

# Thermochemistry

The branch of chemistry which deals with energy changes involved in chemical reactions is called thermochemistry. In thermochemistry the 1st law of thermodynamics is applied in chemical reaction. As we know every substance is associated with a certain amount of energy i.e. Internal energy of the substance.

**Change of Internal Energy in a Chemical Reaction:** - Now consider a chemical reaction taking place at constant temperature and at constant volume. In such case from the 1st law of thermodynamics i.e.  $\Delta U = q + w$ ,  $w = 0$

$$\Delta U = q + 0$$

$$\Delta U = q_v \quad (q_v \text{ is heat exchanged at const. volume})$$

Let  $U_R$  is the internal energy of reactant and  $U_P$  is the internal energy of product.

$$\text{So, } \Delta U = U_P - U_R = q_v \quad (\text{Heat of reaction at const. volume})$$

**Enthalpy Change in a Chemical Reaction:** - Let  $q_p$  be the heat exchanged in the chemical reaction taking place at constant pressure.

Thus the heat exchanged at constant pressure is known as enthalpy change.

$$\text{So, } \Delta H = q_p$$

If  $H_R$  is the enthalpy of reactant and  $H_P$  is the enthalpy of product,

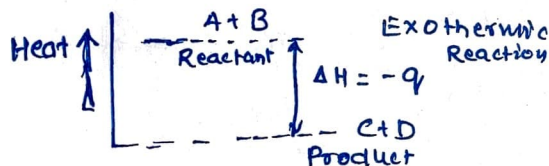
$$\text{then, } \Delta H = H_P - H_R = q_p = \underline{\text{Enthalpy of reaction}}$$

**Heat Transfer:** - Chemical reactions are invariably associated with a transfer of energy.

(i) **Exothermic Reaction** is transferring heat to the surroundings.



$$\Delta H^\circ = -q$$



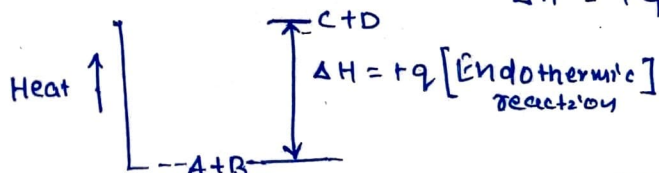
It means the reaction which are accompanied by evolution of heat are called exothermic reaction. In such reactions

$H_P < H_R$  so that  $\Delta H$  is negative

(ii) **Endothermic Reaction** is transferring heat from the surrounding



$$\Delta H^\circ = +q$$



Endothermic reactions are accompanied by absorption of heat.

In these reactions  $H_P > H_R$  so that  $\Delta H$  is positive.

## Relation between Enthalpy of Reaction at Const. Volume and at Const. Pressure

The quantities  $\Delta H$  and  $\Delta U$  are related to each other by the Expression

$$\Delta H = \Delta U + P\Delta V \quad [\Delta V = \text{change in volume}] \quad \text{--- (1)}$$

Since  $q_v = \Delta U$  and  $q_p = \Delta H$

$$\text{or } q_p = q_v + P\Delta V \quad \text{--- (2)}$$

We know for  $n$  moles, the ideal gas equation

$$PV = nRT \quad \text{--- (3)}$$

Let  $n_1$  and  $n_2$  are the number of moles of gaseous reactant and product respectively. If  $n_2 > n_1$ , then increase in the number of gaseous moles

$$= n_2 - n_1 = \Delta n_g$$

Then the corresponding increase in volume ( $\Delta V$ ) will be given by  $(\frac{V}{n}) \Delta n_g$

$$\text{Hence, } P\Delta V = P \left(\frac{V}{n}\right) \Delta n_g = RT \Delta n_g \quad [ \because PV = nRT ]$$

$$\text{Thus, } P\Delta V = \Delta n_g \times RT \quad \text{--- (4)}$$

From equation (2) and (4), we have,

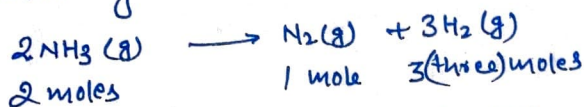
$$q_p = q_v + P\Delta V$$

$$q_p = q_v + RT \Delta n_g$$

where  $\Delta n_g$  is the difference between the number of moles of products and reactants in gaseous state.

Let us understand by few examples

(a) In the reaction involving the dissociation of ammonia into nitrogen and hydrogen



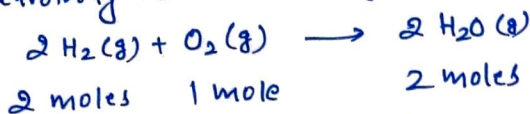
$$\Delta n_g = \text{Product} - \text{Reactant}$$

$$= (1+3) - 2 = 4 - 2 = 2$$

$$q_p = q_v + \Delta n_g RT$$

$$q_p = q_v + 2RT$$

(b) In the reaction involving combination of hydrogen and oxygen.



$$\therefore \Delta n_g = \text{Product} - \text{Reactant}$$

$$= 2 - (2+1)$$

$$= 2 - 3 = -1$$

$$q_p = q_v + \Delta n_g RT$$

$$\therefore q_p = q_v + (-1) RT$$

$$q_p = q_v - RT$$

# Enthalpy

Let us suppose the change of state of a system at constant pressure. In this case there will be change in volume.

The volume of the system increases from  $V_A$  to  $V_B$  at constant pressure  $P$ .

Then the work done by the system is  $W$ .

$$\text{So, } W = -P(V_B - V_A) \quad \text{--- (1)}$$

We know from the 1st law,  $\Delta U = q + W$

$$\therefore \Delta U = q - P(V_B - V_A)$$

$$\text{or } U_B - U_A = q - P V_B + P V_A$$

$$\text{or, } (U_B + P V_B) - (U_A + P V_A) = q \quad \text{--- (2)}$$

The quantity  $(U + PV)$  is known as the enthalpy of the system and it is denoted by  $H$ . So it represents the total energy of the system. Hence,  $H = U + PV$  --- (3)

Since  $U$  is a definite quantity and  $P$  &  $V$  are also definite quantities which define the state of a system. So  $H$  is also a definite quantity depending upon the state of the system.

From equation (2) and (3) we have

$$H_B - H_A = q = \Delta H \quad \text{--- (4)}$$

$\Delta H$  is a definite quantity like  $\Delta U$ ,  $\Delta H$  represents increase in the enthalpy of a system when it changes from state A to state B.

Since  $\Delta H$  is a definite quantity, hence heat  $q$  absorbed under constant pressure is also a definite quantity. We know from eqn (2)

$$\text{So, } (U_B - U_A) + P(V_B - V_A) = q$$

or substituting this value in eqn (4)

we have

$$\Delta H = (U_B - U_A) + P(V_B - V_A)$$

$$\text{or, } \Delta H = \Delta U + P \Delta V$$

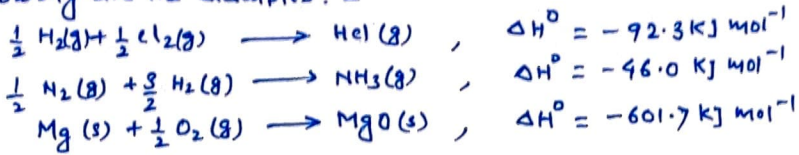
where  $\Delta V$  is the increase in volume.



## Standard Enthalpy of Reaction: -

Enthalpy of reactions determined at 25°C and one atm Pressure are denoted by  $\Delta H^\circ$  and it is known standard enthalpies of reactions.

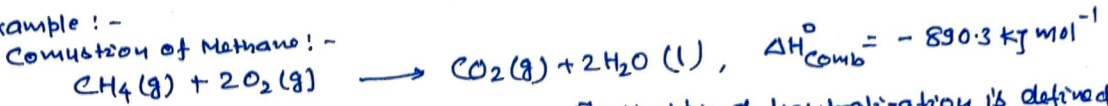
Following are the examples: -



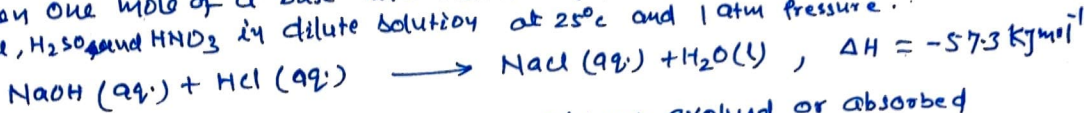
## Standard Enthalpy of Combustion: -

Enthalpy of Combustion is determined when one mole of substance goes under complete combustion at 25°C and 1 atm Pressure.

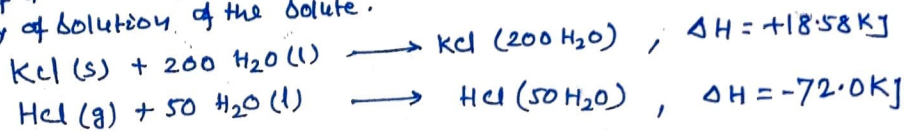
Example: -



**Standard Enthalpy of Neutralization: -** Enthalpy of neutralization is defined as when one mole of a base like NaOH or KOH is neutralized with acid like HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> in dilute solution at 25°C and 1 atm Pressure.



**Enthalpy of Solution: -** The amount of heat evolved or absorbed when 1 mole of a solute is dissolved in a sufficient amount of solvent is called enthalpy of solution of the solute.



## Standard Enthalpy of Formation: -

The standard enthalpy of formation,  $\Delta H_f^\circ$  is defined as the enthalpy change when one mole of a substance is formed from its elements in their standard states.  $\Delta H_f^\circ$  may be negative or positive.

## Determination of Enthalpies of Reaction: -

Enthalpies of reactions at 25°C can be determined if  $\Delta H_f^\circ$  value of reactant and products involved in the reaction are known

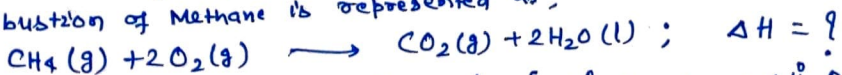
$$\text{Since, } \Delta H^\circ = \sum \Delta H_f^\circ(\text{Products}) - \sum \Delta H_f^\circ(\text{Reactants})$$

In standard state the value of  $\Delta H_f^\circ$  for elements is zero.

**Example: -** Calculate the enthalpy of combustion of Methane at 25°C and 1 atm Pressure

$$\begin{aligned} \text{if } \Delta H_f^\circ \text{CO}_2 &= -393.5 \text{ kJ mol}^{-1}, & \Delta H_f^\circ \text{H}_2\text{O} &= -285.9 \text{ kJ mol}^{-1} \\ \text{and } \Delta H_f^\circ \text{CH}_4 &= -74.8 \text{ kJ mol}^{-1} \end{aligned}$$

The combustion of Methane is represented as,



$$\Delta H^\circ = \left\{ \Delta H_f^\circ(\text{CO}_2) + 2 \Delta H_f^\circ(\text{H}_2\text{O}) \right\} - \left\{ \Delta H_f^\circ(\text{CH}_4) + 2 \Delta H_f^\circ(\text{O}_2) \right\}$$

$$\Delta H^\circ = \left\{ -393.5 + 2 \times (-285.9) \right\} - \left\{ -74.8 + 0 \right\}$$

$$= \left\{ -393.5 \text{ kJ mol}^{-1} - 2 \times 285.9 \right\} + 74.8$$

$$\Delta H^\circ = -393.5 - 571.8 + 74.8$$
$$\Delta H^\circ = -965.3 - 74.8 = -890.5 \text{ kJ mol}^{-1}$$

# The Kirchhoff Eq<sup>n</sup>:

Variation of Enthalpy of reaction with Temperature: -

Varies with temperature. The enthalpy of any physical or chemical process

The enthalpy of the reaction  $\Delta H$ ,



$$\Delta H = \sum H_{\text{Product}} - \sum H_{\text{Reactant}} \\ = (cH_C + dH_D) - (aH_A + bH_B) \quad \text{--- (1)}$$

On differentiating with respect to temperature at constant pressure, we have

$$\left[ \frac{\partial(\Delta H)}{\partial T} \right]_P = c \left( \frac{\partial H_C}{\partial T} \right)_P + d \left( \frac{\partial H_D}{\partial T} \right)_P - a \left( \frac{\partial H_A}{\partial T} \right)_P - b \left( \frac{\partial H_B}{\partial T} \right)_P$$

$$\left[ \frac{\partial(\Delta H)}{\partial T} \right]_P = c C_{pC} + d C_{pD} - a C_{pA} - b C_{pB}$$

$$\left[ \frac{\partial(\Delta H)}{\partial T} \right]_P = \Delta C_p \quad (\because C_p = \left( \frac{\partial H}{\partial T} \right)_P) \quad \text{--- (2)}$$

Where  $\Delta C_p = \text{Sum of heat Capacities of Products} - \text{Sum of heat Capacities of Reactants}$

Now equation (2) is known as Kirchhoff equation.

Kirchhoff equation states that the variation of  $\Delta H$  of a reaction with temperature at constant pressure is equal to  $\Delta C_p$  of the system.

We can write it as follows

$$\left( \frac{\partial(\Delta H)}{\partial T} \right)_P = \Delta C_p \quad \text{or} \quad d(\Delta H) = \Delta C_p \cdot dT \quad \text{--- (3)}$$

Similarly, the temperature-dependence of enthalpy of reaction at constant volume is given by

$$\left[ \frac{\partial(\Delta U)}{\partial T} \right]_V = \Delta C_v \quad \text{or} \quad d(\Delta U) = \Delta C_v \cdot dT \quad \text{--- (4)}$$

If the temperature range is small, Now eq<sup>n</sup> (3) and eq<sup>n</sup> (4) can be easily integrated by assuming that the heat capacities are independent of temperature.

$$\text{Now, } \int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p \cdot dT = \Delta C_p \int_{T_1}^{T_2} dT = \Delta C_p [T]_{T_1}^{T_2} \\ \text{or} \quad \Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1) \quad \text{--- (5)}$$

$$\text{Similarly } \int_{T_1}^{T_2} d(\Delta U) = \int_{T_1}^{T_2} \Delta C_v \cdot dT = \Delta C_v \int_{T_1}^{T_2} dT \\ \text{or, } \Delta U_2 - \Delta U_1 = \Delta C_v (T_2 - T_1) \quad \text{--- (6)}$$

If the temperature range is not small, then the constancy of heat capacities is no longer a valid assumption and we just express the heat capacities as a function of temperature before integration the heat capacity is expressed in the power series in T.

$$\text{i.e. } C_p = \alpha + \beta T + \gamma T^2$$

where  $\alpha$ ,  $\beta$  and  $\gamma$  are constants for a given species.  
Hence

$$\Delta C_p = [(c_{pC} + d_{pD}) - (a_{pA} + b_{pB})] + [(c_{pC} + d_{pD}) - (a_{pA} + b_{pB})] T + \dots \quad (7)$$

from equation (6) and (7) we have.

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2) dT$$

$$\Delta H_2 - \Delta H_1 = \Delta\alpha (T_2 - T_1) + \frac{1}{2} \Delta\beta (T_2^2 - T_1^2) + \frac{1}{3} \Delta\gamma (T_2^3 - T_1^3) \quad (8)$$

The above equation (8) is the integrated Kirchhoff Equation.

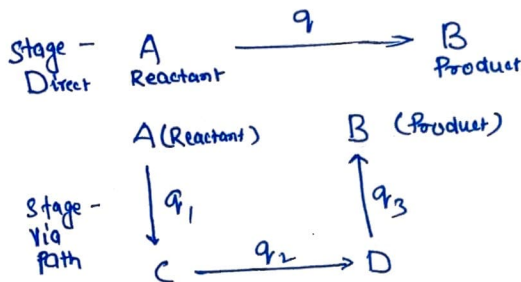


# Hess's Law or Hess's Law of Constant heat Summation

The Hess's Law states that the amount of heat evolved or absorbed in a <sup>chem.</sup> process is the same whether the process takes place in one or several steps.

Let us suppose in a process, the system changes from state A to state B in one step and heat exchanged in this process is  $q$ .

Now the system changes from state A to state B in three steps involving a change from A to C, C to D and finally from D to B. If  $q_1$ ,  $q_2$  and  $q_3$  are heats exchanged in the first, second and third steps respectively, then according to Hess's law  $q_1 + q_2 + q_3 = q$  — (1)

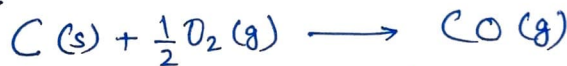


The enthalpy of reaction depends on the initial and final state, not on the intermediates which are formed.

## Application of Hess's Law : —

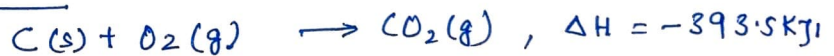
① Calculation of Enthalpies of Reaction: — Hess's law makes it possible to calculate enthalpies of such reaction which are not determined experimentally.

For example, it is extremely difficult to measure the heat evolved when Carbon burns in Oxygen to form CO, Carbon monoxide.

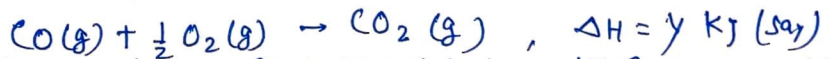


Hess's law states that the heat evolved in the combustion of one mole of Carbon is 393.5 KJ  
(i.e.,  $\Delta H = -393.5$  KJ)

Reaction in One Step: —



or, In two steps: —



$x$  is the heat exchanged in the combustion of Carbon to Carbon monoxide  
 $y$  is the heat exchanged in the combustion of Carbon monoxide ~~has~~ been found to be  $-282.0$  KJ,  
According to Hess's Law,  $x + y = -393.5$  KJ

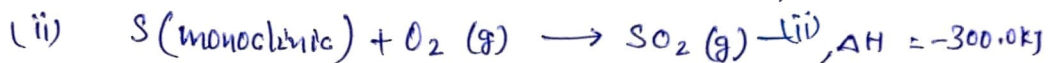
$$x + (-282.0 \text{ KJ}) = -393.5 \text{ KJ}$$

$$x = -393.5 + 282.0 = -111.5 \text{ KJ} \quad (7)$$

(2) Determination of enthalpy of slow reactions:-

Hess's Law is extremely useful in determining enthalpies of extremely slow reactions.

For example:- The formation of rhombic Sulphur into monoclinic Sulphur is so slow that direct measurement of enthalpy is not possible. But the enthalpies of combustion of rhombic sulphur and monoclinic sulphur are known to be  $-297.5$  &  $-300.0 \text{ kJ mol}^{-1}$ .



On subtracting eq<sup>n</sup> (i) from (ii), we have

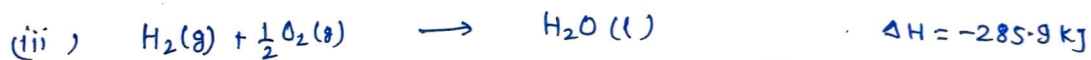


Thus, the transformation of one mole of rhombic sulphur into monoclinic sulphur is accompanied by absorption of  $2.5 \text{ kJ}$  of heat.

(3) Calculation of enthalpies of formation:-

When the formation of Benzene takes place from its elements, i.e. Carbon and hydrogen, their enthalpies of formation of Benzene may be calculated from the enthalpy of combustion of Benzene and the enthalpies of formation of water and Carbon dioxide. Two steps are important.

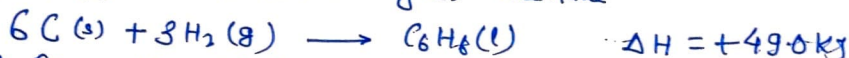
Step I:- The thermochemical eq<sup>n</sup> for the known values are written as



Step II:- Now eq<sup>n</sup> (ii) is multiplied by 6 and eq<sup>n</sup> (iii) is multiplied by 3;



On adding (iv) and (v) then subtracting (i) we have



The enthalpy of formation of Benzene is  $+49.0 \text{ kJ}$



# Bond Energies

Bond energy is defined as the average amount of energy required to break or dissociate one mole of bonds of that type present in the compound. It may be defined as the average of the energy required to break all bonds of one type present in one mole of the gaseous co-valent substance to form products in gaseous state is called bond energies.

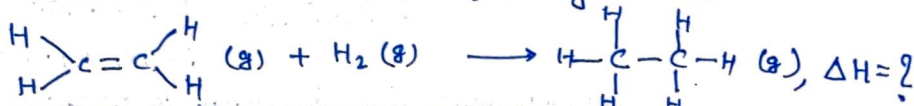
Bond energy is also called the enthalpy of formation of the bond, and it is an additive property.

## Applications

$$\Delta H = (\text{BE})_{\text{Reactant}} - (\text{BE})_{\text{Product}}$$

(1) Determination of Enthalpies of reactions: - The bond energies can be used for determining enthalpies of reaction. This may be illustrated by the following example.

Now we need to determine the enthalpy of the following reaction



In the above reaction the four C-H bonds of  $\text{C}_2\text{H}_4$  remain unaffected. A double bond breaks in ethylene and an H-H bond breaks in  $\text{H}_2$  molecule and one C-C bond and two C-H bonds are formed in  $\text{C}_2\text{H}_6$ .

$$\text{So, } \Delta H = -\Delta H_{\text{C-C}} - 2\Delta H_{\text{C-H}} + \Delta H_{\text{C=C}} + \Delta H_{\text{H-H}}$$

The value of bond and its enthalpy of formation is as

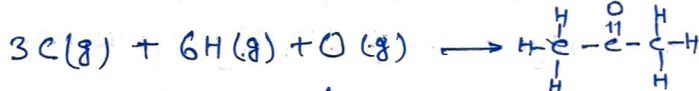
$$\left[ \Delta H_{\text{C-C}} = 347.3 \text{ kJ mol}^{-1}, \Delta H_{\text{C-H}} = 416.2 \text{ kJ mol}^{-1}, \Delta H_{\text{C=C}} = 615.0 \text{ kJ mol}^{-1}, \Delta H_{\text{H-H}} = 435.1 \text{ kJ mol}^{-1} \right]$$

$$\therefore \Delta H = -(\Delta H_{\text{C-C}} + 2\Delta H_{\text{C-H}}) + \Delta H_{\text{C=C}} + \Delta H_{\text{H-H}} \\ = -(347.3 + 832.4) + (615.0 + 435.1) = -129.6 \text{ kJ}$$

This value is very close to experimental value of  $-133 \text{ kJ}$

(2) Determination of Enthalpies of formation of Compounds: -

Let us consider the formation of dimethyl ketone or Acetone



The formation of acetone involves the following steps.

(1) Breaking of three H-H bonds to give six atoms of H  
Breaking of half O-O bond to give one atom of O (Oxygen)  
and sublimation of three atoms of C (s) to give three atoms of C (g).

(2) Formation of two C-C bonds  
Formation of six C-H bonds and one C=O bond

The enthalpy of formation of Acetone is thus given by

$$\Delta H_f = [3(\Delta H_{\text{H-H}}) + \frac{1}{2}(\Delta H_{\text{O-O}}) + 3(\Delta H_{\text{C(s)} \rightarrow \text{C(g)}})] - [2(\Delta H_{\text{C-C}}) + 6(\Delta H_{\text{C-H}}) + \Delta H_{\text{C=O}}]$$

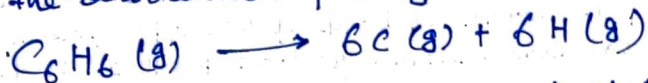
The value of enthalpy of bond formation is as follows: - (Numerical values)

$$\Delta H_{\text{H-H}} = 435.1, \Delta H_{\text{O-O}} = 138.1, \Delta H_{\text{C(s)} \rightarrow \text{C(g)}} = 719.6, \Delta H_{\text{C-C}} = 347.3, \Delta H_{\text{C-H}} = 416.2, \Delta H_{\text{C=O}} = 711.3$$

$$\Delta H_f = [3 \times 435.1 + \frac{1}{2}(138.1) + 3(719.6)] - [2 \times 347.3 + 6 \times 416.2 + 711.3] \\ = -369.95 \text{ kJ mol}^{-1}$$

(3) Determination of resonance energy: -

Let us consider the dissociation of Benzene: -



Benzene ring consist of three single and three double bonds (according to Kekule's str.) the calculated dissociation energy is 5384.1 kJ as illustrated below

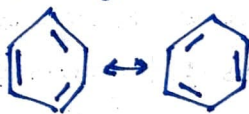
$$\begin{aligned}\Delta H_{\text{disso}} &= 3(\Delta H_{\text{C-C}}) + 3(\Delta H_{\text{C=C}}) + 6(\Delta H_{\text{C-H}}) \\ &= 3 \times 347.3 + 3 \times 615.0 + 6 \times 416.2 \\ &= 5384.1 \text{ kJ mol}^{-1}\end{aligned}$$

The experimental value is known is 5535.1 kJ mol<sup>-1</sup>

So, the actual energy required for the dissociation of Benzene is 151 kJ more than the calculated value 5384.1 kJ

This fact clearly shows that the actual structure of Benzene is more stable than the Kekule structure by 151 kJ

So, the actual structure of Benzene is the resonance hybrids of the two Kekule structure. Kekule str. of Benzene like as follows.



The difference of 151 kJ gives the resonance energy of Benzene.

