Thermochemistry

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CSE-08

*Heat of reaction: The amount of heat released or absorbed in a chemical reaction is known as heat of reaction.

$$\Delta H = H_p - H_r$$

Types:

i) Exothermic reaction: The heat of reaction which are accompanied by the evolution of heat energy are called exothermic reaction. Here $H_p > H_r$ ie $\Delta H = +ve$.

ii) Endothermic reaction: The heat of reaction which are accompanied by the absorbtion of heat are called endothermic reaction Here, $H_p < H_r$ ie $\Delta H = -ve$

*Enthalpy: The heat change in a reaction is known as enthalpy. In other word, the sum of the internal energy and the product of its pressure and volume is enthalpy.

ie, $H = E + PV$. is the enthalpy.

*Internal energy: Every substance has a definite amount of energy known as internal energy. In other word, the total of all possible kinds of energy of a system is known as internal energy. $\Delta E = E_p - E_r$

*Change in enthalpy: If ΔH be the difference of enthalpy of a system in the final state (H_2) and that in the initial state (H_1) then

$$\Delta H = H_2 - H_1$$

$$\Rightarrow \Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1) \quad [\because H = E + PV]$$

$$= (E_2 - E_1) + (P_2V_2 - P_1V_1)$$

$$= \Delta E + P\Delta V. \quad [\text{since enthalpy is measured at constant pressure}]$$

* **Thermochemical equation:** An equation which indicates the amount of heat change in the reaction is called thermochemical equation. $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$; $\Delta H = -57.8$ kcal.

* **Variation of heat of reaction with temperature:**

Kirchoff's equation: The heat of reaction changes with change in temperature of a gas due to variation in its specific heat. The equation representing the variation of heat change of reaction with temperature are known as kirchhoff's equation.

At constant volume, the heat of reaction, ΔE is

$\Delta E = E_2 - E_1$.

E_1 = Internal energy of reactant

E_2 = Internal energy of product

Differentiating with respect to T we get -

$$\left[\frac{d(\Delta E)}{dT}\right]_V = \left(\frac{dE_2}{dT}\right)_V - \left(\frac{dE_1}{dT}\right)_V$$

$$= (C_V)_2 - (C_V)_1. \quad \left[\because \left(\frac{dE}{dT}\right)_V = C_V\right]$$

$$\left[\frac{d(\Delta E)}{dT}\right]_V = \Delta C_V. \quad \text{---(I)}$$

Now, integrating it we get.

$$\int_{E_1}^{E_2} \Delta E_2 - E_1 = \int_{T_1}^{T_2} C_V dT$$

$$\Rightarrow \Delta E_2 - E_1 = C_V [T_2 - T_1] \quad \text{---(II)}$$

At constant pressure the equation is $= \Delta H = H_2 - H_1$ ---(III)

These three equations are called Kirchoff's equation.

* Different types of heat of reaction:

i) Heat of formation: The change in enthalpy that takes place when one mole of the compound is formed from its elements is heat of formation. Example-

$2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)}$ $\quad \Delta H_f = +53.14$ kcal.

$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$ $\quad \Delta H_f = -44$ kcal

ii) Standard heat of formation: The change in enthalpy that takes place when one mole of a compound is formed from its elements, all substances being in their standard states. (298K and 1 atm pressure).

$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \longrightarrow HCl_{(g)}$ $\quad \Delta H_f = -22.08$ kcal.

ii) Heat of combustion: The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.

$C_{(s)} + O_{2(g)} = CO_{2(g)}$ $\quad \Delta H = -94.3$ kcal

iii) Heat of solution: The change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature is heat of solution.

$KCl_{(s)} + H_2O_{(l)} \longrightarrow KCl_{(aq)}$ $\quad \Delta H = -4.9$ kcal.

iv) Heat of neutralisation: The change of heat content of the system when one gram equivalent of an acid is neutralised by one gram equivalent of a base or vice-versa in dilute solution is called heat of neutralisation.

$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O$ $\quad \Delta H = -13.68$ kcal.

v) **Heat of fusion:** The heat change when one mole of a solid substance is converted to the liquid state at its melting point is called heat of fusion

$$H_2O_{(s)} \longrightarrow H_2O_{(l)} \qquad \Delta H = +1.43 \text{ kcal.}$$

vi) **Heat of vaporisation:** The heat change when one mole of liquid is converted into vapour or gaseous state at its boiling point is called heat of vaporisation.

$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \qquad \Delta H = +9.71 \text{ kcal}$$

vii) **Heat of sublimation:** The heat change when one mole of a solid is directly converted into the gaseous state at a temperature below its melting point.

$$I_{2(s)} \longrightarrow I_{2(g)} \qquad \Delta H = +14.92 \text{ kcal.}$$

viii) **Heat of transition:** The change in enthalpy which occurs when one mole of an element changes from one allotropic form to another is called heat of transition.

$$C_{diamond} \longrightarrow C_{amorphous} \qquad \Delta H = +3.3 \text{ kcal}$$

$$P_{white} \longrightarrow P_{red} \qquad \Delta H = -1.028 \text{ kcal}$$

* **The heat of neutralisation of strong acid and strong base is constant:** The heat of neutralisation of strong acid and strong base is -13.7 kcal, no matter which acid or base is employed. This regularity has been explained by the theory of ~~neutralisation~~ ionisation. If HA and BOH represent any strong acid and ~~may~~ any strong base respectively and equivalent amounts of these in dilute soln be mixed. we have,

$$H^+_{(aq)} + A^-_{(aq)} + B^+_{(aq)} + OH^-_{(aq)} \longrightarrow A^-_{(aq)} + B^+_{(aq)} + H_2O_{(l)} \quad \Delta H = -13.7 \text{ kcal}$$

This is because during neutralisation

reaction, the heat of change is due to the formation of water molecule. The heat of neutralisation of an acid and a base is the heat of formation of water from hydrogen and hydroxyl ions. Here anion of acid and cation of base behaves as spectator ion.

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)} \quad \Delta H = -13.7 \text{ kcal}$$

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} \; ; \quad \Delta H = -13.7 \text{ kcal}$$

*Bond energy: The average energy required to break all bonds of a particular type in one mole of the substance is bond energy

$Cl-Cl = 243 \text{ kJ mol}^{-1}$

$O=O = 499 \text{ kJ mol}^{-1}$

*Hess's law: In a chemical reaction if the reactants and the products are fixed, then the change of enthalpy of the reaction will remain same whether the reaction takes place in single step or in several steps. The total enthalpy change in a reaction doesnot depend upon the path by which the reaction is brought out.

→ Example:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H = -393.5 \text{ kJ}$$

i) $C_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{(g)} \quad \Delta H_1 = -110.5 \text{ kJ}.$

ii) $CO_{(g)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H_2 = -283.0 \text{ kJ}.$

$\therefore \Delta H_1 + \Delta H_2 = -110.5 - 283$

$= -393.5 \text{ kJ}.$

→ In fig. A → D is ΔH

A → B is ΔH_1

B → C is ΔH_2

C → D is ΔH_3

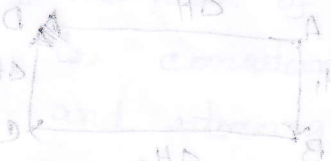
According to this law.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 .$$

* **Lavoisier and Laplace's law:** The quantity of heat required to decompose a compound into its elements, is equal to the heat evolved when that compound is formed from its elements.

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} = CO_{2(g)} \; ; \quad \Delta H = -283.0\,kJ.$$

$$CO_{2(g)} = CO_{(g)} + \tfrac{1}{2}O_{2(g)} \; ; \quad \Delta H = +283.0\,kJ.$$



Mathematical Problems:

Problem 1: The heat of combustion of ethylene at 17°C and at const. volume is −332.19 kCal. Calculate the heat of combustion at const. pressure considering water to be in liquid state. ($R = 2\ cal\ deg^{-1}\ mol^{-1}$)

Solution:

$$C_2H_{4(g)} + 3O_{2(g)} \longrightarrow 2CO_2 + 2H_2O$$

$$\Delta n = (2 - 4) = -2$$

$$T = 273 + 17 = 290K$$

We know, $\Delta H = \Delta E + \Delta n RT$

$$= -332.19 + (-2) \times 2 \times 10^{-3} \times 290$$

$$= -332.19 - 1.16$$

$$= -333.3\ kCal$$

Problem 2: Heat of reaction of $N_2 + 3H_2 \longrightarrow 2NH_3$ at 27°c was found to be -21.976 kcal. what will be the heat of reaction at const. pressure and at 50°c and the molar heat capacities constant.

we know,

$N_2 = 6.8$ cal degree^{-1} mol^{-1}

$H_2 \rightarrow 6.77$ "

$NH_3 \rightarrow 8.86$ "

Solution:

$$\Delta C_p = 2(NH_3) - (N_2 + 3H_2)$$

$$= 2 \times 8.86 - (6.8 + 3 \times 6.77)$$

$$= -9.39 \times 10^{-3} \text{ cal}$$

$$= -9.39 \times 10^{-3} \text{ kcal}.$$

Again, we know, $H_2 - H_1 = C_p (T_2 - T_1)$

$$\Rightarrow -9.39 \times 10^{-3} + 21.976 = C_p (50 - 27)$$

$$\Rightarrow C_p = \frac{21.985}{23}$$

$$= 0.956 \text{ kcal k}^{-1}$$

$\Rightarrow H_2 = H_1 + C_p (T_2 - T_1)$

$= -21.976 + 23 \times 9.39 \times 10^{-3}$

$= 22.192$ kcal

Problem 3: The heat of combustion of ethyl alcohol is -330 kcal. If the heat of formation of CO_2 and H_2O be -94.3 kcal and -68.3 kcal respectively. Calculate heat of combustion of ethyl alcohol.

a) $C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\quad \Delta H = -330.0$ kcal.

b) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta H = -94.3$ kcal

c) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\quad \Delta H = -68.5$ kcal

d) $2C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_2 \longrightarrow C_2H_5OH$ $\quad \Delta H = ?$

$$\Delta H = 2 \times (-94.3) + 3 \times (-68.3) + 330$$

$$= -188.6 - 204.9 + 330$$

$$= -393.5 + 330$$

$$= -63.5 \text{ kcal}$$