text{ kJ/mol}$$

$$\text{CO}_2(\text{g}) \text{ at } 1600^\circ \text{C: } \Delta G^\circ = -396.3 \text{ kJ/mol}$$

$$\text{FeO at } 1600^\circ \text{C: } \Delta G^\circ = -144.6 \text{ kJ/mol}$$

$$R = 8.314 \text{ J/mol}\cdot\text{K} = 1.987 \text{ cal/mol}\cdot\text{K}$$

Problem 3(20 marks): Magnesium is produced by electrolysis(DC current) of MgCl_2 in a molten salt electrolyte at 750°C . The principal reaction is:



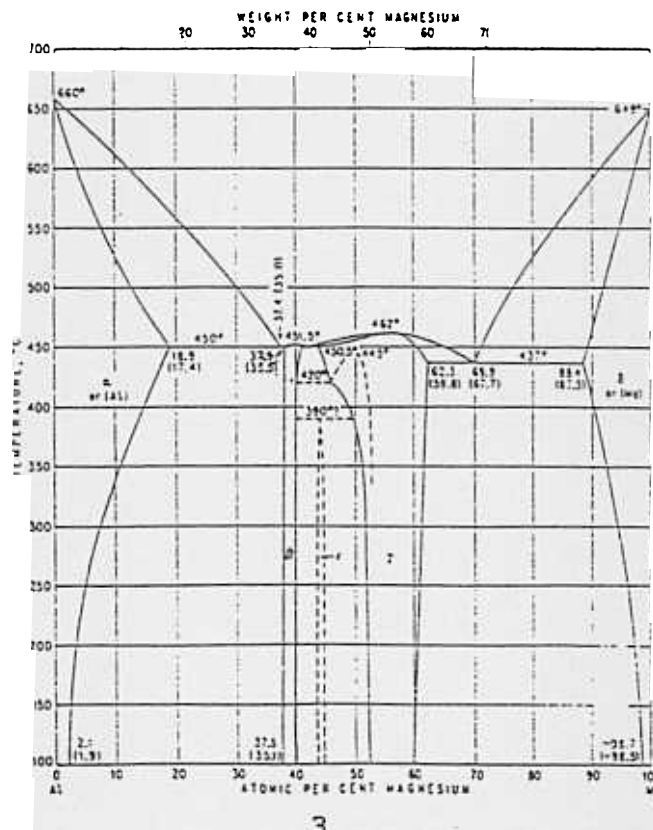
- Calculate ΔH° and ΔG° for the above reaction at 25°C
- Calculate the reversible decomposition voltage of MgCl_2 at 750°C of the above reaction when ΔG° for the above reaction at 750°C is 480 kJ/mol .
- Assuming that the efficiency is 100%, what is the daily(24 hrs) production of magnesium for a cell with a DC current of 150,000 A.

Thermodynamic Data at 25°C : Mg : $\Delta H^\circ = 0$, $\Delta S^\circ = 32.7\text{ J/mol}\cdot\text{K}$; $\text{Cl}_2(\text{g})$: $\Delta H^\circ = 0$, $\Delta S^\circ = 223\text{ J/mol}\cdot\text{K}$; MgCl_2 : $\Delta H^\circ = -641.6\text{ kJ/mol}$, $\Delta S^\circ = 89.6\text{ J/mol}\cdot\text{K}$

Molecular mass: $M_{\text{Mg}} = 24.3\text{ kg/kmol}$; Faraday's Constant: $F = 96500\text{ C/mol}$

Problem 4(20 marks): The lid of aluminum cans is made from an aluminum alloy with 4.5 wt% Mg. Based on the attached Al-Mg phase diagram, explain in detail what happens when such an alloy initially at 750°C is cooled under equilibrium conditions down to room temperature.

Al – Mg Phase Diagram



Problem 5(20 marks):

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

- Discuss the basis behind the construction of the Ellingham diagram.
- Explain the y-axis(why is ΔG° equal to $RT \times \ln p_{O_2}$?)
- Explain the slope changes for the reaction $2Mg + O_2 = 2MgO$
- You want to heat up and melt a piece of silicon metal to $1600^\circ C$, decide on a suitable crucible material.
- What is the value of ΔH° of formation of TiO_2 ?
- Find ΔG° for the reaction $Fe + 0.5O_2 = FeO$ at $1200^\circ C$
- Find ΔG° for the reaction $3Mg + Al_2O_3 = 3MgO + 2Al$ at $1500^\circ C$
- What is the equilibrium oxygen pressure when metallic titanium is in equilibrium with TiO_2 at $1000^\circ C$?
- If you want to reduce pure TiO_2 to pure metallic titanium at $1000^\circ C$ using a CO/CO_2 gas mixture, what is the minimum CO/CO_2 ratio that can achieve such a reduction.

Problem 6(20 marks): In terms of the thermodynamics of a binary liquid mixture, explain the following terms. Also give a short discussion and possible applicability of the same terms.

- Raoult's law
- Henry's law
- Ideal solution
- Regular solution
- Temkin's model

Problem 7(20 marks): The vapour pressure of liquid zinc is given by the approximate equation:

$$\ln P_{Zn}(\text{atm}) = -14800/T + 12.54$$

The heat of melting of zinc at its melting point(693 K) is 7300 J/mol

- Calculate the vapour pressure of liquid zinc at its melting point
- Estimate the normal boiling point of zinc
- Determine the heat of vaporization of liquid zinc
- Derive an expression of the vapour pressure of solid zinc as a function of temperature

State your assumptions.

Data: Gas Constant $R = 8.314\text{ J/mol}\cdot\text{K} = 0.082\text{ l}\cdot\text{atm}/(\text{mol}\cdot\text{K})$

Ellingham Diagram

