Chapter 6. Thermodynamics

Question-1

State and explain Hess's law of constant heat summation by taking a suitable example.

Solution:

The total heat change (ΔH) accompanying a chemical reaction is the same whether the reaction takes place in one step or more steps"

In means that the heat of a reaction depends only on the initial and final states of the system and independent of the path follwed by the system. Carbon can be converted into carbon dioxide either directly or via the formation of carbon monoxide. Formation of CO_2 directly.

$C_{(S)} + O_{2(g)} \longrightarrow CO_{2(g)}$; ΔH = -94 Kcal

Formation of CO_2 via formation of carbon dioxide.

$C_{(s)} + ½\ O_{2(g)} \longrightarrow CO_{(g)}$; ΔH_1 = -26. 4 Kcal

$CO_{(g)} + ½\ O_{2(g)} \longrightarrow CO_{2(g)}$; ΔH_2 = 67.6 Kcal

According to Hess's Law : $\Delta H = \Delta H_1 + \Delta H_2$

-94 = -26.4 + (-67.6)

-94 = -94.

Question-2

What is heat of enthalpy for the transition of S rhombic to S monoclinic (heat of combustion of S (rhombic) and S monoclinic are –71.1 kcal and –71.7 k cal respectively)?

Solution:

$S(rhombic) + O_{2\ (g)} \longrightarrow SO_{2(g)}$; Δ H = -71.1 kcal ---- 1

$S(monoclinic) + O_{2(g)} \longrightarrow SO_{2(g)}$; Δ H = -71.7 kcal ---- 2

Reverse equation (2),

$SO_2 \longrightarrow S(monoclinic) + O_{2(g)}$; Δ H = +71.7 kcal ---- 3

On adding 1 and 3 we get

$S(rhombic) + O_{2(g)} + SO_{2(g)} \longrightarrow SO_{2(g)} + S(monoclinic) + O_{2(g)}$

$S(rhombic) \longrightarrow S(monoclinic)$ + 0.6 kcal (+71.7 + (-71.1) kcal; (Δ H = +0.6kcal).

Question-3

Derive the mathematical formulae of first law of thermodynamics.

Solution:

Let q be the heat supplied to the system

A part of q may be used up by the system itself in increasing its internal energy by ΔE and rest is used for performing external work w.

∴ As per first law, $q = \Delta E + w$

$$\Delta E = q - w$$

If work done is the pressure - volume, then $w = p.dv$ where dv is the change in volume P is the external pressure.

$\Delta E = q - P\,\Delta V$.

Question-4

Show that the heat absorbed at constant volume is equal to the increase in the internal energy of the system, whereas that at constant pressure is equal to the increase in the enthalpy of the system.

Solution:

As per mathematical form of first law of thermodynamics, $\Delta E = q - P\Delta V$.

At constant volume,

$\Delta V = 0$; (ie) $\Delta E = q - o = \Delta E = q$; That is heat absorbed at constant volume is equal to the increase in the internal energy of the system.

From definition,

$H = E + PV$; $\Delta H = \Delta E + \Delta(PV)$

$\Delta H = \Delta E + P\Delta V + V.\,\Delta P$

At constant pressure, $\Delta p = o$;

$\Delta H = \Delta E + P\Delta V$

substitution $\Delta H = q_p - P\Delta V$

$$\Delta H = q_p - P\Delta V + P\Delta V$$

$$\Delta H = q_p.$$

Question-5

What is the relation between enthalpy of reaction and enthalpies of formation?

Solution:

Enthalpy of reaction

ΔH = [Sum of the standard enthalpies of formation of products] - [sum of the standard enthalpies of formation of the reactants]

$= \Sigma\ \Delta H^0 f$ products $- \Sigma\ \Delta H^0 f$ reactants.

Question-6

Given the standard enthalpies of formation of $CO_{(g)}$ and $H_2O_{(g)}$ as –110.5 kJ and –241.8 KJ mol^{-1} respectively. Calculate ΔH^0 and ΔE^0 for the reaction.

Solution:

$C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)}$

$\Delta H^0 = \Sigma\ \Delta H^0{}_f$ products $- \Sigma\ \Delta H^0{}_f$ reactants

$= -110.5 - (-241.8)$

$\Delta H^0 = +131.3$;

$\Delta n = 2-1 = 1$;

$\Delta H^0 = \Delta E^0 + (\Delta n)\ RT$

$\Delta E^0 = \Delta H^0 - (\Delta n)\ RT$

$= +131.3 - (1)\ (8.314 \times^3 k\ Jk^-)(298\ k)$

$= +131.3 - 2.478$ KJ

$= 128.82$ kJ.

Question-7

(a) What is the relationship between enthalpy of reaction and bond energies of reactants and products?

(b) Calculate the enthalpy change (ΔH) of the following reaction:
$2C_2H_{2(g)} + 5O_{2(g)} \rightarrow 4CO_{2(g)} + 2H_2O_{(g)}$, given average bond energies of various bonds
(i.e.) $C - H$, $C \equiv C$, $O = O$, $O - H$ as 414, 810,499, 724 and 460 kJ mole^{-1} respectively.
One C_2H_2 contains two $C - H$ bonds and one $C \equiv C$ bond
One O_2 contains one O=O bonds
One CO_2 contains, two C=C bonds
One H_2O contains two $O - H$ bonds.

Solution:

(a) Enthalpy of reaction = [Sum of bond energies of reactants] - [sum of bond energies products]

(b) Bond energy due to one C_2H_2 molecule = (2 × C - H bond energy) + (1 × C ≡ C bond energy)
= (2 × 414) + (1 × 810) kJmol^{-1}
B. E of one O_2 = (1 × 0 = 0 bond energy) = 499 kJmol^{-1}
B. E of one CO_2 = (2 × 724 kJmol^{-1})
B. E of one H_2O = 1 × 460 kJ mole^{-1}

ΔH = [Total energy required to break the bonds in reactants] - [Energy given out in forming the bonds in products]
$\Delta H = (4\,\Delta H_{C-H} + 2\Delta H_{C\equiv C} + 5\,\Delta H_{O=0}) - [8\,\Delta_{C=0} + 4\,\Delta H_{O\text{-}H}]$
$= (4 \times 414 + 2 \times 810 + 5 \times 499) - (8 \times 724 + 4 \times 460)$
$= 5771 - 7632 = -1861$ KJ.

Question-8

Calculate the heat of reaction for the reduction of ferric oxide by aluminium (thermite reaction) at 25^{0}C. The heat of formation of Fe_2O_3 and Al_2O_3 are – 197.3 and 400.5 kcal respectively.

Solution:

The thermite reaction is as below,

$$2Al + Fe_2O_3 \xrightarrow{} 2Fe + Al_2O_3$$

ΔH (in kcal)

2(0) - 197.3 2(O) - 400.5

ΔHf^0 for any element in its standard state is zero.

$\Delta H^0 = \Delta H_p - \Delta H_R$

$= -400.5 - (-197.3)$

$\Delta H^0 = -203.2$kcal = -850kJ

(1kcal = 4.18 J).

Question-9

Calculate the difference between heats of reaction at constant pressure and constant volume for the reaction at 25^{0}C in kJ.

Solution:

$$2C_6H_6(l) + 15\ O_{2(g)} \xrightarrow{} 12\ CO_{2(g)} + 6H_2O(l)$$

$\Delta n = 12 - 15 = -3$;

$\Delta H = \Delta E + \Delta nRT$; $\Delta H - \Delta E = \Delta nRT$

$= (-)3 \times 8.314\ JK^{-1}mole^{-1}$

$= (-3) \times 8.314 \times 10^{-3} \times 298\ KJ\ mole^{-1}$

$= -7.443\ kJ\ mole^{-1}$.

Question-10

The heat liberated on complete combustion of 7.8g benzene is 327kJ. This heat has been measured at constant volume and at 27^{0}C. Calculate the heat of combustion of benzene at constant pressure. (R = 8.3J mole^{-1} l$_e$$^{-1}$).

Solution:

$C_6H_{6(R)} + 71/2\ O_{2\ (g)} \xrightarrow{\qquad} 6\ CO_{2(g)} + 3H_2O_{(l)}$

Heat liberated on complete combustion of 7.8 g or benzene = 327 kJ

∴Heat liberated on complete combustion of 78 g (1mol) of benzene = 327 kJ

$\Delta n = 6\text{-}7\ ½ = -1.5$

$R = 8.3 \times 10^{-3}$ kJ mole^{-1} K^{-1}

$T = 300$ K

$\Delta H = \Delta E + \Delta ngRT;$

$= -327kJ + (-1.5)\ (8.314 \times 10^{-3})\ (300)$ kJ mole^{-1}

$-327 -3.7413 = 330.7413$ KJ