Bachelor of Metallurgical Engineering 2nd Year 2nd Semester Examination, 2017

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) For one mole of a monatomic ideal gas, G = f (T/P, T).
b) For one mole of a monatomic ideal gas, state = f (H, U).
c) For a ternary solution i-j-k, G' = f (P, V, n_i /n_j, n_j, n_k).
d) An adiabatic expansion of an ideal gas from state 1 to state 2 may take place isothermally as well.
e) In a reversible isothermal expansion with 1 mole of a real gas from state 1 to state 2, the heat input is fully converted into work. 5

ii) A student, by mistake, wrote the reaction A = B as A = A. What is the equilibrium constant of the mistaken reaction? 2

iii) Under what condition the equilibrium constant K of a chemical reaction will be independent of temperature? 2

iv) The ΔG^0 vs T plot 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) The standard free energy of formation of the oxide in the form A + BT.
b) At what p_{O2} the metal will oxidize at 500 K. 5

v) If $dF = Z_1dn_1 + Z_2dn_2 + VdP - SdT$, find, using the concept of Maxwell relation, the derivative that the derivative $(\partial Z_1 / \partial P)_{n_1,n_2,T}$ is equal to. 3

vi) Explain if glass has zero entropy at 0 K in accordance with the 3rd law of thermodynamics. 2

vii) The virial equation for N_2 at 298 K is given as $Z = pV/RT = 1 - (5\times10^{-4})$ P. Calculate

a) The fugacity of nitrogen at 150 atm and 298 K.
b) The pressure at which the fugacity is equal to 80% of the pressure.
c) The free-energy change (ΔG) resulting from the compression of 1 mole of nitrogen at 298 K from 1 atm to 100 atm. 5

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viii) What are the thermodynamic interpretations, in terms of the a) Gibbs free energy and b) vapor pressure, of the statement "The normal melting point of iron is 1809 K". Draw a G vs T and a G vs P plot for iron (solid) and iron (liquid) in support of the free-energy interpretation. 5

ix) Four particles (atoms) of A and B each are kept in two compartments, separated by a partition, of an isolated system. The particles are allowed to mix by snapping the partition. Find the resulting configurational entropy change of the system. 5

x) In a constant temperature (1000 K) and constant volume system, 17 moles of M (s), 10 moles of O_2 (at 0.8 atm) and 3 moles of MO (s) are initially taken and allowed to react according to the reaction

$$M(s) + \tfrac{1}{2} O_2(g) = MO(s) \ldots\ldots\ldots (A)$$

The system is found to attain equilibrium when the number of moles of MO has increased to 13. The system rejects 996520 J of heat to the surrounding (thermostat) in the process. Find

a) the equilibrium constant of reaction (A) at 1000 K
b) the enthalpy change of reaction (A) at 1000 K. 6

2. i) Prove the following:

a) $(\partial H/\partial V)_T = (\alpha/\beta)T - 1/\beta$
b) $(\partial S/\partial T)_V = (\partial S/\partial T)_P - \alpha^2 V/\beta$ 7

ii) Two tube furnaces are arranged in series, first one at 900 K. Copper chips are in the first furnace, and an iron (Fe) sample in the second. Nitrogen containing 1% O_2 is passed through the first furnace, where it reacts with the Cu, forming Cu_2O (s), and attains equilibrium. Then the gas passes through the second furnace where it contacts the iron. What is the lowest permissible temperature in the second furnace without danger of oxidation of the Fe into FeO? Note, P_{total} = 1atm.

Data: $2Cu(s) + \tfrac{1}{2} O_2(g) = Cu_2O(s)$, $\Delta G^0 = -168{,}406 + 71.25\,T$ J
$Fe(s) + \tfrac{1}{2} O_2(g) = FeO(s)$, $\Delta G^0 = -259{,}600 + 62.55\,T$ J 8

3. i) Consider the reduction of M_2O (s) to M (s) in a closed system reactor with pure CO inlet gas at 1000 K, P_{total} = 1atm, and the reaction reaching equilibrium. The following questions are to be answered in terms of the equilibrium constant K for the reaction which occurs and is as follows:

$$M_2O(s) + CO(g) = 2M(s) + CO_2(g)$$

a) What is the reactant efficiency: (mole of CO reacted) / (mole of CO admitted); i.e., how many mol of CO react for each mole of CO admitted?

b) How many moles of CO must be admitted to produce one mole of M (s)? 9

ii) 0.02 moles of iodine vapor at 0.08 atm pressure and 390 K are isothermally compressed. At what pressure iodine vapor will start liquefying? The vapor pressure of liquis iodine is given by

$$\ln p(\text{atm}) = -(7380/T) - 5.181 \ln T + 47.83.$$ 6

4. **Consider the following two separate experiments, both carried out at 800 K and with a** total gas pressure of 1 atm.

Expt. A: Pure CO is fed slowly into a tube furnace containing a mixture of magnetite (Fe_3O_4) and metallic iron (Fe). The gas leaving the bed is 52 mole% CO_2, 48 mole% CO, and is at equilibrium with the iron-magnetite mixture.

Expt. B: This is the same as Expt. A except that the gas flow rate is much higher, so that the gas does not reach equilibrium with the iron-magnetite mixture. The effluent gas is 40% CO_2, 60% CO.

a) Find the Gibbs free energy change in Expt. B, per mole of CO fed to the bed.
b) Using the data of Expt. A, find the standard free energy of formation of Fe_3O_4 at 800 K ($\Delta G^0_{Fe3O4,\, 800\, K}$).

Given,
$\Delta G^0_{CO2,\, 800\, K} = -395{,}555$ J/mol, $\Delta G^0_{CO,\, 800\, K} = -182{,}757$ J/mol. 15

5. A gas mixture composed of CO : CO_2 : Ar in the ratio 2:1:1 is passed through a bed of carbon at 1073 K. Total pressure (p_t) = 1 atm. Find

a) The 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. One gram of $CaCO_3$ is placed in an evacuated rigid vessel of volume 1 liter at room temperature (298 K), and the system is heated. Calculate

a) The highest temperature at which $CaCO_3$ phase is present.

b) The pressure inside the vessel at 1000 K.
c) The pressure inside the vessel at 1500 K.

Data: $CaCO_3$ (s) = CaO (s) + CO_2 (g); $\Delta G^0 = 168{,}400 - 144\,T$ J 15
