Bachelor of Metallurgical Engineering 2nd Year 2nd Semester Examination, 2018

Thermodynamics of Materials

Time: Three Hours   Full Marks-100

Answer Question No. 1 and any Four from the rest.

1. i) Find whether the following statements are True or False. Give short explanations.

   a) The expression $dU + PdV$ is a perfect differential.
   b) The expression $dU + PdV + VdP$ is a perfect differential.
   c) For a ternary solution i-j-k, $G' = f(T, V, n_i/n_j, n_j/n_k, n_k)$.
   d) In a constant pressure heating of an ideal gas from state 1 to state 2, the heat input is fully converted into work.
   e) Starting from the same initial state, an irreversible adiabatic expansion of an ideal gas ends up at the same final state as the reversible adiabatic expansion.   5

   ii) Is it possible to integrate the expression PdV without specifying the path of change of state? Explain.   3

   iii) Give an example of a gas-phase reaction which is simultaneously a constant pressure, constant temperature, and constant volume process?   3

   iv) The ΔG^0 vs T plot (Ellingham diagram) for the reaction $2M(s) + O_2(g) = 2MO(s)$ is found to be linear, yielding a slope of 100 J/K. The line intersects the $\Delta G^0 = 0$ line at 800 K. Find
   a) how much heat will be liberated from or absorbed by the system when 1 mole of MO (s) is formed by reacting M (s) with O_2 under a constant pressure of (i) 1 atm and (ii) 2 atm.
   b) at what p_{O2} the metal M will oxidize at 500 K.   5

   v) Give the expression for the vibrational (internal) energy for the heavy, diatomic gas molecule and derive the corresponding expression for the vibrational heat capacity at constant volume.   3

   vi) Explain why it is difficult for any substance to attain zero entropy at 0 K.   2

   vii) The fugacity of 3 mol of a real gas occupying a volume of 36 liter is 1.95 atm at 300 K. Find its pressure in MPa.   4

   viii) The equilibrium phase diagram of a single component system is drawn by plotting P against T. Explain if the P represents the total pressure of the system or the vapor

pressure or either of them, in the a) solid-liquid equilibrium curve and b) liquid-vapor equilibrium curve. Under what condition a vapor phase exists along with the solid-liquid equilibrium in the diagram.   5

ix) Explain how the total pressure of the system may affect the extent of a chemical reaction at equilibrium, even when the temperature is kept unchanged. For what type of chemical reactions, there is no effect of total pressure?   4

x) Give the integrated form of Van't Hoff equation operating between the two temperatures T_1 and T_2, under the condition that the ΔC_P of the reaction is equal to Δa, a constant. Note that you may also involve the standard enthalpy change ΔH^0_{298} in the integrated equation.
6

2. i) 0.2 mole carbon and 1.2 mole of air are taken in a closed adiabatic system at 298 K and 1 atm. If the carbon is fully oxidized at constant pressure into CO_2 (no CO), what will be the composition (in terms of partial pressure) of the product gas? Specify all the data you need to find out the adiabatic flame temperature (AFT) of the combustion process.
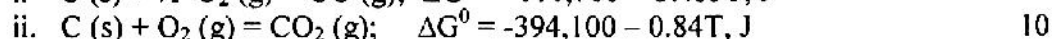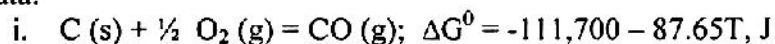5

ii) Air passing through a bed of carbon (C) comes to equilibrium with it and, upon exiting, is analyzed to contain 21% CO.

a) What was the temperature of the bed of carbon?
b) How many moles of air were required to burn 1 mole of carbon?

Note that the exit gas contains CO, CO_2, N_2, and negligible O_2. The total pressure in the system is 1 atm.

Data:
i. $C (s) + \frac{1}{2} O_2 (g) = CO (g)$; $\Delta G^0 = -111,700 - 87.65T$, J
ii. $C (s) + O_2 (g) = CO_2 (g)$; $\Delta G^0 = -394,100 - 0.84T$, J   10

3. i) Find the a) oxygen potential and b) carbon potential of a 40% CO – 60% CO_2 gas mixture at 1000 K and 1 atm total pressure.

Data: See Q. 2 ii) for data.   6

ii) One mole of a monatomic ideal gas is isothermally and reversibly expanded from state 1, given by P_1, V_1, T_1, to state 2 having a volume (V_2) 5 times the initial volume and pressure P_2. The gas occupies a volume V_b when it is reversibly and adiabatically expanded from state 1 to the final pressure P_2. And the gas occupies a volume V_b' when it is irreversibly and adiabatically expanded from state 1 against the final pressure P_2. From the above information, find V_2, V_b, and V_b' in terms of V_1. Also, show V_2, V_b, and V_b in the ascending order.   9

4. i) At 1700 K, it has been reported that SiC (solid) and Si (solid) are in equilibrium with a gas mixture cosisting of 75% SiO and 25% CO at a total pressure of 0.02 atm. Given, in the temperature range 1500-1700 K, the following standard enthalpies of formation:
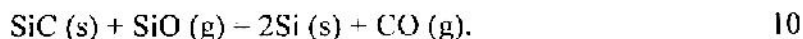
$$\Delta H^0_{SiO\,(g)} = -100,420 \text{ J/mole}$$
$$\Delta H^0_{SiO\,(s)} = -54,390 \text{ J/mole}$$
$$\Delta H^0_{CO\,(g)} = -117,150 \text{ J/mole}$$

a) Using the above data, calculate the ratio of SiO to CO in a gas mixture at equilibrium with SiC (solid) and Si (solid) at 1500 K.

b) Calculate ΔS^0 for the following reaction at 1500 K:

$$\text{SiC (s)} + \text{SiO (g)} - 2\text{Si (s)} + \text{CO (g)}. \hspace{3cm} 10$$

ii) Prove the following:

$$(\partial T/\partial V)_U = (\beta P - \alpha T)/(\beta C_v)$$

(Note, α is the isobaric expansivity and β is the isothermal compressibility.)   5

5. a) Find the standard Gibbs free energy of formation of MnS (solid) from Mn (solid) and S_2 (gas) at 1200 K using the experimental data given in (A) and the established free energy data listed in (B).

(A) Experimental: At 1200 K and 1 atm total pressure , it is found that MnS (solid) and MnO (solid) are in equilibrium with a gas mixture which is 50% H_2O, 0.5% H_2S, and 49.5% N_2.

(B) Standard Gibbs free energies of formation at 1200 K:

     H_2O (gas):   -181,590 J/mole
     H_2S (gas):   -31,380 J/mole
   MnO (solid):   -297,060 J/mole

b) Making use of information given or calculated in a), find the molar ratio of H_2S to H_2 in a gas mixture at equilibrium with Mn (solid) and Mns (solid) at 1200 K.

c) Would it be thermodynamically efficient to use H_2 to reduce MnO to metal at 1200 K? Justify your answer.   15

[Turn over

6. Consider the hydrogen reduction of tin oxide at temperature below the melting point of tin:

$$\frac{1}{2} SnO_2 (s) + H_2 (g) = \frac{1}{2} Sn (s) + H_2O (g)$$
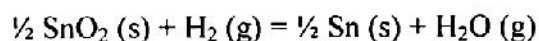
The standard enthalpy of reaction (ΔH^0) is given by the following equation:

$$\Delta H^0 = 53{,}500 - 17.0\, T + 3.2 \times 10^{-3}\, T^2 - 5.3 \times 10^5\, T^{-1}, J.$$

Also, the standard molar entrpies at 298 K are as follows:

	S^0_{298}, J/mol.K
SnO_2 (s)	52.3
H_2 (g)	130.5
Sn (s)	51.5
H_2O (g)	188.7

a) Using the data given above, find an equation giving ΔS^0 as a function of T.

b) Find the composition of a H_2/H_2O gaseous mixture in equilibrium with Sn and SnO_2 at 500 K.   15