National Exams May 2012

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).

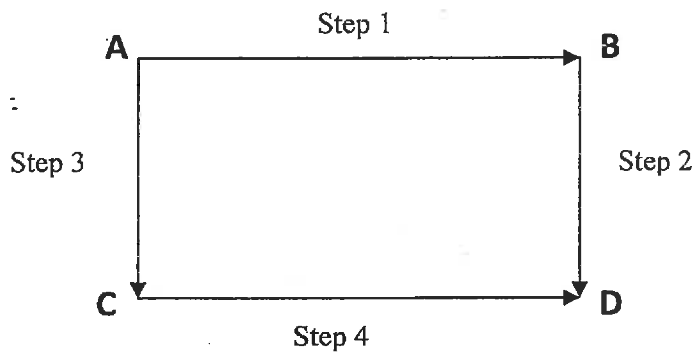
3. If doubt exists as to the interpretation of any question, the candidate is urged to submit with the answer paper a clear statement of any assumptions made.

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 5 pages including Ellingham diagram.

Question 1: (a) 4, (b) 4, (c) 4, (d) 4, (e) 2, (f) 2
Question 2: (a) 2, (b) 2, (c) 2, (d) 2, (e) 2, (f) 2, (g) 2, (h) 2, (i) 2, (j) 2
Question 3: (a) 4, (b) 4, (c) 4, (d) 4, (e) 4
Question 4: (a) 3, (b) 3, (c) 3, (d) 3, (e) 2, (f) 2, (g) 2, (h) 2
Question 5: (a) 10, (b) 10
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): 1 mol of a monatomic ideal gas is taken from state A (P_A = 100 kPa, V_A= 10 L) to state D (P_D = 50 kPa, V_D= 30 L) by two different paths as shown below:



Path 1: Step 1: State A (P_A = 100 kPa, V_A= 10 L) to state B (P_B = 100 kPa, V_B= 30 L)
Step 2: State B (P_B = 100 kPa, V_B= 30 L) to state D (P_D = 50 kPa, V_D= 30 L)

Path 2: Step 3: State A (P_A = 100 kPa, V_A= 10 L) to state C (P_C = 50 kPa, V_C= 10 L)
Step 4: State C (P_C = 50 kPa, V_C= 10 L) to state D (P_D = 50 kPa, V_D= 30 L)

(a) Calculate heat flow in the system (q), work done on the system (w), change in internal energy of the system (ΔE) and change in enthalpy of the system (ΔH) for Step 1. (4 marks)
(b) Calculate heat flow in the system (q), work done on the system (w), change in internal energy of the system (ΔE) and change in enthalpy of the system (ΔH) for Step 2. (4 marks)
(c) Calculate heat flow in the system (q), work done on the system (w), change in internal energy of the system (ΔE) and change in enthalpy of the system (ΔH) for Step 3. (4 marks)
(d) Calculate heat flow in the system (q), work done on the system (w), change in internal energy of the system (ΔE) and change in enthalpy of the system (ΔH) for Step 4. (4 marks)
(e) Calculate heat flow in the system (q), work done on the system (w), change in internal energy of the system (ΔE) and change in enthalpy of the system (ΔH) for Path 1. (2 marks)
(f) Calculate heat flow in the system (q), work done on the system (w), change in internal energy of the system (ΔE) and change in enthalpy of the system (ΔH) for Path 2. (2 marks)

Problem No. 2 (20 marks): 1 mol of a compound A is heated from -10 °C to 50 °C at 1 atm pressure. Constant pressure molar heat capacities of solid A, liquid A and vapour A are 118.4, 134.8 and 82.4 J $mol^{-1}K^{-1}$ respectively. The standard enthalpy change of fusion of compound A is 9.9 kJ mol^{-1} at 5.4 °C and the standard enthalpy change of vaporization of compound A is 33.9 kJ mol^{-1} at 25 °C.

(a) Calculate the change in entropy for solid A from -10 °C to 5.4 °C. (2 marks)
(b) Calculate the change in entropy for phase transformation at 5.4 °C. (2 marks)
(c) Calculate the change in entropy for liquid A from 5.4 °C to 25 °C. (2 marks)
(d) Calculate the change in entropy for phase transformation at 25 °C. (2 marks)
(e) Calculate the change in entropy for vapour A from 25 °C to 50 °C. (2 marks)
(f) Calculate the total change in entropy from -10 °C to 50 °C. (2 marks)
(g) Calculate the change in enthalpy for solid A from -10 °C to 5.4 °C. (2 marks)
(h) Calculate the change in enthalpy for liquid A from 5.4 °C to 25 °C. (2 marks)
(i) Calculate the change in enthalpy for vapour A from 25 °C to 50 °C. (2 marks)
(j) Calculate the total change in enthalpy from -10 °C to 50 °C. (2 marks)

Problem No. 3 (20 marks): Given the following data for standard enthalpy of formation at 25 °C:

Compound	Standard enthalpy of formation
CH_4	-75 kJ mol^{-1}
CH_3OH	-238 kJ mol^{-1}
C_4H_{10}	-125 kJ mol^{-1}
C_8H_{18}	-208 kJ mol^{-1}
CO_2	-394 kJ mol^{-1}
H_2O	-286 kJ mol^{-1}

(a) Calculate the heat of combustion per mole of methane (CH_4). (4 marks)
(b) Calculate the heat of combustion per mole of methanol (CH_3OH). (4 marks)
(c) Calculate the heat of combustion per mole of n-butane (C_4H_{10}). (4 marks)
(d) Calculate the heat of combustion per mole of n-octane (C_8H_{18}). (4 marks)
(e) Which fuel generates highest amount of heat per unit weight of the fuel. (4 marks)

Problem No. 4 (20 marks): Consider the formation of sulfuric acid at 25 °C and 1 atm by the following reactions:

$S + O_2 = SO_2$ (1)
$2SO_2 + O_2 = 2SO_3$ (2)
$SO_3 + H_2O = H_2SO_4$ (3)

Given the following data for standard enthalpy of formation and standard entropy:

Compound	Standard enthalpy of formation (ΔH_f^o)	Standard entropy of formation (S^o)
S	0 kJ mol^{-1}	32 J K^{-1} mol^{-1}
O_2	0 kJ mol^{-1}	205 J K^{-1} mol^{-1}
SO_2	-297 kJ mol^{-1}	248 J K^{-1} mol^{-1}
SO_3	-396 kJ mol^{-1}	257 J K^{-1} mol^{-1}
H_2O	-286 kJ mol^{-1}	70 J K^{-1} mol^{-1}
H_2SO_4	-814 kJ mol^{-1}	157 J K^{-1} mol^{-1}

(a) Calculate ΔH^o for reactions (1), (2) and (3). (3 marks)
(b) Calculate ΔS^o for reactions (1), (2) and (3). (3 marks)
(c) Calculate ΔG^o for reactions (1), (2) and (3). (3 marks)
(d) Calculate equilibrium constant (K) for reactions (1), (2) and (3). (3 marks)
(e) Write a balanced reaction for the formation of H_2SO_4 from S, O_2 and H_2O. (2 marks)
(f) Calculate ΔH^o for the balanced reaction in Part (e). (2 marks)
(g) Calculate ΔS^o for the balanced reaction in Part (e). (2 marks)
(h) Calculate ΔG^o for the balanced reaction in Part (e). (2 marks)

Problem No. 5 (20 marks): A gaseous mixture of 25 % CO, 25 % CO_2, 25 % H_2 and 25 % H_2O is brought to a Temperature T and 1 atm. Equilibrium composition of the gas mixture is determined by the following reaction:

$$CO_2 + H_2 = CO + H_2O \quad (1)$$

(a) Calculate the equilibrium composition of the gaseous phase at 700 °K. (10 marks)
(b) Calculate the equilibrium composition of the gaseous phase at 1500 °K. (10 marks)

Given: ΔG^o at 700 °K = .14 kJ and ΔG^o at 1500 °K = -9.6 kJ.

Problem No. 6 (20 marks): Consider a galvanic cell based on the following reaction:

$$Fe\ (s) + Cu^{2+}\ (aq) \longrightarrow Fe^{2+}\ (aq) + Cu\ (s) \quad (1)$$

(a) Calculate the standard cell potential (E^o) at 25 °C. (5 marks)
(b) Calculate the standard free energy (ΔG^o) for the cell at 25 °C. (5 marks)
(c) Calculate the equilibrium constant for the redox reaction at 25 °C. (5 marks)
(d) Calculate the cell potential (E) at 25 °C if concentration of Cu^{2+} is 0.5 M and concentration of Fe^{2+} is 1.5 M. (5 marks)

Given: Standard reduction potentials at 25 °C for half reactions:

$Fe^{2+} + 2e^-$	$\longrightarrow$	Fe	-0.44 V
$Cu^{2+} + 2e^-$	$\longrightarrow$	Cu	0.34 V

Problem No. 7 (20 marks): Use the attached Ellingham Diagram to answer the following questions:

a) What is the partial pressure of oxygen in equilibrium with Cu and Cu_2O at 900 °C? (4 marks)
b) What is the ratio of partial pressures of CO to CO_2 for equilibrium of Cr and Cr_2O_3 in a CO-CO_2 atmosphere at 1300 °C? (4 marks)
c) What is the ratio of partial pressures of H_2 to H_2O for equilibrium of Ti and TiO_2 in a H_2-H_2O atmosphere at 1000 °C? (4 marks)
d) What is ΔG^o (kJ/mol) at 650 °C for the reaction: $Ti + SiO_2 = TiO_2 + Si$? (4 marks)
e) Explain why there is no discontinuity in the Ellingham diagram at points where phase transformations take place? (4 marks)

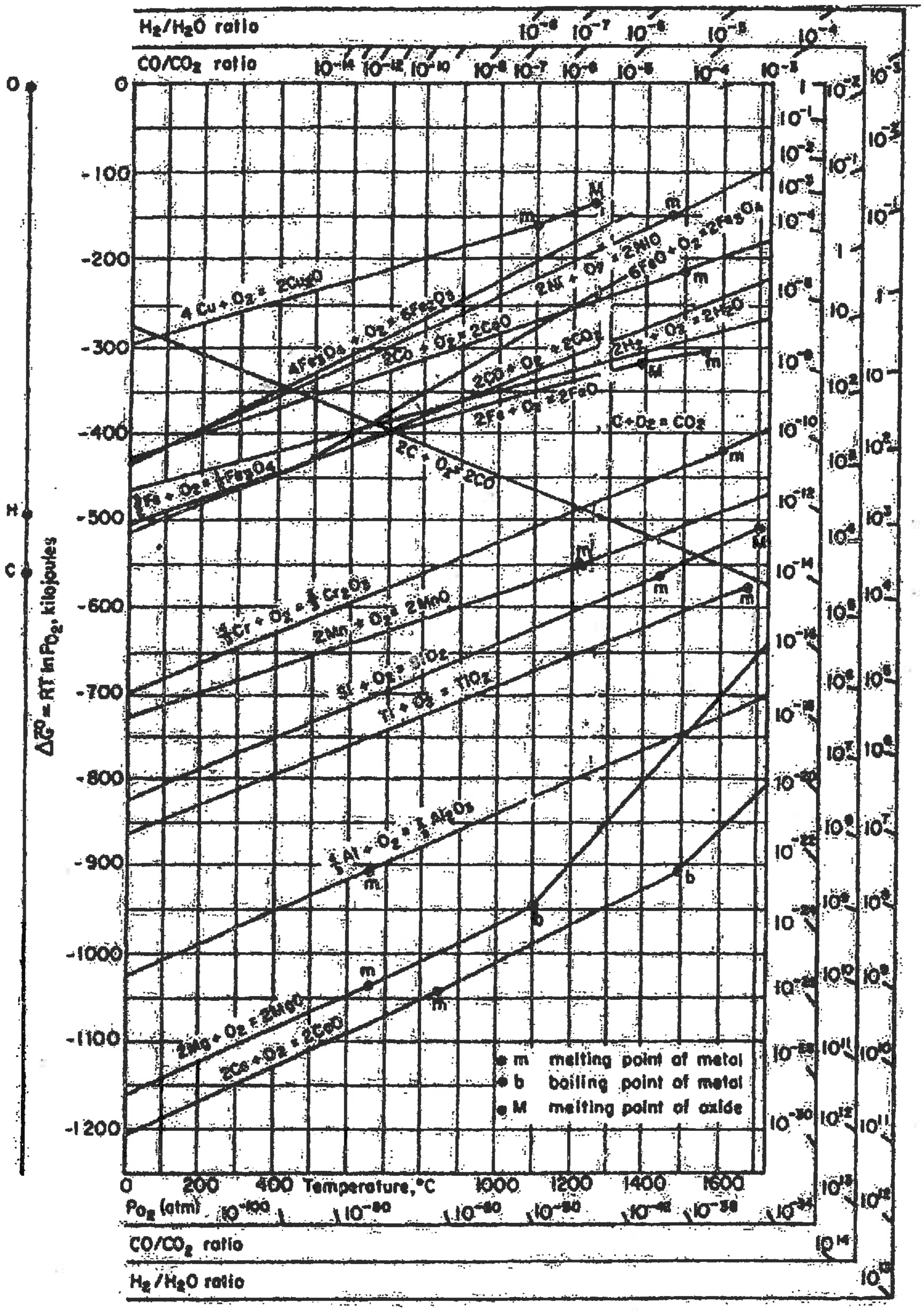


Figure 9–3. Ellingham diagram for some oxides; Richardson nomographic scales are included. (Adapted from D. R. Gaskell, *Introduction to Metallurgical Thermodynamics*, 2nd ed., Hemisphere Publishing, New York, 1981.)