By- SHAILENDRA SHUKLA SIR

THERMOCHEMISTRY

(1) Enthalpy of formation ($\Delta_f H$)

"The enthalpy change (heat evolved or absorbed), when one mole of a compound is formed by combination of its elements is called enthalpy of formation of the compound ($\Delta_f H$)".

If the enthalpy of formation of the compounds is measured in standard state (298 K temperature, 1atm pressure), then it is termed as the standard enthalpy of formation of the compounds ($\Delta_f H^0$).

For example, when one mole of CO_2 is formed by combination of carbon and oxygen in standard state (298 K temperature, 1atm pressure), 393.5 kj heat is released. Hence, standard enthalpy of formation of CO_2 will be -393.5 kj/mole.

$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) + 393.5\ kj;\ \Delta_f H^0 = -393.5\ kj/mole$

Similarly, standard enthalpy of formation of water is -285.8 kj/mole.

$H_2.(g) + \frac{1}{2} O_2\,(g) \rightarrow H_2O\,(l) + 285.8\ kj;\ \Delta_f H^0 = -285.8\ kj/mole$

Since, the process of formation of a compound may either be exothermic or endothermic, the standard enthalpy of formation of the compounds may be positive or negative.

By convention, the standard enthalpy of formation of the elements are taken to be zero.

(2) Enthalpy of the reaction ($\Delta_r H$)

"The enthalpy change (heat evolved or absorbed), when total number of moles of reactants represented in balanced chemical equation, react completely to form products is called enthalpy of the reaction ($\Delta_r H$)".

If enthalpy of reaction is measured in standard state (298 K temperature, 1 atm pressure), then it is called standard enthalpy of reaction ($\Delta_r H^0$).

For example, when one mole of CO_2 is formed by combination of carbon and oxygen in standard state (298 K temperature, 1atm pressure), 393.5 kj heat is released. Hence, standard enthalpy of the reaction involved will be -393.5 kj.

$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) + 393.5\ kj;\ \Delta_r H^0 = -393.5\ kj$

Similarly, standard enthalpy of reaction for the combustion of methane is -890 kj.

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) + 890\ kj;\ \Delta_r H^0 = -890\ kj$

CHEMISTRYFORCOMPETITION.COM

Since, the reactions may either be exothermic or endothermic, the standard enthalpy of the reaction may be positive or negative.

The standard enthalpy of the reactions is found to be equal to the difference of the summation of standard enthalpy of the formation of products and the summation of the standard enthalpy of the formation of the reactants. Thus, the standard enthalpy of the reaction,

$$\Delta_r H^0 = \sum \Delta_f H^0 \text{ (products)} - \sum \Delta_f H^0 \text{ (reactants)}$$

For example, for following reaction-

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(l)$$

The standard enthalpy of the reaction,

$$\Delta_r H^0 = [\Delta_f H^0\{CO_2(g)\} + 2\times\Delta_f H^0\{H_2O(l)\}] - [\Delta_f H^0\{CH_4(g)\} + 2\times\Delta_f H^0\{O_2(g)\}]$$

(3) Enthalpy of combustion

"The enthalpy change (amount of heat evolved) when one mole of a substance is burnt completely in presence of excess of air is called the enthalpy of combustion of the substance ($\Delta_c H$)."

If enthalpy of combustion is measured in standard state (298 K temperature, 1atm pressure), then it is called standard enthalpy of combustion ($\Delta_c H^0$) of the substance.

For example, when one mole of carbon is burnt completely in presence of excess of air in standard state (298 K temperature, 1atm pressure), 393.5 kj heat is released. Hence, standard enthalpy of the combustion of carbon will be -393.5 kj.

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) + 393.5\text{ kj};\ \Delta_c H^0 = -393.5\text{ kj/mole}$$

Similarly, standard enthalpy of combustion of methane is -890 kj/mole.

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(l) + 890\text{ kj};\ \Delta_c H^0 = -890\text{ kj/mole}$$

Since, the combustion of the substances is always exothermic, the enthalpy of combustion is always negative.

Hess's law of constant heat summation

This law is the direct consequence of first law of thermodynamics. According to this law,

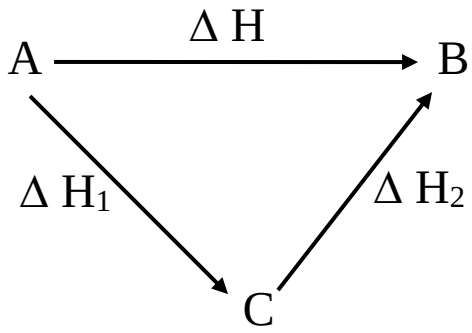
"Whether a process is carried out by one method or by another method, in one step or in several steps, the enthalpy change (amount of heat evolved or absorbed) is always constant and is independent of the path followed during the process."

Let, in a chemical reaction, reactant A convert directly into product B in a single step process and the enthalpy change during the process is ΔH. If the same change is carried out in a two step process through an intermediate product C, the

CHEMISTRY FOR COMPETITION.COM

enthalpy change during both the steps are ΔH_1 and ΔH_2 respectively, then from Hess's law of constant heat summation-

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



$$\Delta \mathbf{H} = \Delta \mathbf{H_1} + \Delta \mathbf{H_2}$$

Fig.- Hess's Law of Constant Heat Summation

Verification- Hess's law can be verified by taking the example of formation of CO_2. In fact, CO_2 can be prepared by following two methods-

(1) Ist method (single step process)-

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g); \quad \Delta H = -393.5\ kj$$

(2) IInd method (Two step process)-

$$C\,(s) + \tfrac{1}{2}\,O_2\,(g) \rightarrow CO(g); \quad \Delta H_1 = -110.5\ kj$$
$$CO\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow CO_2\,(g); \quad \Delta H_2 = -283.0\ kj$$

Here,

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

Hence, the Hess's law is verified.

Applications of Hess's Law- Hess's law is useful for determining enthalpy change during all the processes. Using this law, the chemical reactions can be added, subtracted, multiplied or divided from one another. It is helpful in determination of-

(1) Enthalpy of formation of the compounds
(2) Enthalpy of reactions
(3) Enthalpy of combustion
(4) Lattice enthalpy of a compound
(5) Bond enthalpy of different bonds
(6) Resonance enthalpy

CHEMISTRYFORCOMPETITION.COM

Numericals based on Hess's Law

Ques.- Find the enthalpy of formation of methane (CH_4) from following data-

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.5$ kj

(2) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$; $\Delta H = -285.8$ kj

(3) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; $\Delta H = -890.3$ kj

Ans.- Given that-

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.5$ kj

(2) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$; $\Delta H = -285.8$ kj

(3) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; $\Delta H = -890.3$ kj

The required equation for the enthalpy of formation of CH_4 is as under-

$$C(s) + 2H_2(g) \rightarrow CH_4(g); \quad \Delta H = ?$$

In order to get this equation, multiplying equation (2) by 2 and adding to the equation (1), we get-

$[H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l); \quad \Delta H = -285.8 \text{ kj}] \times 2$

$C(s) + O_2(g) \rightarrow CO_2(g); \quad \Delta H = -393.5$ kj

---

(4) $C(s) + 2H_2(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \quad \Delta H = -965.1$kj

Subtracting eq. (3) from eq. (4), we get-

$C(s) + 2H_2(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \quad \Delta H = -965.1$kj

$-[CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \quad \Delta H = -890.3$ kj]

$$C(s) + 2H_2(g) \rightarrow CH_4(g); \quad \Delta H = -74.8 \text{ kj}$$

Thus, enthalpy of formation of CH_4 will be -74.8 $kjmol^{-1}$.

Ques.- The enthalpy of formation of $CO_2(g)$ and $H_2O(l)$ are -393.5 and -285.8 $kjmol^{-1}$ respectively. If enthalpy of combustion of ethane is -1564.5 $kjmol^{-1}$, then find the enthalpy of formation of ethane (C_2H_6).

Ans.- Given that-

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.5$ kj

(2) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$; $\Delta H = -285.8$ kj

(3) $C_2H_6(g) + \frac{7}{2} O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta H = -1564.5$ kj

The required equation for the enthalpy of formation of CH_4 is as under-

$$2C(s) + 3H_2(g) \rightarrow C_2H_6(g); \quad \Delta H = ?$$

In order to get this equation, multiplying equation (1) by 2 and eq. (2) by 3 and adding, we get-

CHEMISTRY FOR COMPETITION.COM

$[C\ (s) + O_2\ (g) \rightarrow CO_2\ (g);\ \Delta H = -393.5\ kj] \times 2$

$[H_2.(g) + \frac{1}{2} O_2\ (g) \rightarrow H_2O\ (l);\ \Delta H = -285.8\ kj] \times 3$

---

(4) $2C\ (s) + 3H_2\ (g) + \frac{7}{2} O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l);\ \Delta H = -1644.4kj$

Subtracting eq. (3) from eq. (4), we get-

$2C\ (s) + 3H_2\ (g) + \frac{7}{2} O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l);\ \Delta H = -1644.4kj$

$-[C_2H_6\ (g) + \frac{7}{2} O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l);\ \Delta H = -1564.5\ kj]$

$2C\ (s) + 3H_2\ (g) \rightarrow C_2H_6\ (g);\ \Delta H = -79.9\ kj$

Thus, enthalpy of formation of C_2H_6 will be -79.9 $kjmol^{-1}$.

(4) Enthalpy of atomization ($\Delta_a H$)-

"The enthalpy change (heat required) in separation of all the atoms present in one mole molecules of a substance is called enthalpy of atomization of the substance."

For example, enthalpy of atomization of hydrogen is 433 $kJmol^{-1}$

$H{-}H\ (g) \rightarrow 2H(g);\ \Delta_a H = +433\ kJmol^{-1}$

Similarly, enthalpy of atomization of chlorine is 242.5 $kJmol^{-1}$

$Cl{-}Cl\ (g) \rightarrow 2Cl(g);\ \Delta_a H = +242.5\ kJmol^{-1}$

For a diatomic molecule, the enthalpy of atomization is equal to the bond dissociation enthalpy of the molecule.

(5) Enthalpy of neutralization ($\Delta_{neu} H$)-

"The enthalpy change (amount of heat evolved) when one gram equivalent of an acid is neutralized completely by a base in very dilute solution is called enthalpy of neutralization of the acid."

For example,

$HCl\ (aq.) + NaOH\ (aq.) \rightarrow NaCl\ (aq.) + H_2O\ (l) + 57.32\ kj$

$\Delta_{neu} H = -57.32\ kj/gram\ eqv.\ wt.$

The enthalpy of neutralization of all the strong acids with strong bases is always constant and it is - 57.32 kj/gram equivalent weight. It is because of the fact that, it always involves the combination of 1 mole each of H^+ and OH^- ions to form one mole of water molecules.

$HCl\ (aq.) + NaOH\ (aq.) \rightarrow NaCl\ (aq.) + H_2O\ (l)$

or

$H^+(aq.) + Cl^-(aq.) + Na^+(aq.) + OH^-(aq.) \rightarrow Na^+(aq.) + Cl^-(aq.) + H_2O\ (l)$

or

$H^+(aq.) + OH^-\ (aq.) \rightarrow H_2O\ (l) + 57.32\ kj$

$\Delta_{neu} H = -57.32\ kj/gram\ eqv.\ wt.$

CHEMISTRYFORCOMPETITION.COM

Similarly, for following reaction-

$$HNO_3\ (aq.) + KOH\ (aq.) \rightarrow KNO_3\ (aq.) + H_2O\ (l)$$

or

$$H^+(aq.) + NO_3^-(aq.) + K^+(aq.) + OH^-(aq.) \rightarrow K^+(aq.) + NO_3^-(aq.) + H_2O\ (l)$$

or

$$H^+(aq.) + OH^-\ (aq.) \rightarrow H_2O\ (l) + 57.32\ kj$$

$$\Delta_{neu}H = -57.32\ kj/gram\ eqv.\ wt.$$

If acid or base or both are weak, a part of heat released is used up in dissociation of them. Hence, enthalpy change is relatively lesser. For example, for following reaction-

$$CH_3COOH\ (aq.) + NaOH\ (aq.) \rightarrow CH_3COONa\ (aq.) + H_2O\ (l) + 55.23\ kj$$

$$\Delta_{neu}H = -55.23\ kj/gram\ eqv.\ wt.$$

Here, 2.09 kj heat is used up in dissociation of CH_3COOH and is called enthalpy of dissociation of CH_3COOH.

On this basis, the enthalpy of neutralization of the weak acids with weak bases are found to be the least. For example,

$$CH_3COOH\ (aq.) + NH_4OH\ (aq.) \rightarrow CH_3COONH_4\ (aq.) + H_2O\ (l) + 49.8\ kj$$

$$\Delta_{neu}H = -49.8\ kj/gram\ eqv.\ wt.$$

(6) Bond dissociation enthalpy ($\Delta_{diss}H$)-

"The enthalpy change (heat required) for breakage of one mole bonds of a definite type in gaseous state is called bond dissociation enthalpy ($\Delta_{diss}H$) of the respective bond."

For a diatomic molecule, the enthalpy of atomization is equal to the bond dissociation enthalpy of the molecule. For example, bond dissociation enthalpy of hydrogen is 433 $kJmol^{-1}$

$$H{-}H\ (g) \rightarrow 2H(g); \quad \Delta_{diss.}H = +433\ kJmol^{-1}$$

Similarly, bond dissociation enthalpy of chlorine is 242.5 $kJmol^{-1}$

$$Cl{-}Cl\ (g) \rightarrow 2Cl(g); \quad \Delta_{diss.}H = +242.5\ kJmol^{-1}$$

If a molecule contains two or more bonds of same kind, then different amount of energy are required to break these bonds successively. For example, for H_2O mplecule, the bond dissociation enthalpies of two O-H bonds are 497.8 and 428.5 $kJmole^{-1}$ respectively.

$$H_2O\ (g) \rightarrow H(g) + OH(g); \quad \Delta_{diss.}H = +497.8\ kJmol^{-1}$$

$$OH\ (g) \rightarrow H(g) + O(g); \quad \Delta_{diss.}H = +428.5\ kJmol^{-1}$$

In such case average of bond dissociation enthalpies of different bonds are taken and it is called bond enthalpy of the respective bond. Thus,

$$\text{Bond enthalpy of O-H bond} = \frac{497.8 + 428.5}{2}\ kJmol^{-1}$$

$$= 463.15\ kJmol^{-1}$$

CHEMISTRYFORCOMPETITION.COM

For a diatomic molecule, bond dissociation enthalpy corresponds to the bond enthalpy of the molecule.

Determination of Enthalpy of Reaction from Bond Enthalpy Data-

The enthalpy of the reaction is found to be equal to the difference of the summation of bond enthalpies of the reactants and the summation of the bond enthalpies of the products. Thus, the enthalpy of the reaction,

$$\Delta_r H = \sum \Delta_{diss.}H \text{ (reactants)} - \sum \Delta_{diss.}H \text{ (products)}$$

For example, for following reaction-

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$$

The enthalpy of the reaction,

$$\Delta_r H = [4\times\Delta_{diss.}H(C\text{-}H) + 2\times\Delta_{diss.}H(O=O)] - [2\times\Delta_{diss.}H(C=O)2 + 4\times\Delta_{diss.}H(O\text{-}H)]$$

Ques.- The bond dissociation enthalpy of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcalmol^{-1} respectively. Find the enthalpy of following reaction-

$$H_2\,(g) + Cl_2\,(g) \rightarrow 2HCl\,(g)$$

Ans.- The enthalpy of the reaction is given by the expression,

$$\Delta_r H = \sum \Delta_{diss.}H \text{ (reactants)} - \sum \Delta_{diss.}H \text{ (products)}$$

$\therefore$ For the given reaction-

$$H_2\,(g) + Cl_2\,(g) \rightarrow 2HCl\,(g)$$

$$\Delta_r H = [\Delta_{diss.}H(H\text{-}H) + \Delta_{diss.}H(Cl\text{-}Cl)] - [2\times\Delta_{diss.}H(H\text{-}Cl)]$$
$$= [104 + 58] - [2 \times 103]$$
$$= (162 - 206)\text{ kcal}$$
$$= -44\text{ kcal}$$

Ques.- The bond dissociation enthalpy of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcalmol^{-1} respectively. Find the enthalpy of formation of HCl.

Ans.- The reaction involved for enthalpy of formation of HCl is as under-

$$\frac{1}{2}H_2\,(g) + \frac{1}{2}Cl_2\,(g) \rightarrow HCl\,(g)$$

Here, the enthalpy of the reaction would correspond to the enthalpy of formation of HCl. Thus,

$$\Delta_f H\,(HCl) = \sum \Delta_{diss.}H \text{ (reactants)} - \sum \Delta_{diss.}H \text{ (products)}$$
$$= [\tfrac{1}{2}\times\Delta_{diss.}H(H\text{-}H) + \tfrac{1}{2}\times\Delta_{diss.}H(Cl\text{-}Cl)] - [\Delta_{diss.}H(H\text{-}Cl)]$$
$$= [(\tfrac{1}{2}\times 104) + (\tfrac{1}{2}\times 58)] - [103]$$
$$= [(52 + 29) - 103]\text{ kcal}$$
$$= -22\text{ kcalmol}^{-1}$$

CHEMISTRYFORCOMPETITION.COM