EX/PG/METIM-MATE/T/113A/23,25/2017

M. Tech. Mat. Engg. & M. Met. Engg. (I.M.) 1st Semester Examination, 2017

Physicochemical Principles of Metallurgical Processes

Time: Three Hours | Full Marks-100

Answer question number 1 and any four from the rest.

1. i) Explain whether the following statements are True or False; give short explanations:

   a) For a ternary gas mixture i-j-k, State = f(T, P, V, n_i, n_j,).
   b) For 4 moles of a ternary liquid solution i-j-k, H = f(S/P, P, n_i/n_j, n_i/n_k).
   c) For 1 mole of a monatomic ideal gas, State = f(H/U, T).
   d) In an adiabatic free expansion, the internal energy of an ideal gas does not change. 5

   ii) How will you contrast an isolated system with an adiabatic system in terms of heat interaction (δq), work interaction (δw) and change in internal energy (dU). 3

   iii) Starting from dH = TdS + VdP, show that for a reversible adiabatic process with n moles of an ideal gas

   $$\Delta H = nC_P (T_2 - T_1).$$ 4

   iv) Two moles of a monatomic ideal gas, with the molar heat capacity $C_P = (5/2)R$, are taken in a closed system at 600 K and 3 atm pressure. The gas is irreversibly and adiabatically expanded against 2 atm (external) pressure to a final volume V_2. Find V_2. 5

   v) To show that the cyclic integration $\oint(\delta q_{rev}/T)$ is equal to zero for any reversible cycle, consider a reversible cycle comprised of four alternate isothermal and constant pressure steps and prove. Consider n moles of ideal gas as the system. 5

   vi) Write three statements of the 2nd law of thermodynamics dealing with the impossibility of processes/cycles. 3

   vii) The virial equation for N_2 at 298 K is given as $Z = pV/RT = 1 - (5\times10^{-4})\,P + (3\times10^{-6})\,P^2$. Calculate the fugacity of nitrogen at 150 atm and 298 K. 4

   viii) The molar free energy of a metal at 1 atm pressure is considered to vary with temperature as follows:

   $$G = 30{,}000 + 175\,T - 25\,T\ln T$$

   Find the molar enthalpy H and molar heat capacity C_P of the metal at 500 K. 5

ix) The standard free energy of formation of a metal oxide M_2O_3 is given as $\Delta G^0 = A + BT$ joule. Find the temperature, in terms of A and B, at which the oxide will dissociate into M and O_2

a) under 1 atm O_2
b) under 0.25 atm O_2

Also, find the standard free energy change (ΔG^0) of the Ellingham reaction for the oxide. 6

2. a) A gas mixture containing 50% argon, 40% CO_2 and 10% CO is passed through a bed of carbon at 1100 K. Total pressure (p_t) = 1 atm. Calculate the mol% of CO and CO_2 in the exit gas at equilibrium.
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

b) Prove that for a fixed mass and fixed composition system

$$(\partial U/\partial T)_P = c_V + V\alpha\,[(T\alpha/\beta) - P]$$ 5

3. a) Fifty grams of palladium oxide (PdO) is placed in a tube furnace at 1200 K, and air is passed through the furnace slowly enough to permit equilibrium between the gas and solid phases before the gas leaves the tube furnace. P_{total} = 1 atm. After the passage of 1 mole of air, the sample is found to have lost 3.0 gm. Calculate the standard free energy of formation of PdO (s) from Pd (v) and O_2 (g) at 1200 K.
Data: Atomic weight of Pd = 106.4. 10

b) A JU engineer claims to have invented a cycle in which the system takes up 3000 kJ of heat from the hot reservoir at 500 K and rejects 1200 kJ of heat to the cold reservoir at 300 K. Is the engineer's claim acceptable according to the 2nd law of thermodynamics? 5

4. a) 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. 6

b) 1 mole of H_2 and 1 mole air (air contains 80% N_2 and 20% O_2) are mixed at 298 K and burned under adiabatic and constant pressure condition. Calculate the AFT.
Data:
i. $H_2(g) + \frac{1}{2} O_2(g) = H_2O(g)$; $\Delta H^0_{298\,K} = -246{,}000$ J

ii. $C_{P,H2O}(g) = 30.00$ J/deg.mol
iii. $C_{P,H2}(g) = 27.37$ J/deg.mol
iv. $C_{P,N2}(g) = 20.79$ J/deg.mol
iv. $C_{P,O2}(g) = 29.96$ J/deg.mol
(Note, all data may not be needed). 9

5. a) At a pressure of 1 atm, the melting temperature of lead is 600 K and its latent heat of fusion at this temperature is 4810 J/mol. If 1 mole of supercooled liquid lead spontaneously freezes at 590 K and 1 atm pressure, calculate the entropy produced, *i.e.*, the $\Delta S_{universe}$.
Data:
$C_{P,Pb(l)} = 32.4 - 3.1 \times 10^{-3}$ T, J/K.mol
$C_{P,Pb(s)} = 23.6 + 9.75 \times 10^{-3}$ T, J/K.mol 9

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

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

6. a) Nickel oxide (NiO) is to be chlorinated in a reactor. It is required that 90% conversion of the input chlorine gas be achieved during a single pass of the gas through the reactor at 900 K. What total gas pressure is required? Will the conversion efficiency increase with the increase in the total pressure?
Data:

$Ni(s) + \frac{1}{2} O_2(g) = NiO(s)$, $\Delta G^0 = -244{,}550 + 98.5\ T$ J
$Ni(s) + Cl_2(g) = NiCl_2(s)$, $\Delta G^0 = -314{,}650 + 159.1\ T$ J 12

b) Explain why glass does not have zero entropy at 0 K. 3
