# THERMOCHEMISTRY

## ❑ THERMOCHEMISTRY :

All chemical processes are associated with energy changes in chemical reactions. A thermochemical equation, represents both the material change and the energy. While writing a thermochemical equation, the heat evolved in case of exothermic reaction, or the heat absorbed in case of endothermic reaction, is indicated on the product side of the balanced chemical equation. For example,

(i) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$ $\Delta H = -285.91$ kJ

(ii) $C(\text{graphite}) + 2S\ (\text{rhombic}) \rightarrow CS_2$ $\Delta H = +91.96$ kJ

The most stable physical state of the reacting species and the products is also indicated in brackets. Thus, a thermochemical equation gives complete information about the material change and the associated heat change. It is clear that the first reaction is exothermic and the second one endothermic.

- **Examples of exothermic reactions**

Coal is burnt simply for the large amount of energy available during its combustion :

When water is added to quick lime (CaO) for preparing whitewash, a considerable amount of heat is produced during the reaction. The heat produced warms up the water.

When we add dilute hydrochloric acid to a test tube containing granulated zinc, hydrogen gas is evolved. The reaction is accompanied by evolution of heat.

- **Examples of endothermic reactions**.

When a small quantity of ammonium chloride ($NH_4Cl$) is dissolved in water in a test tube, the tube becomes colder than before. During this chemical reaction heat is absorbed from the surroundings (test tube).

When the crystals of sodium thiosulphate ($Na_2S_2O_3.5\ H_2O$) commonly called hypo, are dissolved in water, a cooling effect takes place.

One mole of nitrogen reacts with one mole of oxygen to form two moles of nitric oxide. 180.5kJ of heat is absorbed at constant temperature and the reaction may be expressed as:

or $N_2(g) + O_2(g) \rightarrow 2NO(g)$

## ❑ STANDARD ENTHALPY OF REACTION :

Enthalpy of reaction is defined as the quantity of heat evolved or absorbed. When molar quantities of substances react in amounts represented by chemical equation at constant pressure and temperature, the substances being in their standard states.

For example : $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ $\Delta H = -183.92$ kJ

Thus, when one mole of gaseous hydrogen reacts with one mole of gaseous chlorine, 183.92 kJ of heat is evolved. This is the heat of the reaction for the above chemical reaction.

$\Delta H_r = \Sigma H_{\text{products}} - \Sigma H_{\text{reactants}}$

- **Factors Affecting Heat or Enthalpy Change** : The enthalpy change of reaction ($\Delta H$) depends upon the following factors :
- **Physical state of the reactants and the products** : The $\Delta H$ of a reaction depends upon the physical states of reactants and products. For example, when hydrogen and oxygen gases combine to give liquid water, the heat of reaction is different than when they combine to form gaseous water.

$H_2(g) + O_2(g) \rightarrow H_2O(\ell)$ $\Delta H = -285.83$ kJ

$H_2(g) + O_2(g) \rightarrow H_2O(g)$ $\Delta H = -241.82$ kJ

- **Quantities of reactants** : The amount of heat evolved or absorbed depends upon the amount of reactants. For example, the heat of combustion of 2 moles of carbon is double than heat of combustion of 1 mole of carbon.
- **Allotropic modification** : The amount of heat evolved or absorbed for different forms of the same substance are different. For example,

  $C(diamond) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -395.41$ kJ

  $C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.51$ kJ
- **Temperature** :The heat of reaction depends upon the temperature of reactants and products.

  $H_2O(\ell) \rightarrow H_2O(g)$ $\Delta H =$ at 298K

  $H_2O(\ell) \rightarrow H_2O(g)$ $\Delta H =$ at 373K
- **Pressure or volume:** The heat of reaction depends upon the conditions of constant pressure or volume. As,

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

  $\Delta H$ may be equal, greater than or less than $\Delta U$.

  Thus, a reaction, which is exothermic in one direction will be **endothermic in reverse direction.**
- **Standard Enthalpy of Reaction** : As the heat of a reaction varies with temperature it is desirable to fix up a standard or a reference state. A substance is said to be in standard state when it is present in its most stable state at 298 K under a pressure of one atmosphere.

  The heat change that occurs when a process is carried out at 298K and one atmospheric pressure is called standard heat change. It is represented as $\Delta H$ where the superscript ( ) indicates the standard state. If the reactants and products are in their standard states, then the enthalpy of a reaction is termed as the standard enthalpy of reaction

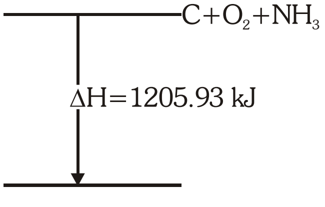
  **Note : The thermodynamic standard state can be established at any temperature, but most book tabulate standard enthalpy at 298.15K.The superscript (°) indicate rather pressure of 1 bar. Thus there can be one standard state at each temperature.**

## HESS'S LAW OF CONSTANT HEAT SUMMATION :

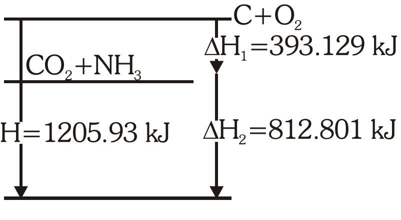
This law put forth by Hess states that "the resultant enthalpy change in a reaction is the same whether it occurs in one or several steps".

We illustrate this law by considering a example :

(i) The formation of urea from carbon, oxygen and ammonia may take place directly in one step or in two steps as shwon below :



(i) One step reaction



(ii) Two step reaction

The enthalpy change when the reaction takes place in two steps is given by

$\Delta H_1 + \Delta H_2 = -393.129 - 812.801 = -1205.93$ kJ

This is seen to be equal to $\Delta H$, the change involved in one step reaction.

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**Enthalpy of Formation :**

The heat evolved or absorbed when **1 mole** of a substance is formed from its constituent elements under constant pressure and temperature conditions is called enthalpy of formation. It is denoted by $\Delta H_f$ .

For example, heat of formation of carbon dioxide and methane may be expressed as :

$$C(\text{graphite}) + O_2 \rightarrow CO_2(g)$$

$$C(\text{graphite}) + 2H_2 \rightarrow CH_4(g)$$

These equations should always be written for one mole as per the definition of the substance to be formed. If for balancing, we require the coefficient 2, 3.... etc., in the equation then $\Delta H_f$ values should also be multiplied by the same number as discussed earlier.

**Ex.** Calculate the standard heat of formation of carbon disulphide ($\ell$). Given that the standard heats of combustion of carbon (s) sulphur (s) and carbon disulphide ($\ell$) are 393.3, –293.72 and –1108.76kJ mol$^{-1}$ respectively.

**Sol.** The given data can be written in thermochemical equation form as :

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ} \quad ......(i)$$

$$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H = -293.72 \text{ kJ} \quad ......(ii)$$

$$CS_2(\ell) + 3O_2(g) \longrightarrow CO_2(g) + SO_2(g) \qquad \Delta H = -1108.76 \text{ kJ} \quad ......(iii)$$

The required equation is:

$$C(s) + 2S(g) \longrightarrow CS_2(\ell) \qquad \Delta H = ?$$

Multiplying equation (ii) by 2 and adding to equation (i) we get,

$$2S(s) + 2O_2(g) \longrightarrow 2SO_2(g) \qquad \Delta H = -587.44 \text{ kJ}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ}$$

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$$2S(s) + C(s) + O_2(g) \longrightarrow 2SO_2(g) + CO_2(g) \qquad \Delta H = -980.74 \text{ kJ}$$

Subtracting equation (iii) from the above equation we have,

$$2S(s) + C(s) + O_2(g) \longrightarrow 2SO_2(g) + CO_2(g) \qquad \Delta H = -980.74 \text{ kJ}$$

$$CS_2(\ell) + 3O_2(g) \longrightarrow CO_2(g) + SO_2(g) \qquad \Delta H = -1108.76 \text{ kJ}$$

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$$C(s) + 2S(g) \longrightarrow CS_2(\ell) \qquad \Delta H = -128.02 \text{ kJ}$$

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**Standard enthalpy of formation :** The heat of formation $\Delta H_f$ depends upon the condition of temperature, pressure and physical state (gas, liquid or solid) of the reactants and the products. Therefore the heat change accompanying the formation of one mole of a compound from its elements when all the substances are in their standard states (1 atm pressure and 298 K), is called the standard heat of formation. It is expressed as $\Delta H_f^\circ$.

Since no heat changes are involved in the formation of elements form themselves in their standard states, the standard enthalpy of formation of all elements is zero.

For example, the standard enthalpy of formation ($\Delta H_f^\circ$) for $H_2O_{(\ell)}$ is - 286 kJ mol$^{-1}$ i.e., when one mole of liquid water is formed from its elements $H_{2(g)}$ and $O_{2(g)}$ at 298 K and 1 atm pressure, then 286 kJ mol$^{-1}$ of heat is released. The negative value of $\Delta H_f^\circ$ indicates the formation of a stable compound.

### ◆ Standard heat of reaction from standard heats of formation :

The knowledge of standard heats of formation of various substances can be used to calculate the heats of reactions under standard conditions. The standard heat of any reaction ($\Delta H$ ) is equal to the difference between the $\Delta H_f^\circ$ of all the reactants i.e.,

$\Delta H$ = Sum of the standard heats of formation of products - Sum of the standard heats of formation of reactants.

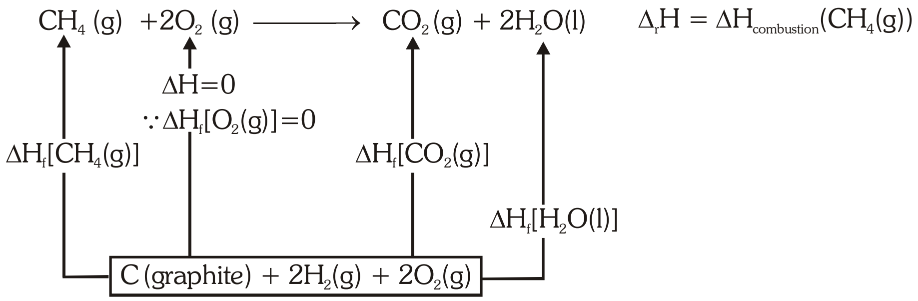
i.e., $\Delta H^\circ = \Sigma\Delta H_f^\circ{}_{\text{(products)}} - \Sigma\Delta H_f^\circ{}_{\text{(reactants)}}$

For a reaction,

$$aA + bB \rightarrow cC + dD$$
$$\Delta H = \Sigma\Delta H_f^\circ{}_{\text{(products)}} - \Sigma\Delta H_f^\circ{}_{\text{(reactants)}}$$
$$= [c\Delta H_f^\circ\,(C) + d\Delta H_f^\circ\,(D)] - [a\Delta H_f^\circ\,(A) + b\Delta H_f^\circ\,(B)]$$

Consider the combustion of $CH_4$, the enthalpy change of the reaction is equal to the entahlpy of combustion of $CH_4$.

$$\Delta H_r = [\Delta H_f\,(CO_{2(g)}) + 2.\Delta H_f\,(H_2O_{(\ell)})] - [2\Delta H_f\,(O_{2(g)}) + \Delta H_f\,(CH_4)]$$



### ❑ ENTHALPY OF COMBUSTION :

Enthalpy of combustion of a given compound is defined as follows :

It is the enthalpy change when one mole of this compound combines with the requisite amount of oxygen to given products in their stable forms.

For example, the standard enthalpy of combustion of methane at 298.15 K is –890.36 kJ mol$^{-1}$. This implies the following reaction :

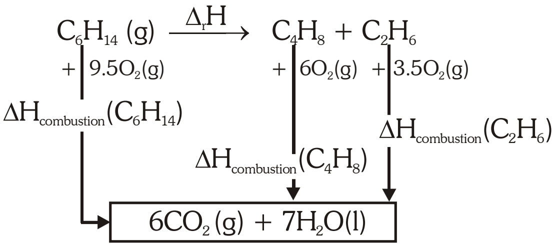
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) \qquad \Delta H = -\ 890.36 \text{ kJ mol}^{-1}$$

The standard enthalpy of combustion of methane at 298.15 K may be writen as

$$\Delta_c H\,(CH_4,\ g,\ 298.15\text{ K}) = -\ 890.36 \text{ kJ mol}^{-1}$$

### ❑ APPLICATION OF ENTHALPY OF COMBUSTION :

Consider a reaction of disproportination of $C_6H_{14}$ into $C_4H_8$ and $C_2H_6$. The following diagram show how enthalpy of combustions can be used to estimate entlalpy of reaction.



From the inspection of the above diagram, it is clear that

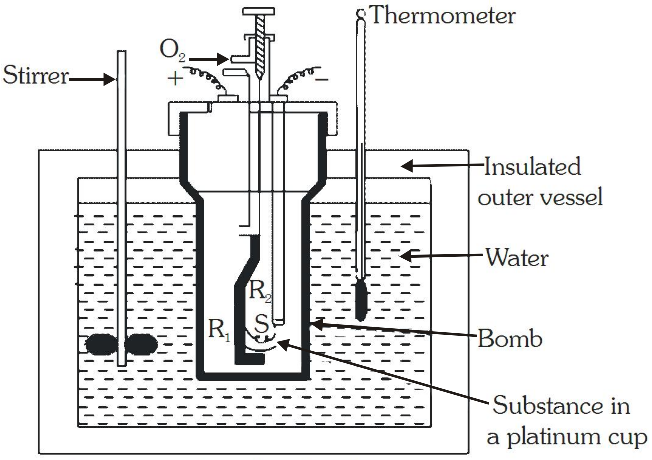
$$\Delta H_{\text{reaction}} = \Delta H_{\text{combustion}}(C_6H_{14}) - \Delta H_{\text{combustion}}\,(C_4H_8) - \Delta H_{\text{combustion}}\,(C_2H_6)$$

Hence $\Delta H_{\text{reaction}} = \Delta H_{\text{combustion}}(\text{Reactant's}) - \Delta H_{\text{combustion}}\,(\text{Products})$

## ❑ EXPERIMENTAL DETERMINATION OF ENTHALPY OF COMBUSTION :

### (1) CONSTANT VOLUME BOMB CALORIMETER

The heat changes in chemical reactions are measured with the help of calorimeters. Depending upon the requirements of experiments different types of calorimeters are used. In general, reactions taking place at constant volume and involving gases are carried out in a closed container with rigid walls that can withstand high pressures such as a bomb calorimeter. The body of the bomb calorimeter is made of heavy steel. The steel vessel is coated inside with gold or platinum to avoid oxidation of steel during the chemical reactions. The vessel is fitted with a tight screw cap.



Constant volume bomb calorimeter

There are two electrodes $R_1$ and $R_2$, which are connected to each other through a platinum wire S, which remains dipped in a platinum cup just below it. The substance under investigation is taken in platinum cup (few grams). The vessel is then filled with excess of oxygen at a pressure of about 15200 to 19000 mm of Hg and sealed. It is now dipped in an insulated water bath provided with a mechanical stirrer and a thermometer, sensitive enough to read upto 0.01 C (Beckmann's thermometer). The initial temperature of water is noted and the chemical reaction (combustion) is initiated by passing electric current through the platinum wire. The heat evolved during the chemical reactions raises the temperature of water, which is recorded from the thermometer. By knowing the heat capacity of the calorimeter and also the rise in temperature, the heat of chemical reaction or heat of combustion at constant volume can be calculated by using the expression.

$$\Delta U = -\ C \quad \Delta T \quad (M/w)$$

where, C = Heat capacity of calorimeter system $\Delta T$ = Rise in temperature M = Molecular mass of substance w = Mass of substance taken.

**Ex.** 0.138 gm sample of solid magnesium (molar mass = 24.3 g $mol^{-1}$) is burned in a constant volume bomb calorimeter that has a heat capacity of 1.77 kJ/°C. The calorimeter contains 300 mL of water (density = 1g/mL) and its temperature is raised by 1.126°C. Calculate enthalpy of combustion of magnesium at 289 K.

**Sol.** We have, $q_{water} = m_{water}\ C_{water}\ \Delta T$

or $q_{water} = 300 \quad 1 \quad 4.184 \quad 1.126 = 1413\ J = 1.413\ kJ$

$$q_{bomb} = (m_{bomb}\ .\ C_{bomb})\ \Delta T$$

$$= 1.77 \quad 1.126 = 1.992\ kJ$$

$$q_{comb} = -(q_{water} + q_{bomb})$$

$$= -(1.413 + 1.992) = -3.405\ kJ$$

$$\Delta U = \frac{q_{comb}}{m_{subs}/M_{subs}} = \frac{-3.405\ kJ}{\frac{0.138}{24.3}} = -599.6\ kJ\ mol^{-1}$$

The combustion reaction is

$Mg(s) + 1/2O_2\ (g) \rightarrow MgO(s) \qquad \Delta n_g = -1/2$

$$\Delta H = \Delta U + (\Delta n_g)\ RT$$

$$= -599.6 + (-1/2)\ (8.314 \quad 10^{-3})\ (298)$$

$$= -599.6 - 1.24 = -600.84\ kJ\ mol^{-1}$$

## (2) CONSTANT PRESSURE BOMB CALORIMETER :

The only difference with the constant volume calorimeter is that the bomb is fitted with a piston which is maintained at constant pressure.

Thus the heat liberated during the chemical reaction $q_p$ directly gives enthalpy of reaction by the expression

$$\Delta H = -\ C \quad \Delta T \quad (M/w)$$

where, C = Heat capacity of calorimeter system, ΔT = Rise in temperature, M = Molecular mass of substance w = Mass of substance taken.

## ❑ MAXIMUM TEMPERATURE ATTAINED IN A BOMB CALORIMETER :

During explosion ion bomb calorimeter, Heat released from the bond temporarily remain inside the bomb, and temperature of calorimeter system rises to a very high value. For small period the process can be considered as adiabatic process since the heat librated still accumulates in container, and become available to product's formed during the reaction as well as remaining reactants.

$\Delta_r U = \quad \Sigma n_i C_{vi}(T_f - T_i)$ in a constant volume bomb calorimeter

$\Delta_r H = \quad \Sigma n_i C_{pi}(T_f - T_i)$ in a constant volume bomb calorimeter

Here $C_{pi}$ and $C_{vi}$ are molar constant pressure and constant volume heat capacities of products and unreacted reactants and $n_i$ are number of moles of respective substance.

## ❑ CALORIFIC VALUE OF A FUEL

Nutritional value of foods, and the usefulness of fuels is determined by the heat (energy) they produce on heating. The energy released by the combustion of foods or fuels is usually compared in terms of their combustion energy per gram. It is known as calorific value. It is defined as the amount of heat produced in calories (or joules) when one gram of a substance (food or fuel) is completely burnt. The calorific value is usually expressed in kcal per gram or kilojoules per gram (1 kcal = 4.184 kJ).

For example when Methane burns

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 891 \text{ kJ energy}$$

therefore calorific value of meathan is $891/16 = 55.6$kJ/gm

The fuel are graded according to their calorific value. Greater the calorfic value of a fuel, greater is the prize. Hydrogen has greatest calorific value.

## ❑ BOND ENTHALPY

In chemical reactions the formation of a chemical bond is accompanied by the release of energy. Conversely energy has to be supplied for the breaking of a bond. Bond strengths are commonly described by their bond dissociation energy which is the energy required to break one mole of a bond of particular type. This is a definite quantity and is expressed in kJ $mol^{-1}$. For diatomic molecules the bond dissociation energy is same as bond energy, whereas in polyatomic molecules the bond energy is taken as the mean average of the various bond dissociation energies of the bonds of a given type.

Thus bond energy is avarage energy needed to break one mole of a particular bond in a gaseous molecule to convert it into gaseous atoms.

The thermochemical data is useful in determining the bond energies of different bonds.

For example the bond energy of C-H bond in methane can be calculated form its heat of formation. The heat for formation of methane from carbon and hydrogen gaseous atoms has been found to be $-1663$ $kJmol^{-1}$.

$$C(g) + H(g) \rightarrow CH_4\ (g) \qquad \Delta H = -1663 \ kJmol^{-1}$$

Methane has four C-H bonds and the energy required to break all the four C-H bonds is 1663 kJ. Therefore the average C-H bond energy is

$$1663/4 = \ 413.25 \ kJmol^{-1}$$

## ❑ APPLICATION OF BOND ENTHALPY IN ESTIMATION ENTHALPY OF REACTIONS

Bond energies can be utilized to quickly estimate enthalpy of reactions. The enthalpy obtained from bond energy data often match very well with actual enthalpy obtained from other methods like enthalpy of combustion, or formation enthalpy data.

$$\Delta H = \text{B.E(reactant's)} - \text{B.E.(product's)}$$

example : 1 - consider the reaction

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6\ (g)$......................(i)

$C_2H_4\ (g) \rightarrow 2C(g) + 4H(g)$ ......................(ii)

$H_2 \rightarrow 2H(g)$ ..........................................(iii)

$C_2H_6(g) \rightarrow 2C(g) + 6H(g)$.....................(iv)

Now (i) = (i) + (iii) – (iv)

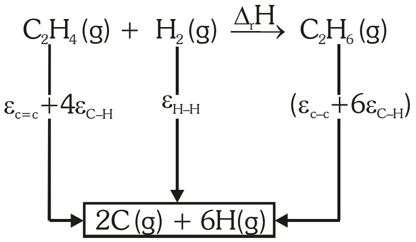
clearly from the equations the given formula is justified

Example :

2 - Figure in the following the enthalpies are indicated for.

$\Delta_r H_{\text{Theortical}} = \varepsilon_{c=c} + 4\varepsilon_{c-c} - 6\varepsilon_{c-c} - \varepsilon_{c-c}$

$\Rightarrow \quad \Delta_r H_{\text{Theortical}} = \text{B.E.(reactant's)} - \text{B.E. (product's)}$



## ❑ RESONANCE ENERGY, CONCEPT AND CALCULATION USING BOND ENENGY :

When two or more double bond are in conjugation, there is possiblity of delocalization of electron through conjugation. The Phenomenon is called resonance. Due to resonance, the molecule gain stability. The actual structure of molecule is avarage of many possible canonical structures possible for molecule.

Resonance energy is difference in energy of most stable canonical sturcture and energy of actual molecule. When ever there is possibility of resonance in molecule, the molecule become more stable and bond breaking become difficult.

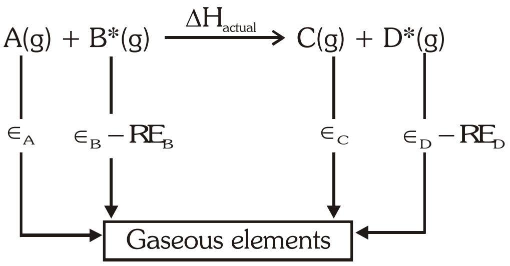
Resonance energy can be calculated using the formula

ΔH (Actual) - ΔH(theoretical) = Resonance energy of products - Resonance energy of reactants

The proof of above formula is given by following diagram.

Consider a reaction $A(g) + B^*(g) \rightarrow C(g) + D^*(g)$ where (*) showing that molecules exhibit phenomena of resonance. Remember where ever resonance take place, bond breaking become difficult.

Actual energy required to break a bond is equal to $\in_{\text{actual}} = \in_{\text{theoretical}}$ - resonance energy



$\Delta H_{\text{actual}} = \in_A + \in_B - R.E_B - \{\in_C + \in_D - R.E_D\}$

$\Delta H_{\text{actual}} = (\in_A + \in_B - \in_C - \in_D) + R.E_D - R.E_B$

$\Rightarrow \quad \Delta H_{\text{actual}} - \Delta H_{\text{Theoretical}} = R.E_D - R.E_B$

$[\Delta H_{\text{actual}} - \Delta H_{\text{Theoretical}} = R.E_{\text{Products}} - R.E_{\text{reactants}}]$

keep it in mind that resonance energy are expressed as -ive number because due to resonance, the molecule gain stability. Due to resonance in a molecule, bond breaking become difficult hence actual energy required to break a bond = theoretical bond energy - resonance energy.

## ❑ ENTHALPY OF SOLUTION :

When a solute is dissolved in a solvent a solution is formed. During dissolution of a solute in any solvent, a certain amount of heat is either absorbed or evolved. Such heat changes under constant pressure conditions are known as the enthalpy of solution. 'The change in enthalpy when one mole of a solute is dissolved in a specified quantity of a solvent at a given temperature is called enthalpy of solution'.To avoid the amount of solvent, heat of solution is usually defined for an infinite dilute solution. Thus, heat of solution at infinite dilution is the heat change when one mole of a substance is dissolved in such a large quantity of solvent so that further dilution does not give any further heat change.

Here 'aq' represents aqueous meaning a large excess of water. For substances, which dissolve with the absorption of heat (endothermic), the enthalpy of solution is positive while for the substances which dissolve by liberating heat (exothermic), the enthalpy of solution is negative. For example, when KCl is dissolved in water, heat is absorbed. Thus, the enthalpy of solution of KCl is positive. For a 200 times dilution (water : KCl = 200 : 1), the enthalpy change during the process, So, the enthalpy of solution of KCl at a dilution of 200 is 18.6 kJ $mol^{-1}$. The dissolution of $CaCl_2(s)$ in water is an exothermic process. So, the enthalpy of solution of calcium chloride ($CaCl_2$) is negative. At a dilution of 400, the enthalpy change for the reaction, So, the enthalpy of solution of $CaCl_2(s)$ at a dilution of 400 is –75.3 kJ $mol^{-1}$.

$$KCl(s) + 200H_2O \rightarrow KCl(aq)\ (200H_2O) \qquad \Delta H = +18.6 kJ\ mol^{-1}$$

$$CaCl_2(s) + 400H_2O \rightarrow KCl(aq)\ (400H_2O) \qquad \Delta H = -75.3 kJ\ mol^{-1}$$

### ◆ Important points to remember about enthalpy of solution :

It is generally negative for anhydrous salts

It is generally positive for salts which do not have water of hydration like NaCl

It is generally positive for hydrated salts like $CuSO_4.5H_2O$

If lattice energy|U|is more than |Hydration energy|of gaseous ions, enthalpy of solution is positive.

If lattice energy|U|is less than |Hydration energy|of gaseous ions, enthalpy of solution is negative.

Note that even when $\Delta H_{solution}$ is positive, salts are freely soluble in water due to favourable Gibb's free energy change.

## ❑ ENTHALPY OF HYDRATION :

This is defined as the heat change (evolved or absorbed) when one mole of the anhydrous salt combines with the required number of moles of water to form the specific hydrated salt.

$$CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s)\ ;\ \Delta H_{Hydration} = -78.21\ kJ\ mol^{-1}$$

Hydration is generally exothermic change.

If integral heat of solution of the hydrated and anhydrous salt is known, then heat of hydration can be calculated.

**For example :**

(a) $CuSO_4(anhydrous) + 800\ H_2O(\ell) \longrightarrow CuSO_4\ (800\ H_2O)\ ;\ \Delta H = -66.50\ kJ$

(b) $CuSO_4.5H_2O(s) + 795H_2O\ (\ell) \longrightarrow CuSO_4\ (800\ H_2O)\ ;\ \Delta H = 11.71\ kJ$

Thus, (a – b) gives

$$CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s)\ ;\ \Delta H_{Hydration} = -78.21\ kJ$$

## ❑ ENTHALPY OF NEUTRALISATION :

The reaction in which an acid and a base react to give a salt and water is called neutralization reaction. Neutralization reactions are exothermic in nature. The heat change when one gram equivalent of an acid is completely neutralised by a base or vice versa in dilute solution, is called heat of neutralization. Examples of heat of neutralization are :

Neutralization of HCl with NaOH

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(\ell)$ $\Delta H = -57.1$ kJ

Neutralization of $CH_3COOH$ with NaOH

$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa + H_2O(\ell)$ $\Delta H = -55.9$ kJ

It is important to note that the term gram equivalent is used in the definition of heat of neutralization. This is because neutralization involves 1 mole of $H^+$ ions and 1 mole of $OH^-$ ions to form 1mole of water and 57.1 kJ of heat is liberated.

$H^+(aq) + OH^- \longrightarrow H_2O(\ell)$ $\Delta H = -57.1$kJ

Now, one gram equivalent of various acids on complete dissociation liberates one mole of $H^+$ ions. But one mole of the acid may produce more than one mole of $H^+$ ions in solution depending upon its basicity; for example 1mol of $H_2SO_4$ gives 2 mol of $H^+$ ions and 1mol of $H_3PO_4$ gives 3 mol of $H^+$ ions on complete dissociation. But 1gram equivalent of both ($H_2SO_4$ or $H_3PO_4$) produces only 1 mol of $H^+$ ions.Thus, it is more appropriate to use the term gram equivalent in the definition of enthalpy of neutralization.

The average enthalpy of neutralization of any strong acid by a strong base is found to be –57.7. This is because strong acids and strong bases are completely ionized in aqueous solutions. The aqueous solution of one gram equivalent of all strong acids contains the same number of $H^+$ ions. Similarly, aqueous solution of one gram equivalent of all strong bases also contains same number of $OH^-$. The neutralization reactions between strong acids and strong bases in aqueous solutions involve simply the combination of $H^+$ ions (from an acid) and $OH^-$ ions (from a base) to form unionized water molecules. For example, the reaction between hydrochloric acid and sodium hydroxide. The neutralization can be represented as :

$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq)\ Cl^-(aq) + H_2O(\ell)$ $\Delta H = -57.1$ kJ

Cancelling common ions :

$H^+(aq) + OH^- \longrightarrow H_2O(\ell)$ $\Delta H = -57.1$ kJ

## ❑ EXPERIMENTAL DETERMINATION OF ENTHALPY OF NEUTRALIZATION :

In this experiment, an aqueous hydrochloric acid solution will be added to an aqueous sodium hydroxide solution. The neutralization reaction will occur until either $H^+$ or $OH^-$ is entirely consumed. The reactant which is consumed completely is called the limiting reactant.

The molar enthalpy of neutralization is defined as

$$\Delta H_{neut} = q_{neut}/n$$

Where $q_{neut}$ is the heat of neutralization, measured calorimetrically, and n is the moles of the limiting reactant.

**Approach** ∵ Add a known volume of 3.00 M aqueous HCl to a known volume of 1.00 M aqueous NaOH.

- Observe the temperature of the system before and after the neutralization reaction occurs.
- Calculate the change in temperature ($\Delta T$) for the system.
- Use the temperature change and heat capacities (C) for the calorimeter and aqueous solution to calculate the heat of neutralization.
- Divide the heat of neutralization by the moles of the limiting reactant to determine the molar enthalpy of neutralization.

$$\Delta H_{neut} = -\frac{C\Delta T}{n}$$

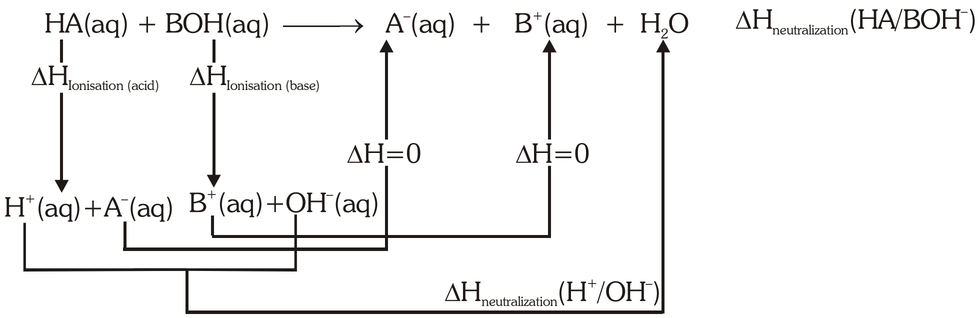
## ❑ THE ENTHALPY OF NEUTRALIZATION OF WEAK ACID AND WEAK BASE :

Consider the neutralisation of weak acid HA with weak base BOH.

Where, $\Delta H_{\text{ionisation}}$ (HA) = Enthalpy of ionization of acid HA

$\Delta H_{\text{ionisation}}$ (BOH) = Enthalpy of ionization of base BOH

$\Delta H_{\text{neutralisation}}$ ($H^+/OH$) = Enthalpy change for the reaction of $H^+$ and $OH^-$ to form water.

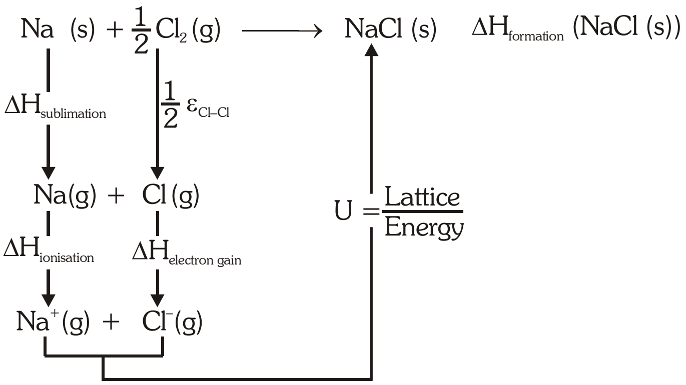


Thus for weak acid :

$$\Delta H_{\text{neut}}\,(BOH/HA) = \Delta H_{\text{ion.}}\,(HA) + \Delta H_{\text{ion}}\,(BOH) + \Delta H_{\text{neut}}\,(H^+\ OH^-)O$$

## ❑ BORN - HABER CYCLE FOR NaCl :

This cycle is based on thermochemical changes taking place in the formation of a lattice. This cycle can be used to determine lattice energy which cannot be directly measured. It is defined as that energy released when one mole of the ionic compound (lattice) is formed from its isolated ions in the gaseous state under standard condition.



BORN-HABER CYCLE FOR NaCl

$$nA^{m+}(g) + mB^{n-}(g) \longrightarrow A_nB_m(s)$$

$$\Delta H = -\,U \text{ (lattice energy)}$$

Formation of NaCl(s) lattice involves thus,

$$S + I + \frac{\varepsilon_{Cl-Cl}}{2} - E - U = q$$

hence, U can be calculated.

here, S = enthalpy of sublimation of Na(s) = $\Delta H_{\text{sublimation}}$

I = ionisation of energy of Na(g) = $\Delta H_{\text{ionization}}$

$\varepsilon$ = bond energy of $Cl_2$

U = lattice energy

q = enthalpy of formation of NaCl(s) = $\Delta H_{formation}$

If lattice is $MgX_2$ (s) then

$$S + (I_1 + I_2) + \varepsilon - 2E - U = q$$

where, $(I_1 + I_2)$ = total ionisation energy to form $Mg^{2+}(g)$.

**Ex.** Calculate lattice energy for the change,

$Li^+(g) + Cl^-(g) \longrightarrow LiCl(s)$

Given that

$\Delta H_{subl.}$ of Li = 160.67 kJ $mol^{-1}$,

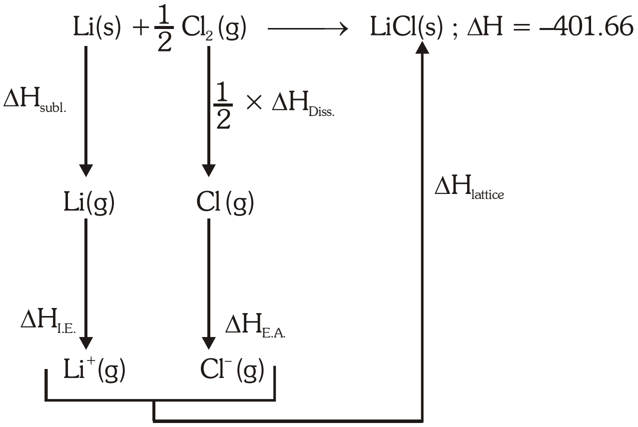
$\Delta H_{Dissociation}$ of $Cl_2$ = 244.34 kJ $mol^{-1}$,

$\Delta H_{ionisation}$ of Li(g) = 520.07 kJ $mol^{-1}$,

$\Delta H_{E.A}$ of Cl(g) = – 365.26 kJ $mol^{-1}$,

$\Delta H_f$ of LiCl(s) = – 401.66 kJ $mol^{-1}$.

**Sol.** Considering the different changes that occur in the formation of solid lithium chloride based on the data given the lattice energy of the above can be constituted as:



$$\Delta H_f = \Delta H_{subl.} + \Delta H_{I.E.} + \frac{1}{2}\Delta H_{Diss.} + \Delta H_{E.A} + \Delta H_{lattice}$$

or $$\Delta H_{lattice} = \Delta H_f - \Delta H_{subl.} - \Delta H_{I.E.} - \frac{1}{2}\Delta H_{Diss.} - \Delta H_{E.A}$$

$$= -839.31 \text{ kJ mol}^{-1}$$

## ❑ ENTHALPY OF ATOMISATION :

Enthalpy change to covert 1 mole of molecule into gaseous atoms is called enthalpy of atomisation :

Example :

$CH_4(g) \longrightarrow C(g) + 4H(g)$ ; $\Delta H_{atomisation}$ $(CH_4(g))$

$C_2H_6(g) \longrightarrow 2C(g) + 6H(g)$ ; $\Delta H_{atomisation}$ $(C_2H_6(g))$

$H_2(g) \longrightarrow 2H(g)$ ; $\Delta H_{atomisation}$ $(H_2(g))$

**Ex.** The bond dissociation enthalpies of $H_2(g)$ and $N_2$ (g) are + 435.95 kJmol$^{-1}$ and + 941.8 kJ mol$^{-1}$ and enthalpy of formation of $NH_3(g)$ is –46.024 kJ mol$^{-1}$.

(a) What is the enthalpy of atomization of $NH_3(g)$ ?

(b) What is the bond enthalpy of N – H bond ?

**Sol.** (a) The desired equation is

$$NH_3(g) \rightarrow N(g) + 3H(g)$$

we can consider the reaction as

$$NH_3(g) \xrightarrow{\Delta H_1} N(g) + 3H(g) \xrightarrow{\Delta H_2} \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

$$\therefore \quad \Delta H_1 + \Delta H_2 = +46.024 \text{ kJ mol}^{-1}$$

$$\text{Now } \Delta H_2 = -\frac{3}{2}(435.95) - \frac{1}{2}(941.80)$$

$$\therefore \quad \Delta H_1 = 46.024 + \frac{3}{2}(435.925) + \frac{1}{2}(941.8)$$

$$\text{or} \quad \Delta H_1 = 46.024 + 653.925 + 470.9$$

$$\text{or} \quad \Delta H_1 = 1170.849 \text{ kJ mol}^{-1}$$

$$\text{or} \quad \Delta H_1 = 1.170849 \text{ MJ mol}^{-1}$$

(b) The average bond enthalpy of N – H bond

$$= \frac{1170.849}{3} = 390.283 \text{ kJ mol}^{-1}$$

## ❑ ENTHALPY OF ELECTRON GAIN :

Enthalpy change when 1 mole electrons are added to gaseous species is called electron gain enthalpy.

Example :

$$Cl(g) + e \longrightarrow Cl^-(g) \quad ; \Delta H_{\text{electron gain}}$$

$\Delta H_{\text{electron gain}}$ is usually negatigve for non metals.

However electron gain enthalpy of negatively charged gaseous species is positive.

$$O^- + e \longrightarrow O^{2-} \quad ; \quad \Delta H_{\text{electron gain}} = +\text{ive}$$

## ❑ IONISATION ENTHALPY :

Enthalpy change when one mole of gaseous atom is converted into gaseous ion be removing one mole electron from ground state is called ionisation enthalpy.

Example :

$$Na(g) \longrightarrow Na^+(g) + e \quad ; \Delta H_{\text{Ionization}}(Na(g))$$

$$H(g) \longrightarrow H^+(g) + e \quad ; \Delta H_{\text{Ionization}}(H(g))$$

❑ Different types of standard enthalpy changes (Based on IUPAC recommendations).

| | Transition Enthalpy | Example | Definition | Symbol |
|---|---|---|---|---|
| 1. | Enthalpy of formation | $K(s) + \frac{1}{2} Cl_2(g) \longrightarrow KCl(s)$ | One mole of the compound formed from its elements | $\Delta_f H$ or $\Delta H_f$ |
| 2. | Enthalpy of combustion | $C_2H_6(g) + O_2(g) \longrightarrow CO_2(g) + 3H_2O(\ell)$ | One mole of the compound (fuel) is burnt completely in oxygen | $\Delta_c H$ or $\Delta H_c$ |
| 3. | Enthalpy of fusion | $H_2O(s) \longrightarrow H_2O(\ell)$ | One mole of the liquid is formed from the solid without a change in temperature | $\Delta_{fus} H$ or $\Delta H_{fus}$ |
| 4. | Enthalpy of vaporisation | $H_2O(\ell) \longrightarrow H_2O(g)$ | One mole of the vapour formed from the liquid without a change in temperature | $\Delta_{vap} H$ or $\Delta H_{vap}$ |
| 5. | Enthalpy of sublimation | $I_2(s) \longrightarrow I_2(g)$ | One mole of the vapour formed the solid | $\Delta_{sub} H$ or $\Delta H_{sub}$ |
| 6. | Enthalpy of atomisation | $H_2(g) \longrightarrow 2H(g)$ | One mole of the substance broken into isolated atoms in the gas phase | $\Delta_{at} H$ or $\Delta H_{at}$ |
| 7. | Enthalpy of reaction | $A \longrightarrow B$ | Enthalpy change taking place in a reaction | $\Delta_r H$ or $\Delta H_r$ |
| 8. | Enthalpy of neutralisation | $HCl(aq) + NaOH(aq) \longrightarrow H_2O + NaCl(aq)$ | One mole of water formed by the neutralisation of an acid by a base | $\Delta_n H$ or $\Delta H_n$ |
| 9. | Enthalpy of ionisation | $Na(g) \longrightarrow Na^+(g) + e^-$ | One mole atoms ionised - all species in gaseous phase | $\Delta_{ion} H$ or $\Delta H_{ion}$ |
| 10 | Electron-gain enthalpy | $X(g) + e^- \longrightarrow X^-(g)$ | One mole of anions being formed all species in the gaseous phase | $\Delta_{eg} H$ or $\Delta H_{eg}$ |
| 11 | Lattice enthalpy | $NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$ | One mole of a crystal completely separated into isolated particles in the gaseous phase | $\Delta_L H$ or $\Delta H_L$ or U |
| 12 | Bond dissociation enthalpy (bond A – B) | $HCl(g) \longrightarrow H(g) + Cl(g)$ | One mole of bonds broken - all species in the gaseous phase | $\Delta H_{A-B} = \varepsilon_{A-B}$ |
| 13 | Enthalpy of solution | $NaCl(s) + H_2O(excess) \longrightarrow NaCl(aq)$ | One mole of the solute dissolved in excess of solvent so that further dilution produces no enthalpy change | $\Delta_{sol} H$ or $\Delta H_{sol}$ |
| 14 | Enthalpy of hydration | $X^{\pm}(g) \longrightarrow X^{\pm}(aq)$ | One mole of the ion in gaseous phase is hydrated | $\Delta_{hyd} H$ or $\Delta H_{hyd}$ |
| 15 | Enthalpy of mixing | pure substances → mixture | One mole each of the two or more substances is mixed | $\Delta_{mix} H$ or $\Delta H_{mix}$ |

## MEMORY TIPS

- Heat change expressed at constant pressure = $\Delta H$

  Heat change expressed at constant volume = $\Delta E$

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

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

  $\Delta$ = No. of moles of product – No. of moles of reactants ; as represented by stoichiometry of change.

  (count only gaseous phase molecule for $\Delta n$)

- **Kirchoff's Equation** : Variation of $\Delta H$ and $\Delta E$ with temperature

  $$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

  $$\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$$

  $$\Delta C_p = \sum C_{p\ \text{Products}} - \sum C_{p\ \text{Reactants}}$$

  $$\Delta C_v = \sum C_{v\ \text{Products}} - \sum C_{v\ \text{Reactants}}$$

  $\Delta C_p$ and $\Delta C_v$ are changes in molar heat capacities at constant and volume respectively during the change.

- **Standard Heat Enthalpy (H )**

  $$H_{\text{(Compound)}} = \Delta H_{\text{(Formation of compound)}}$$

- **Heat of solution for electrolytes ($\Delta H_s$)**

  $$\Delta H_s = \Delta H_i + \Delta H_h$$

  $\Delta H_i$ and $\Delta H_h$ are heat of ionisation and heat of hydration respectively

- **Heat of neutralization**

  $$H^+ + OH^- \rightleftharpoons H_2O \text{ ; } \Delta H \text{ (neutralization)} = -13.7 \text{ kcal} = -57.27 \text{ kJ}$$

## SOLVED PROBLEMS (OBJECTIVE)

**Ex.1** From the following data at 25°C

| Reaction | $\Delta_r$ H°/KJ mol$^{-1}$ |
|---|---|
| $1/2\ H_2(g) + 1/2O_2(g) \rightarrow OH(g)$ | 42.09 |
| $H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$ | –241.84 |
| $H_2(g) \rightarrow 2H(g)$ | 435.88 |
| $O_2(g) \rightarrow 2O(g)$ | 495.04 |

Calculate $\Delta_r$ H° for the following reactions

(a) $OH(g) \rightarrow H(g) + O(g)$

(b) $H_2O(g) \rightarrow 2H(g) + O(g)$

(c) $H_2O(g) \rightarrow H(g) + OH(g)$

**Sol.** **(a)** The desired equation is

$OH(g) \rightarrow H(g) + O(g)$

We are to develop the desired equation by using the four given equations

(i) $\frac{1}{2}H_2(g) \rightarrow H(g)$ $\qquad \Delta_rH° = \frac{435.88}{2}$

(ii) $OH(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}O_2(g)$ $\qquad \Delta_rH° = -42.09$

(iii) $\frac{1}{2}O_2(g) \rightarrow O(g)$ $\qquad \Delta_rH° = \frac{495.04}{2}$

By adding equation (i), (ii) & (iii),

we get

$OH(g) \rightarrow H(g) + O(g)$

$$\Delta_rH° \rightarrow \frac{435.88}{2} - 42.09 + \frac{495.04}{2}$$

or $\Delta_rH° = 423.37$ kJ/mol. **Ans.**

**(b)** The desired equation is

$H_2O(g) \rightarrow 2H(g) + O(g)$

(i) $\frac{1}{2}O_2(g) \rightarrow O(g)$ $\qquad \Delta_rH° = \frac{495.04}{2}$

(ii) $H_2(g) \rightarrow 2H(g)$ $\qquad \Delta_rH° = 435.88$

(iii) $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ $\qquad \Delta_rH° = 241.88$

The net equation is,

$H_2O(g) \rightarrow 2H(g) + O(g)$ $\qquad \Delta_rH° = 925.28$ kJ/mol **Ans.**

(c) The desired equation is

$H_2O(g) \rightarrow H(g) + OH(g)$

(i) $H_2O(g) \rightarrow 2H(g) + O(g)$ $\qquad \Delta_rH° = 925.28$ kJ/mol

(ii) $H(g) + O(g) \rightarrow OH(g)$ $\qquad \Delta_rH° = 423.37$ kJ/mol

By adding eq$^n$ (i) and (ii)

$H_2O(g) \rightarrow H(g) + OH(g)$ $\qquad \Delta_rH° = 1348.65$ kJ/mol **Ans.**

**Ex.2** From the given data prove that graphite is more stable allotrope of carbon than diamond from the given data

$C_{dia} + O_2 \rightarrow CO_2 \qquad \Delta H_1 = -94500$ cal

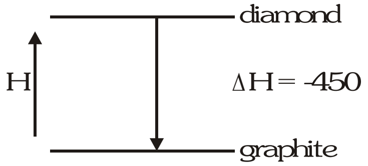
$C_{gra} + O_2 \rightarrow CO_2 \qquad \Delta H_2 = -94050$ cal

**Sol.** $C_{dia} + O_2(g) \rightarrow CO_2 \qquad \Delta H_1 = -94500$ cal

$C_{gra} + O_2(g) \rightarrow CO_2 \qquad \Delta H_2 = -94050$ cal

on substraction

$C_{dia} \rightarrow C_{gra} \qquad \Delta_r H^o = -450$ cal



since heat content of diamond > graphite

Therefore diamond is less stable than graphite.

**Ex.3** At 25° C, 1 mole $MgSO_4$ was dissolved in water. The heat evolved was found to be 91.211 kJ. One mole of $MgSO_4 . 7H_2O$ on dissolution gives a solution of the same composition accompained by an absorption of 13.807 kJ. Find the enthalpy of hydration, i.e., ΔH for the reaciton

$MgSO_4(s) + 7H_2O(\ell) \rightarrow MgSO_4 . 7H_2O(s)$

Given that

(i) $MgSO_4 (s) + aq \rightarrow MgSO_4 (aq) \qquad \Delta_r H_1 = -91.211 \text{ kJ mol}^{-1}$

(ii) $MgSO_4 . 7H_2O (s) + aq \rightarrow MgSO_4 (aq) \qquad \Delta_r H_2 = +13.807 \text{ kJ mol}^{-1}$

**Sol.** $MgSO_4 . 7H_2O (s) + aq \rightarrow MgSO_4 (aq) \qquad \Delta_r H_2 = +13.807 \text{ kJ mol}^{-1}$ ...........(ii)

Equation (i) can be written as follows :

$MgSO_4(s) + 7H_2O(\ell) + aq \rightarrow MgSO_4(aq) \qquad \Delta_r H = -91.211 \text{ kJ mol}^{-1}$ ...........(iii)

eqn (iii) – (ii) will give

$MgSO_4(s) + 7H_2O(\ell) \rightarrow MgSO_4 . 7H_2O(s)$

$\Delta_r H = -91.211 - 13.807 = -105.018 \text{ kJ mol}^{-1}$.

**Ex.4** Enthalpy of neutralization of HCl by NaOH is –57.32 kJ $mol^{-1}$ and by $NH_4OH$ is –51.34 kJ $mol^{-1}$. Calculate the enthalpy of dissociation of $NH_4OH$.

**Sol.** Given that

$H^+(aq) + NH_4OH(aq) \rightarrow NH_4^+ (aq) + H_2O(\ell) \qquad \Delta_r H = -51.34 \text{ kJ mol}^{-1}$

we may consider neutralization in two steps :

(i) ionization

$NH_4OH(aq) \rightarrow NH_4^+(aq) + OH^-(aq) \; \Delta_r H_1$ ?

(ii) neutralization

$H^+ (aq) + OH^-(aq) \rightarrow H_2O(\ell) \qquad \Delta_r H_2 = -57.32 \text{ kJ mol}^{-1}$

Thus, $\Delta_r H = \Delta_r H_1 + \Delta_r H_2$

Therefore,

$$\Delta_r H_1 = \Delta_r H - \Delta_r H_2$$

$$= -51.34 + 57.32 = 5.98 \text{ kJ/mol}^{-1}$$

**Ex.5** Calculate $\Delta_r H^\circ$ for the reaction

$Ag^+(aq) + Cl^-(aq) = AgCl (s)$ at 25°C.

Given :

$\Delta_f H^\circ (Ag^+, aq) = 105.58 \text{ kJ mol}^{-1}$,

$\Delta_f H^\circ (Cl^-, aq) = -167.16 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ$

$(AgCl, s) = -127.07 \text{ kJ mol}^{-1}$

**Sol.** For the reaction

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

We have

$\Delta_rH° = (AgCl, s) – \Delta_fH° (Ag^+, aq) – \Delta_fH° (Cl^-, aq)$

$= [–127.07 – 105.58 – (–167.16)]$

$= –65.49$ kJ mol$^{-1}$

**Ex.6** The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are –2839.2, –2275.2 and –5536 kJ mol$^{-1}$ respectively. Calculate the resonance energy of benzene, compared with Kekule structure. The bond enthalpy of C – H bond is given as equal to 410.87 kJ mol$^{-1}$.

**Sol.** Bond enthalpy of C – C bond

= Enthalpy required to break $C_2H_6$ into gaseous atoms –6   bond enthalpy of C – H bond

= 2839.2 kJ mol$^{-1}$ – 6   410.87 kJ mol$^{-1}$

= 373.98 kJ mol$^{-1}$

Bond enthalpy of C = C bond = Enthalpy requried to break $C_2H_4$ into gaseous atoms –4   bond enthalpy of C – H bond

= 2275.2 kJ mol$^{-1}$ – 4   410.87 kJ mol$^{-1}$

= 631.72 kJ mol$^{-1}$

For the formation of benzene having Kekule structure, we have to form 3 C – C bonds, 3 C = C bonds and 6 C – H bonds for which enthalpy released is

[3 (–373.98) + 3(–631.72) + 6(–410.87)]

= –5482.32 kJ mol$^{-1}$

But the given value of $\Delta_fH$ is

$\Delta_fH$ (actual) = –5536 kJ mol$^{-1}$

Hence resonance energy compared to Kekule structure

= $\Delta_fH$ (actual) – $\Delta_fH$ (Kekule structure)

= (–5536 + 5482.32)

= –53.68 kJ mol$^{-1}$

**Ex.7** Using bond enthalpy data given below, estimate enthalpy of formation of acetic acid.

| **Bond** | **Bond enthalpies** |
|---|---|
| C – H | 413.38 kJ mol$^{-1}$ |
| C – C | 347.69 kJ mol$^{-1}$ |
| C = O | 728.02 kJ mol$^{-1}$ |
| C – O | 351.46 kJ mol$^{-1}$ |
| O – H | 462.75 kJ mol$^{-1}$ |

**Enthalpy of atomization**

| | |
|---|---|
| C | 718.39 kJ atom$^{-1}$ |
| H | 217.94 kJ atom$^{-1}$ |
| O | 247.52 kJ atom$^{-1}$ |

The observed $\Delta_fH°$ for acetic acid is –438.15 kJ mol$^{-1}$. Compute the resonance energy of acetic acid.

**Sol.** The desired reaction for the formation of $CH_3COOH$ is

$2C(s) + 2H_2(g) + O_2(g) \rightarrow CH_3COOH (\ell)$

$\Delta_rH° = –3 \quad 413.38 – 1 \quad 347.69 – 728.02 – 351.46 – 462.75 + 2 \quad 718.39 + 4 \quad 217.94 + 2 \quad 247.52$

= – 326.48 kJ mol$^{-1}$

Resonance energy $= \Delta H°_{obs} – \Delta H°$

= –438.15 + 326.48

= –111.67 kJ mol$^{-1}$

**Ex.8** The specific heats of iodine vapour and solid are 0.031 and 0.055 cal/g respectively. If heats of sublimation of iodine is 24 cal/g at 200 C, what is its value at 250°C ?

**Sol.** Given

$I_{2_{(s)}} \longrightarrow I_{2_{(v)}}$ ; $\Delta H = 24$ cal/g at 200°C

$\Delta C_{P(cal/g)} = C_P$ of product – $C_P$ of reatant

$= 0.031 - 0.055$

$= -0.024$ cal/g

Now $\Delta H_2 - \Delta H_1 = \Delta C_P\ (T_2 - T_1)$

$\Delta H_2 - 24 = -0.024 \quad (523 - 473)$

$\therefore \quad \Delta H_2 = 24 - 1.2 = 22.8$ cal/g.

**Ex.9** The molar heat of formation of $NH_4NO_{3_{(s)}}$ is –367.54 kJ and those of $N_2O_{(g)}$, $H_2O_{(\ell)}$ are 81.46 and –285.8 kJ respectively at 25 C and 1 atmosphere pressure. Calculate ΔH and ΔE of the reaction $NH_4NO_{3_{(s)}} \longrightarrow N_2O_{(g)} + 2H_2O_{(\ell)}$

**Sol.** We have to find ΔH for

$NH_4NO_{3_{(s)}} \longrightarrow N_2O_{(g)} + 2H_2O_{(\ell)}$ ; $\Delta H = ?$

$$\Delta H_{reaction} = \Delta H_{Products} - \Delta H_{Reactants}$$

$$= \Delta H_{N_2O} + \Delta H_{H_2O} \times 2 - \Delta H_{NH_4NO_3}$$

Given, $\Delta H_{N_2O} = +81.46$ kJ , $\Delta H_{H_2O} = -285.8$ kJ , $\Delta H_{NH_4NO_3} = -367.54$ kJ

$\therefore \quad \Delta H_{reaction} = +81.46 + 2(-285.8) - (-367.54)$

$\Delta H = -122.6$ kJ

Further $\Delta H = \Delta E + \Delta nRT$ $\quad (\Delta n = 1 - 0 = 1,\ R = 8.314$ J, $= 298$ K)

$\therefore \quad -122.6 \quad 10^3 = \Delta E + 1 \quad 8.314 \quad 298$

$\therefore \quad \Delta E = -125077$ joule

$= 125.077$ kJ

**Ex.10** When 2 mole of $C_2H_{6_{(g)}}$ are completely burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of $C_2H_{6_{(g)}}$.$\Delta H_f$ for $CO_{2_{(g)}}$ and $H_2O_{(l)}$ are –395 and –286 kJ mol$^{-1}$ respectively.

**Sol.** We have to find

$2C(s) + 3H_{2_{(g)}} \rightarrow C_2H_{6_{(g)}}$ ; $\Delta H = ?$ ....(1)

Given, $C_{(s)} + O_{2_{(g)}} \rightarrow CO_{2_{(g)}}$ ; $\Delta H = -395$ kJ ....(2)

$H_{2_{(g)}} + \frac{1}{2}O_{2_{(g)}} \rightarrow H_2O_{(l)}$; $\Delta H = -286$ kJ ....(3)

$C_2H_{6_{(g)}} + \frac{7}{2}O_{2_{(g)}} \rightarrow 2CO_{2_{(g)}} + 3H_2O_{(l)}$; $\Delta H = -\frac{3129}{2}$ kJ $= -1564.5$ kJ ....(4)

Multiplying Eq. (2) by 2 and Eq. (3) by 3, then adding

$2C_{(s)} + 3H_{2_{(g)}} + \frac{7}{2}O_{2_{(g)}} \rightarrow 2CO_{2_{(g)}} + 3H_2O_{(l)}$; $\Delta H = -1648$ kJ ....(5)

Subtracting Eq. (4) from Eq. (5)

$C_2H_{6_{(g)}} + \frac{7}{2}O_{2_{(g)}} \rightarrow 2CO_{2_{(g)}} + 3H_2O_{(l)}$; $\Delta H = -1564.5$ kJ

– – – – +

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$2C_{(s)} + 3H_{2_{(g)}} \rightarrow C_2H_{6_{(g)}}$; $\Delta H = -83.5$ kJ

$\therefore \quad \Delta H_f$ of $C_2H_6 = -83.5$ kJ

**Ex.11** The heats of combustion of $C_2H_{4(g)}$, $C_2H_{6(g)}$ and $H_{2(g)}$ are –1409.5, –1558.3 and –285.6 kJ respectively. Calculate heat of hydrogenation of ethylene.

**Sol.** We have to find

$$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}; \qquad \Delta H = ?$$

Given,

$$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 3CO_{2(g)} + 2H_2O_{(g)}; \qquad \Delta H = -1409.5\text{ kJ} \qquad ......(1)$$

$$C_2H_6 + \frac{7}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}; \qquad \Delta H = -1558.3\text{ kJ} \qquad ......(2)$$

$$H_2 + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}; \qquad \Delta H = -285.6\text{ kJ} \qquad ......(3)$$

Adding Eqs. (1) and (3)

$$C_2H_{4(g)} + \frac{7}{2}O_{2(g)} + H_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}; \qquad \Delta H = -1695.1\text{ kJ} \qquad ......(4)$$

Subtracting Eq. (2) from (4)

$$\begin{array}{lll}
C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}; & \Delta H = -1558.3\text{ kJ} & ......(5)\\
- \qquad - \qquad - \qquad - & \qquad + & \\
\hline
C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}; & \Delta H = -136.8\text{ kJ} &
\end{array}$$

∴ Heat of hydrogenation of $C_2H_4$ = 136.8 kJ

**Ex.12** $\Delta H$ for combustion of ethane and ethyne are –341.1 and –310.0 kcal respectively. Which is better gas welder and why ?

**Sol.** A better gas welder is one which posses high calorific value, i.e., heat produced by 1 g of fuel.

$\Delta H_{\text{combustion}}$ for $C_2H_6$ = –341.1 kcal

∴ Calorific value = $\frac{-341.1}{30}$ kcal/g = –11.37 kcal/g

$\Delta H_{\text{combustion}}$ for $C_2H_2$ = –310.0 kcal

∴ Calorific value = $\frac{-310.0}{26}$ kcal/g = –11.92 kcal/g

∴ $C_2H_2$ is better gas welder.

**Ex.13** The heat of formation of methane is –17.9 kcal. If the heats of atomisation of carbon and hydrogen are 170.9 and 52.1 kcal per mole, calculate the C–H bond energy in methane.

**Sol.** Given that

$$C(s) + 2H_2(g) \rightarrow CH_4(g); \qquad \Delta H = -17.9\text{ kcal}$$

Energy change in reactants :

Heat of atomisation of 1 mole of C = 170.9 kcal

Heat of atomisation of 4 moles of H = 4   52.1 kcal

Energy change in product :

Heat of formation of 4 moles of C–H bonds = 4   x kcal.

(where x is the energy of formation of C–H bonds in kcal/mole).

Since the algebraic sum of all the heat changes is equal to the heat of formation of the above given equation, we have

170.9 + 4   52.1 + 4x = –17.9; x = –99.3 kcal

Thus the bond energy = +99.3 kcal/mole.

**Ex.14** Calculate the heat of formation of benzene from the following data, assuming no resonance. Bond energies :

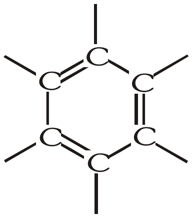
C–C = 83 kcal,   C=C = 140 kcal,   C–H = 99 kcal

Heat of atomisation of C = 170.9 kcal

Heat of atomisation of H = 52.1 kcal

**Sol.** We have to calculate ΔH for the reaction

$$6C(s) + 3H_2(g) \rightarrow C_6H_6(g)$$



ΔH = ?

For reactants :

Heat of atomisation of 6 moles of C = 6   170.9 kcal

Heat of atomisation of 6 moles of H = 6   52.1 kcal

For products :

Heat of formation of 6 moles of C – H bonds = –6   99

Heat of formation of 3 moles of C – C bonds = –3   83

Heat of formation of 3 moles of C = C bonds = –3   140

On adding, we get heat of formation of $C_6H_6$, i.e.,

ΔH = 6   170.9 + 6   52.1 – 6   99 – 3   83 – 3   140 = 75.0 kcal.