Bachelor of Metallurgical Engineering 2nd Year 2nd Semester Examination, 2019

Thermodynamics of Materials

Time: Three Hours | Full Marks-100

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

1. i) Give an example of a gas-phase reaction carried out at a constant temperature which is simultaneously a constant pressure and a constant volume process. 3

ii) Why are the Ellingham diagrams for oxides drawn on the basis of 1 mole O_2, not 1 mole metal or 1 mole metal oxide? 3

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

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

v) How will you contrast Joule-Thomson cooling with adiabatic cooling? Find the Joule-Thomson coefficient (μ) for an ideal gas. 3

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

vii) Give the integrated form of the Van't Hoff equation ($d(\ln K)/dT = \Delta H^0/RT^2$) operating between two temperatures T_1 and T_2 (and the corresponding equilibrium constants K_{T1} and K_{T2}), under the condition that the ΔC_P of the reaction is equal to Δa, a constant. Note that you may involve the standard enthalpy change ΔH^0_{298} in the integrated equation. 5

viii) Define the partial molar enthalpy, $\bar{H}_i$, in a derivative form, as used in a) chemical equilibrium criterion and b) finding heat of reaction. 3

ix) Consider that the air in your examination hall contains 4% moisture and the temperature of the hall is 311 K. Find the activity of H_2O in the air, with respect to a) pure liquid H_2O as standard state and b) 1 atm H_2O (gas) as standard state. Given, for the phase change H_2O (liq) = H_2O (vapor), $\Delta G^0 = 41090 - 110.12\,T$ J. 4

x) The standard Gibbs free energies (ΔG^0) of formation of SnO_2 (s) and H_2O (gas) at 800 K are -415,053 J/mole and -203,510 J/mole, respectively. a) Find ΔG for the process of

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oxidizing 1 mole of Sn (liquid) with H_2O at 0.5 atm pressure to form SnO_2 (s) and H_2 (gas) at 0.5 atm pressure. b) Is this process feasible? 6

xi) In which molar ratio will you mix CO and CO_2 to produce a carbon potential of 0.3 at 1000 K and 1 atm total pressure. (See Q. 5 for data) 4

2. i) When coal is gasified with air or oxygen, the process is strongly exothermic; when gasified with steam, the process is strongly endothermic. Thus the process can be thermally balanced by using oxygen and steam together.

Assume that pure C at 298 K, O_2 at 298 K, and H_2O (g) at 500 K are fed to a reactor which yields a gas at 1200 K composed entirely of CO and H_2. The reactor, which is a constant pressure system, is well insulated so that $q = 0$ for the process.

Find the consumption rates of O_2 and H_2O *each* in moles per mole of C fed to the reactor.

Given: Standard enthalpies of formation at 298 K:

CO	-110.54 kJ/mol
H_2O (g)	-241.83 kJ/mol

Enthalpy changes, $H_T - H_{298}$:

	T = 500 K	T= 1200 K
O_2	6.09 kJ/mol	29.77 kJ/mol
H_2O (g)	6.92 kJ/mol	13.56 kJ/mol
H_2	5.88 kJ/mol	26.80 kJ/mol
CO	5.92 kJ/mol	28.43 kJ/mol
C (s)	2.38 kJ/mol	16.23 kJ/mol

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ii) Prove that

$$\alpha^2 V^2 T / C_P = (\partial V/\partial P)_S - (\partial V/\partial P)_T$$ 4

3. i) A four-step, reversible, cyclic heat engine uses one mole of an ideal monatomic gas as working medium and comprises two constant-temperature steps (at 500 K and 300 K, respectively) and two constant-pressure steps (at 1 atm and 12 atm, respectively).

a) Find ΔS for each of the four steps.
b) What fraction of heat input at high temperature (500 K) is converted into work in the complete cycle.
c) Would the result in b) increase or decrease if the lower temperature were 350 K instead of 300 K? (Preferably do not repeat all previous calculations.)

(Attach a P-V diagram of the cycle to your answer) 10

ii) Refer to the two Ellingham diagrams drawn in Figure 1.

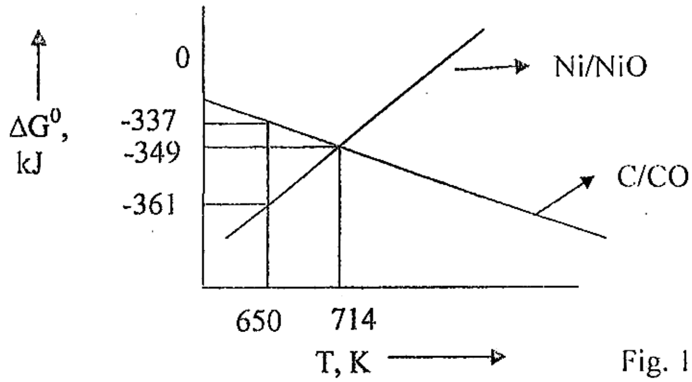

Fig. 1

a) What total pressure is required to reduce NiO (s) by C at 650 K?
b) What temperature is required to reduce NiO (s) by C at 1 atm total pressure? 5

4. i) The standard enthalpy change (ΔH^0) for the reaction Ti (s) + 2 Cl_2 (g) = $TiCl_4$ (g) is given by the following equation:

$$\Delta H^0 = -726{,}340 + 14.2\,T \text{ J.}$$

Derive from this equation another equation giving ΔS^0 as a function of T. Given, ΔG^0 of the reaction at 298 K is -701,190 J. 8

ii) a) Express the thermodynamic efficiency (%) of gas (CO_2) utilization in terms of the equilibrium constant K and total pressure P for the following carbon gasification reaction with pure CO_2:

$$CO_2\,(g) + C(s) = 2CO\,(g)$$

b) Find, from the expression found in a), the efficiency corresponding to K = 1 and P = 1 atm. 7

5. A gas mixture composed of CO_2 : CO : Ar in the ratio 7:3:1 is passed through a bed of carbon at 948 K. Total pressure (p_t) = 1 atm. Find

a) The mol% of CO, CO_2, and Ar in the exit gas at equilibrium.
b) The mole of carbon burnt per mole of inlet gas mixture.

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 15

6. Sander and Healey studied the reaction

$$CaS (s) + \frac{1}{2} O_2 (g) = CaO (s) + \frac{1}{2} S_2 (g)$$

and experimentally found the equilibrium constant $K_{1700} = 300$. Find the standard entropy S^0_{CaS} at 298 K .

Data:

	ΔH^0_{298}, J/mol	S^0_{298}, J/K.mol	$H^0_{1700} - H^0_{298}$, J/mol	$S^0_{1700} - S^0_{298}$, J/K.mol
CaS (s)	-542,665	?	82,840	96.2
O_2 (g)		205	47,970	57.6
CaO (s)	-635,550	39.7	72,970	87.7
S_2 (g)		228	51,150	62.4

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