S.Y.B.Sc. Physical Chemistry

PRACTICE PROBLEMS ON THERMODYNAMICS

1	Calculate the free energy changes at 300 K when the change in enthalpy of the reaction is – 94.47 kJ and entropy change is – 188.9 J in the same reaction. Say whether the reaction *is* spontaneous or non-spontaneous. (**Ans**. ΔG = – 37.8 KJ, since it is – ve, the process is spontaneous)
2	For a certain process ΔG = – 3.824 kJ and ΔH = – 5.031 kJ at 450K. Calculate for the process: i) ΔS and ii) $\left[\frac{\partial}{\partial T}(\Delta G)\right]_p$ at 450K (**Ans**. i) ΔS = – 2.682 JK^{-1} , ii) $\left[\frac{\partial}{\partial T}(\Delta G)\right]_p$ = 2.682 JK^{-1})
3	For the reaction : $HgS_{(red)} = HgS_{(black)}$; $\Delta G = 17138 - 25.46\ T$ Calculate the temperature at/above which the transition will be spontaneous. Calculate the ΔG and ΔH at 300K. (**Ans**. T = 673 K , ΔG = 9.5kJ mol^{-1} ΔH = 1.862 kJ mol^{-1})
4	Calculate the free energy change of a process whose change in enthalpy at 373 K is –264.93 kJ and the temperature coefficient of the process is 19.58 J. (**Ans.** ΔG = –257.63 kJ)
5	The free energy change accompanying a given process is – 91.21 kJ mol^{-1} at 293 K and – 89.12 kJ mol^{-1} at 303K. Calculate the enthalpy change for the process at 298K. (**Ans**. ΔH = –152.447 kJ)
6	Calculate the standard free energy change (ΔG^0) for the reaction $2H_2O_{(g)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$ given that at 1000 K, and 1 torr pressure, the degree of dissociation is 3.0×10^{-7} (R = 8.314 $J.deg^{-1}$ $mole^{-1}$) (**Ans.** ΔG = 380.445 kJ)
7	The standard free energy change (ΔG^0) for the reaction $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO$ is 71.128kJ. Calculate the equilibrium constant for the reaction at 2000 K (R = 8.314 $J.deg^{-1}$ $mole^{-1}$) (**Ans.** K_p = 0.0139)
8	Find the value of K_p, for the reaction **$CO_{(g)}$ + $H_2O_{(g)}$ $\rightleftharpoons$ $HCOOH_{(g)}$.** The standard free energies of $CO_{(g)}$, $H_2O_{(g)}$ and $HCOOH_{(g)}$ are respectively **–137.23**, **–228.45** and **–333.55 kJ** at 298 K. What will he the course of the reaction? (**Ans.** As $K_p = 5.248 \times 10^{-4}$, which is very small, hence reaction will proceed in backward direction)
9	At 300 K and one torr pressure N_2O_4 is 20% dissociated to NO_2. Calculate std. free energy change (ΔG^0) for the reaction (R = 8.314J deg^{-1} $mole^{-1}$) (**Ans.** (ΔG^0) = 4.48 KJ)

10	The equilibrium constant K_p for the reaction $H_2(g) + S(g) \rightleftharpoons H_2S(g)$, at 1218 K is 20.2 and the enthalpy change is 88.5 J $deg^{-1}mole^{-1}$. Calculate the equilibrium constant at 1318 K . (**Ans.**$K''_p = 10.41$)
11	The equilibrium constant (K_p) for the reaction $N_2+3H_2 \rightleftharpoons 2NH_3$ is 1.64×10^{-4} at 673 K and 0.144×10^{-4} at 773K. Calculate the heat of formation of one mole of ammonia from its elements in this temperature range. (**Ans**. $\Delta H = 52.5895$ kJ)
12	For the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ The value of $K_p = 1.597 \times 10^{-8}$ at 673 K. Calculate the value of K_c (**Ans**. $K_c = 0.499$)
13	For a chemical reaction the values of ΔH and ΔS are – 94.45 KJ and – 188.93 J/deg. respectively. These values do not change much with the temperature. What is the free energy change for this reaction at 300 K and 1000 K. (**Ans.** – 37.787 KJ and – 93.63 KJ)
14	If the vapour pressure of liquid water at 354.9 K is 0.5 pascal. Find ΔG at this temperature for the process $H_2O_2 \rightarrow H_2O_{(g)}$ (**Ans.** 2043.6 J)
15	The standard entropy of $A_{(g)}$ as a function of temperature is given by: **$S^o = 8.68 + 11.44 \log TK$**. Find the change in free energy suffered by a 1 mole of $A_{(g)}$ when its temperature is changed from 298 K to 348 K at a constant pressure of 1 pascal. (**Ans.** – 7816.6 J/mole)
16	Find whether $Br_{2(g)}$ will oxidize $H_2S_{(g)}$ to give $S_{(s)}$ at 25^0C and 1 Pascal pressure if the std. free energies of formation (ΔG^0) of H_2S, $Br_{2(g)}$ and $HBr_{2(g)}$ are –32.98, 3.135 and – 53.17 KJ/mole respectively at the temperature. **(Ans**. The oxidation takes place as change is spontaneous, ΔG = – 76.49 KJ)
17	For a reaction $CaCO_{3(s)} \rightarrow CO_{2(g)}$; ΔG^0 at 25°C = 130 KJ and at 25^0 C = 160.5 e.u. Calculate (a) ΔG at 0.01 pascal pressure at the same temperature and (b) ΔG at 35^0C temperature, assuming that ΔS^0 is independent of temperature. **(Ans.** (a) 118.7 KJ (b) 128.326 KJ)
18	Calculate the free energy change for the reaction $CO + H_2O \rightarrow CO_2 + H_2$ at 25^0 C, if free energy of formation of CO , H_2O, CO_2 and H_2 are –133.76; –392.92; –228.23 and –238.26 respectively. (**Ans**. 60.2 KJ)
19	For the reaction $N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$, the standard free energy change is given by $\Delta G^0 = 21600 – 2.5\ T$. Calculate K_p for the reaction. **(Ans.** 2.63×10^{-3})

20	For the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ K = 42.9 at 900K . Calculate the standard free energy change (ΔG^0) of the reaction at 900K. **(Ans**. (ΔG^0) = – 28.132kJ)
21	For the reaction ½ $H_{2(g)}$ + ½ $Cl_{2(g)} \rightleftharpoons HCl_{(g)}$ the standard free energy at 298K is –95.37 kJ. Calculate the equilibrium constant for the dissociation of HCl into its elements at 298K. (**Ans. K'** = 2.01×10^{-17})
22	At 298K and 1 bar pressure, nitrogen tetroxide N_2O_4 is dissociated to the extent of 18.46%. Calculate the standard free energy change at 298K. The reaction is $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ (**Ans. (ΔG^0)** = 4.851kJ)
23	At 30^0C for the dissociation , $SO_2Cl_{2(g)} = SO_{2(g)} + Cl_{2(g)}$, the free energy change ΔG^0 is 8.29 kJ. Calculate the percentage dissociation at the total equilibrium pressure of 10 bar. (**Ans.** 6.088%)
24	The equilibrium constant K_p for the dissociation: $2H_2S \rightleftharpoons 2H_{2(g)} + S_{2(g)}$ is $K_p = 1.18 \times 10^{-2}$ at 138 K and the enthalpy change , ΔH is 177.4 kJ. Calculate the equilibrium constant at 1573K. (**Ans.** K_{p2} = 0.1277)
25	For the reaction: $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ K_c = 50.0 at 721 K and K_c = 66.9 at 629K. Calculate the ΔU and ΔH of the reaction over this temperature range. (**Ans.** $\Delta H = \Delta E$ = 11.101 kJ)
26	For the reaction, $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$ ΔH^0 = 196.3 kJ and ΔG^0= 139.9 kJ at 298K. Assuming ΔH^0 to be independent of temperature, calculate the ΔG^0 at 700K. (**Ans.** ΔG^0 = 638.2 kJ)
27	For the reaction: $CO_{2(g)} + 2NH_{3(g)} \rightleftharpoons (NH_2)_2CO_{(s)} + H_2O_{(l)}$ ΔH and ΔS at 298K are respectively – 136.644 kJ and – 425.88 JK^{-1} . Calculate the maximum temperature at which reactions will be spontaneous. **(Ans**. 313.8 K)
28	What is the change in free energy of a chemical process whose change in enthalpy at 373K is 269.114 kJ and the entropy change is - 220 JK^{-1} (**Ans**. – 187.05kJ)
29	For the reaction : $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ at 298 K, the partial pressures at equilibrium of N_2 , H_2 and NH_3 are respectively 0.2, 0.4 and 0.6 bar. Calculate (i) K (ii) ΔG^0. Is the reaction spontaneous? (**Ans:** (i)28.13 (ii) – 8.268 kJ ΔG^0 – ve , hence spontaneous)
30	For the reaction $A_{2(g)} + B_{2(g)} \rightleftharpoons$ 2AB, the equilibrium constant is doubled when the temperature increases from 298 to 308 K. Calculate ΔH for the reaction. (**Ans**. 53kJ mol^{-1})

31	At 298 K, for the reaction, $6C_{(s)} + 6H_{2(g)} = C_6H_{12(l)}$: $\Delta H = -157.7$ kJ, $\Delta S =$ 206.3JK. Calculate the free energy of formation of C_6H_{12} at 298 K. (**Ans.** – 219.17 kJ)
32	For the reaction $C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$ $\Delta H = 131.38$ kJ , $\Delta S = 133.8k\,JK^{-1}$ Will the reaction be spontaneous at 1000 K? (**Ans.** $\Delta G = -2420$ J, hence spontaneous)
33	For the reaction , $H_2S_{(g)} + \frac{3}{2} O_{2(g)}$ $H_2O_{(g)} + SO_{2(g)}$ ΔG^0 at 500K is – 470.15 kJ. Calculate the equilibrium constant for the reaction. (**Ans.**1.l2 x 10^{50})

34) 23 g of an aqueous solution of ethyl alcohol contains 2.3g ethyl alcohol.If the change of chemical potential of ethyl alcohol is -8kJ find the change of chemical potential of water

35) For the reaction

$$N_2(g) + 3Cl_2(g) \longleftrightarrow 2NCl_3(g)$$

The equilibrium constant for the dissociation of NCl_3 is 5.76 X 10^7 at 400^0C.Calculate the standard free change for the reaction.

36) For the reaction

$$N_2(g) + O_{2(g)} \longleftrightarrow 2NO(g)$$

Heat of formaton of No is 9.097 X 10^4J.if K_p for the reaction is 1.21 x 10^{-3} at 1800K, find K_p at 2000K.