Thermodynamics

SUBJECTIVE PROBLEMS:

Q 1.

The enthalpy for the following reaction (ΔH^o) at 25°C are given below:

(i) 1/2 $H_2(g)$ + 1/2 $O_2(g)$ → OH(g) 10.06 kcal

(ii) $H_2(g)$ → 2H(g) 104.18 kcal

(iii) $O_2(g)$ → 2O(g) 118.32 kcal

Calculate the O-H bond energy in the hydroxyl radical. **(IIT JEE 1981 – 2 Marks)**

Q 2.

The standard heats of formation at 298 K for $CCI_4(g)$, $H_2O(g)$, $CO_2(g)$ and HCI(g) are -25.5, -57.8, -94.1 and -22.1 kcal/mol respectively. Calculate ΔH°_{298} for the reaction

$CCI_4(g) + 2H_2O \rightarrow CO_2(g) + 4HCI(g)$ **(IIT JEE 1982 – 2 Marks)**

Q 3.

The molar heats of combustion of $C_2H_2(g)$, C(graphite) and $H_2(g)$ are 310.62 kcal, 94.05 kcal and 68.32 kcal, respectively. Calculate the standard heat of formation of $C_2H_2(g)$.

(IIT JEE 1983 – 2 Marks)

Q 4. The heat energy, q, absorbed by a gas ΔH, is true at what condition(s).

(IIT JEE 1983 – 2 Marks)

Q 5.

Give the following standard heats of reaction :

(i) heat of formation of water = -68.3 kcal;

(ii) heat of combustion of acetylene = - 310.6 kcal;

(iii) heat of combustion of ethylene = -337.2 kcal;

Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25°C).

(IIT JEE 1984 – 4 Marks)

Q 6.

The bond dissociation energies of gaseous H_2, CI_2 and HCI are 104, 58 and 103 kcal/mole respectively. Calculate the enthyalpy of formation of HCI gas. **(IIT JEE 1985 – 2 Marks)**

Q 7.

The standard molar heats of formation of ethane, carbon dioxide and liquid water are -21.1, -94.1 and -68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane. **(IIT JEE 1986 – 2 Marks)**

Q 8.

An intimate mixture of ferric oxide, Fe_2O_3, and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc of the mixture. Heats of formation and densities are as slow : **(IIT JEE 1988 – 2 Marks)**

H_f (AI_2O_3) = 399 kcal/mole;

H_f (Fe_2O_3) = 199 kcal/mole;
Density of Fe_2O_3 = 5.2 g/cc;
Density of Al = 2.7 g/cc.

Q 9.

An athlete is given 100 gm of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilizes 50 percent fo this gained energy in the event. In order to avoids storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ/mole. **(IIT JEE 1989 – 2 Marks)**

Q 10.

The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are -241 -3800 and -3920 kJ/mole respectively. Calculate the heat of hydrogenation of cyclohexene. **(IIT JEE 1989 – 2 Marks)**

Q 11.

Using the data (all values are in kcal mol^{-1} at 25°C) given below, calculate the bond energy of C-C and C-H bonds. **(IIT JEE 1990 – 5 Marks)**

$\Delta H^o_{combustion}$ (ethane)	=	-372.0
$\Delta H^o_{combustion}$ (propane)	=	-530.0
$\Delta H^o C_{(s)} \rightarrow C(g)$	=	172.0
Bond energy of H-H	=	104.0
ΔH^o_f of $H_2O(l)$	=	-68.0
ΔH^o_f of $CO_2(g)$	=	-94.0

Q 12.

A gas mixture of 3.67 litres of ethylene and methane on complete combustion at 25°C produces 6.11 litres of CO_2. Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are -1423 and -891 kJ mol^{-1} at 25°C. **(IIT JEE 1991 – 5 Marks)**

Q 13.

Determine the enthalpy change of the reaction.
$C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$, at 25°, using the given heat of combustion values under standard conditions

Compound	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	C(graphite)
ΔH^o (kJ/mol)	-285.8	-890.0	-1560.0	-393.5

The standard heat of formation of $C_3H_8(g)$ is -103.8 kJ/mol. **(IIT JEE 1992 – 3 Marks)**

Q 14.

In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and 6x litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen?

Assume that losses due to incomplete combustion, etc, are the same for both the fuels and the gases behave ideally. **(IIT JEE 1993 – 3 Marks)**

Heats of combustion :

$CH_4 = 809$ kJ/mol; $C_4H_{10} = 2878$ kJ/mol

Q 15.

The polymerization of ethylene to linear polyethylene is represent by the reaction

(IIT JEE 1994 – 2 Marks)

$nCH_2 = CH_2 \rightarrow [CH_2 - CH_2]$

where n has a large integral value. Given that the average enthalpies of bond dissociation for C = C and C-C at 298 K are + 590 and + 331 kJ mol^{-1}, respectively, calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

Q 16.

The standard molar enthalpies of formation of cyclohexane(l)and benzene(l) at 25°C are- 156 and+ 49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene(l) at 25°C is -1 19 kJ mol^{-1}. Use these data to estimate the magnitude of the resonance energy of benzene

(IIT JEE 1996 – 2 Marks)

Q 17.

The enthalpy change involved in the oxidation of glucose is 72880 kJ mol^{-1}, Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after eating 120 g of glucose. **(IIT JEE 1997C – 2 Marks)**

Q 18.

Compute the heat of formation of liquid methyl alcohol in kilojoules per mole, using the following data. Heat of vaporization of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states; H, 218 kJ1mol; C, 715 kJ1mol; 0,249kJ 1mol. Average bond energies :

C-H = 415kJ/mol, C-O =365 kJ/mol, O-H=463 kJ/mol **(IIT JEE 1997- 5 Marks)**

Q 19.

Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. (Ionisation energy for Al = 5137 kJ mol^{-1}; $\Delta H_{hydration}$ for Al^{3+} = 4665 kJ mol^{-1}; $\Delta H_{hydration}$ for CI = -381 kJ mol^{-1}.) **(IIT JEE 1997- 2 Marks)**

Q 20.

From the following data, 'calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of CO_2(g), H_2O(1) and propene(g) are - 393.5, - 285.8 and 20.42 kJ mol-I respectively. The enthalpy of isomerisation ofcyclopropane to propene is - 33.0kJ mol^{-1}. **(IIT JEE 1998 - 5 Marks)**

Q 21.

Estimate the average S-F bond energy in SF_6. The values of standard enthalpy of formation of SF_6(g), S(g)and F(g) are : - 1100,275 and 80 kJ mol^{-1} respectively.

(IIT JEE 1999 - 3 Marks)

Q 22.

A sample of argon gas at 1 am pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process.$C_{V\,m}$ for argon is 12.48 JK^{-1} mol^{-1}.

(IIT JEE 2000 - 4 Marks)

Q 23.

Show that the reaction CO(g) + 1/2 O_2(g) → CO_2 (g) at 300 K, is spontaneous and exothermic, when the standard entropy change is4.094 kJ mol^{-I} K^{-I}. The standard Gibbs free energies of formation for CO_2 and CO are -394.4 and, -137.2kJ mol-I, respectively.

(IIT JEE 2000 - 3 Marks)

Q 24.

Diborane is a potential rocket fuel which undergoes combustion according to the reaction.

(IIT JEE 2000 - 2 Marks)

B_2H_6 (g) +3 O_2 (g) → B_2O_3 (s) + 3.H_2O (g)

From the following data, calculate the enthalpy change for the combustion of diborane.

2B(s) + 3/2 O_2 (g) → B_2O_3(s) ΔH = - 1273 kJ mol^{-1}

H_2(g) + 1/2 O_2(g) → $H_2O(\ell)$ ΔH = 44kJ mol^{-1}

2B(s) + 3H_2 (g) → B_2H_6(g) ΔH = 36 kJ mol^{-1}

Q 25.

When 1-pentyne (A) is treated with 4 N alcoholic KOH at 17S°C, it is converted slowly into an equilibrium mixture of 1.3% I-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1,2- pentadiene (C). The equilibrium was maintained at 175°C. Calculate AGO for the following equilibria :

B ⇌ A ΔG_1° =? B ⇌ C ΔG_2° =?

From the calculated value of ΔG_1° and ΔG_2° indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C).

(IIT JEE 2001 - 10 Marks)

Q 26.

Two moles of a perfect gas undergo the following processes

(IIT JEE 2002 -5 Marks)

(a) a reversible isobaric expansion from (1.0 am, 20.0L) to (l.0 atm40.0 L);

(b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);

(c) a reversible isothermal compression from (0.5 am, 40.0 L) to (1.0 atm, 20.0 L).

(i) Sketch with labels each. of the processes on the same P-V diagram.

(ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.

(iii) What will be the values of AU, AH and AS for the overall process?

Q 27.

C_v value of He is always 3R/2 but C_v value-of H_2 is 3R/2 at low temperature and 5R/2 at moderate temperature and more than 5R/2 at higher temperature explain in two to three lines.

(IIT JEE 2003 - 2 Marks)

Q 28.

An insulated container contains 1 mol of a liquid, molar volume 100 ml, at 1 bar. When liquid is steeply pressed to 100 bar, volume decreases to 99 ml. Find. ΔH and ΔU for the process.

(IIT JEE 2004 - 2 Marks)

Q 29. In the following equilibrium N_2O_4 (g) ⇌ $2NO_2$(g) **(IIT JEE 2004 - 2 Marks)**

When 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.

Given : $\Delta G_f^\circ(N_2O_4)$ = 100kJ; ΔG_f° (NO_2) = 50 kJ

(i) Find ΔG of the reaction at 298 K.

(ii) Find the direction of the reaction

Q 30.

For the reaction, $2CO + o_2 \rightarrow 2CO_2$; ΔH = -560kJ. Two moles of CO and one mole of 0, are taken in a container of volume 1 L. They completely form two moles of CO_2, the gases, deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500K. (1 L atm = 0.l kJ)

(IIT JEE 2006 - 6Marks)