

## National Exams May 2009

### 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 including graph paper and Ellingham diagram

Question 1: (a) 10, (b) 10

Question 2: (a) 20

Question 3: (a) 10, (b) 10

Question 4: (a) 5, (b) 5, (c) 10

Question 5: (a) 5, (b) 5, (c) 5, (d) 5

Question 6: (a) 5, (b) 5, (c) 5, (d) 5

Question 7: (a) 4, (b) 4, (c) 4, (d) 4, (e) 4

**Problem No. 1(20 marks):** Scrap aluminium is recycled by taking the scrap 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/metric tonne aluminum) required to heat up and melt scrap aluminum.
- Calculate the vapour pressure(atm) of sodium in equilibrium with an aluminum melt with 0.005 mol% Na. The activity coefficient of sodium in aluminum is 320 and the vapour pressure of pure sodium at 750 °C is 0.23 atm.

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

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

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

**Problem No. 2(20 marks):** Calculate the adiabatic flame temperature when pure  $\text{CH}_4(\text{gas})$  at 25 °C is fully combusted with stoichiometric amount of air. The air(assume 21 mole%  $\text{O}_2$  and 79 mole%  $\text{N}_2$ ) is pre-heated to 500 °C before it reacts with the methane.

Table of Data

	Molecular Mass g/mole	Standard Enthalpy of Formation (kJ/mole)	Average Heat Capacity (J/mole·°C)
$\text{CH}_4(\text{g})$	16	-75	38
$\text{H}_2\text{O}(\text{g})$	18	-242	39
$\text{CO}_2(\text{g})$	44	-394	51
$\text{O}_2(\text{g})$	32	0	34
$\text{N}_2(\text{g})$	28	0	32

**Problem No. 3(20 marks):** Hematite( $\text{Fe}_2\text{O}_3$ ) is reduced to metallic iron by carbon, and the resulting gaseous reaction product is a mixture of CO and  $\text{CO}_2$  with two parts of CO to one part of  $\text{CO}_2$  per volume.

- calculate the heat of reaction at  $25^\circ\text{C}$  per mole of iron(Fe) produced
- calculate the heat of reaction at  $1000^\circ\text{C}$  per mole of iron(Fe) produced

	$\Delta H_f^\circ(25^\circ\text{C})$ kJ/mol	$C_p(\text{J/mol}\cdot\text{K})$
$\text{Fe}_2\text{O}_3$	-1207	141
Fe	0	$16.32 + 28.4 \times 10^{-3} T$
C	0	$11.2 + 9.5 \times 10^{-3} T$
$\text{CO}(\text{g})$	-110.5	$28.4 + 4.1 \times 10^{-3} T - 0.46 \times 10^{-5} / T^2$
$\text{CO}_2(\text{gas})$	-394	37.2

!Heat capacities are given as a function of temperature in Kelvin  
 $K = 273.15 + ^\circ\text{C}$

**Problem No. 4(20 marks):** Limestone decomposes according to the following reaction:



At  $25^\circ\text{C}$  the following data are given:

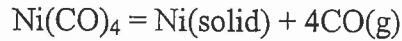
	$\text{CaCO}_3$	CaO	$\text{CO}_2(\text{g})$
$\Delta H_f^\circ$ (kJ/mol)	-1207	-635	-394
$S^\circ$ (J/mol $\times$ K)	92	38	214

- Calculate the heat of reaction(kJ/mol) at  $25^\circ\text{C}$
- Calculate  $\Delta G^\circ$ (kJ/mol) of the above reaction at  $25^\circ\text{C}$
- Assuming that  $\Delta C_p$  for this reaction is zero, what is the equilibrium  $\text{CO}_2$  pressure when solid  $\text{CaCO}_3$  is heated to  $850^\circ\text{C}$

Data:

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

**Problem No. 5(20 marks):**  $\text{Ni}(\text{CO})_4(\text{gas})$  decomposes according to the following reaction upon heating

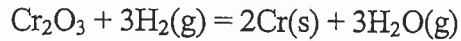


For this reaction, the following data are given:

T °C	$\Delta H^\circ$ kJ	$\Delta G^\circ$ kJ
25.000	160.745	38.552
50.000	160.541	28.314
75.000	160.278	18.094
100.000	159.967	7.895
125.000	159.620	-2.282
150.000	159.243	-12.437
175.000	158.842	-22.568

- Calculate  $\Delta S^\circ$  (J/mol·K) for this reaction at 25 °C. Does the value make sense, explain
- Calculate the equilibrium constant at 150 °C
- What conditions do you think promotes this decomposition reaction, give what you think are ideal conditions, explain
- $\text{Ni}(\text{CO})_4$  gas can be formed by reacting solid nickel with gaseous CO at 25 °C. If you had to design this reactor, in terms of heating or cooling, what would you have to consider and how much heating or cooling would you need to have per mole of Ni reacting to form  $\text{Ni}(\text{CO})_4$ .

**Problem No. 6(20 marks):** The standard Gibbs Free energy of the following reaction



is given by

$$\Delta G^\circ(\text{kJ/mol}) = 408.6 - 0.12 \times T(\text{K})$$

- find the equilibrium constant at 1500 K
- what is the maximum partial pressure(atm) of water vapour in otherwise pure  $\text{H}_2$  in which chromium can be heated to 1500 K without oxidizing. The total pressure is 1 atm
- derive from the data whether the oxidation of chromium metal with water vapour is exothermic or endothermic
- indicate in general terms how the equilibrium for the above reaction is affected by a change in the total pressure from 1 to 2 atm(explain)

**Problem No. 7(20 marks):** Use the Ellingham Diagram to answer

- What is  $\Delta G^\circ(\text{kJ/mol})$  at 1000 °C for the formation of solid MnO from pure manganese(Mn) and oxygen gas
- If you have pure solid Fe and pure solid FeO in equilibrium at 1000 °C what would the equilibrium oxygen pressure be(use two methods to find this)
- If you want to reduce FeO to metallic Fe at 1000 °C using a CO/CO<sub>2</sub> gas mixture, what is the minimum percentage of CO in that gas mixture.
- What is  $\Delta G^\circ(\text{kJ/mol})$  for the reaction:  $3\text{TiO}_2 + 4\text{Al} = 2\text{Al}_2\text{O}_3 + 3\text{Ti}$  at 1600 °C
- What is the equilibrium ratio for  $\text{H}_2/\text{H}_2\text{O}$  for the reduction of  $\text{Cu}_2\text{O}$  to metallic Cu at 400 °C

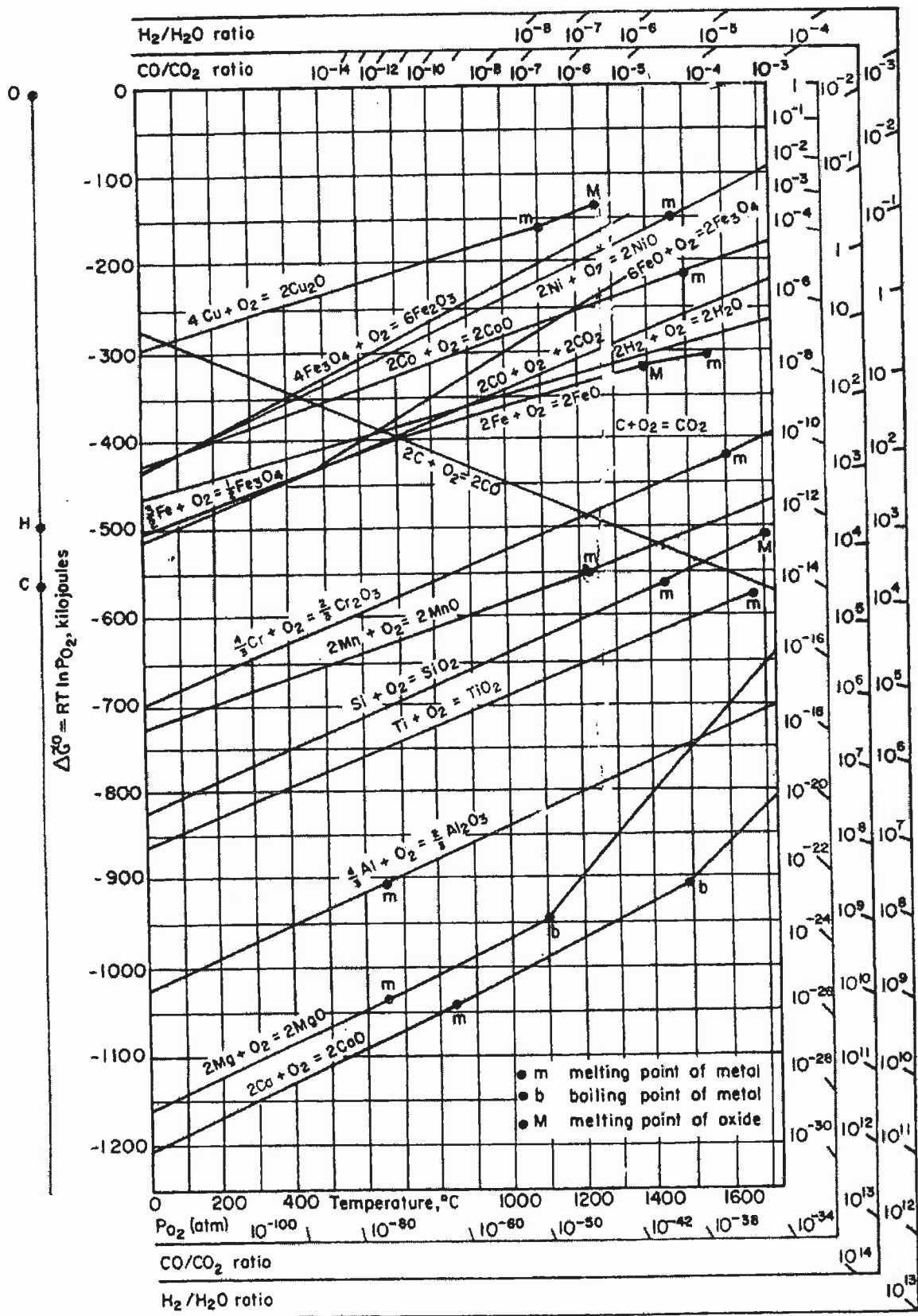


Figure 9-3. Ellingham diagram for some oxides; Richardson nomographic scales are included. (Adapted from D. R. Gaskell, *Introduction to Metallurgical Thermodynamics*, 2nd ed., Hemisphere Publishing, New York, 1981.)