Chapter-11

THERMOCHEMISTRY

Thermodynamics:

Study of heat involvement both in chemical and physical processes is called thermodynamics.

It is macro level study of heat involvement in the process.

Thermochemistry:

Study of heat involvement in a chemical process is called thermo chemistry. Thus thermo chemistry is a branch of thermodynamics. It is micro level study of heat involvement in the process.

In a chemical, reaction chemical energy changes to various other forms of energies.

- In many reactions chemical energy changes to heat energy e.g. combustion reactions, neutralization reactions etc.
- In some reactions chemical energy changes to light energy e.g. burning of kerosene oil in lantern, natural gas in gas lamp, magnesium ribbon etc.
- In some reactions chemical energy changes to electrical energy e.g. in dry cells (Allahdin battery cell, Chanda battery cell etc) redox reaction occurs and electrical energy is obtained.
- In some reactions chemical energy changes to mechanical energy e.g. burning of fuel in automobiles.
- In some reactions chemical energy changes to sound energy e.g. burning of hydrogen gas.

Science, Society Relationship:

Various forms of energy are heat, light, electromagnetic radiations, electric, sound, mechanical, potential and kinetic energy.

Albert Einstein in 1905 proposed his classic theory which states that matter and energy are inter-convertible and are equivalent.

For equivalence of matter and energy he gave a relationship which is $E = mc^2$
According to this expression, the conversion of one gram of matter to energy yields 2.2×19^{13} cal. This amount of heat could raise the temperature of 250,000 tons (5×10^8 lb) of water from 0^oC to 100^oC. This shows that a very small amount of matter produces a huge amount of energy. However in ordinary chemical reactions an extremely small amount of matter changes to energy e.g. during the combustion of 3000 tons of coal only 1 g of matter is converted to energy. So in ordinary chemical reactions no detectible loss occurs in mass and thus law of conservation of matter get hold.

Exothermic Reactions:

The reactions in which heat is evolved (liberated) are called exothermic reactions.

e.g (i) $C_{(s)} + O_{2(g)}$ $\rightarrow$ $CO_{2(g)}$ $\Delta H = -393.51$ kJ

     or $C_{(s)} + O_{2(g)}$ $\rightarrow$ $CO_{2(g)}$ $+ 393.51$ kJ

Endothermic Reactions:

The reactions in which heat is absorbed are called endothermic reactions.

e.g $H_2 + I_2$ $\rightarrow$ 2HI $\Delta H = +53$ kJ

     or $H_2 + I_2 + 53kJ \rightarrow$ 2HI
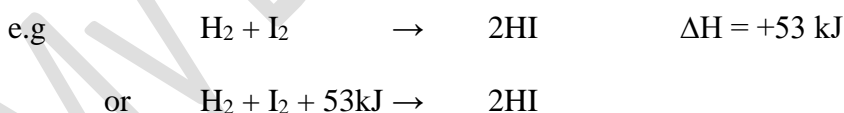
Spontaneous and Non-Spontaneous Changes:

The changes which occur at expense of systems own energy and without any external help are called ***spontaneous changes***.

The changes which occur at expense of energy provided by external agency are called ***non-spontaneous changes***.

Usually exothermic reactions are spontaneous also natural processes are spontaneous, while endothermic reactions are non-spontaneous process.

Some examples of spontaneous process

Melting of ice	$H_2O_{(s)}$	$\rightarrow$	$H_2O_{(l)}$
Burning of natural gas	$CH_4 + 2O_2$	$\rightarrow$	$CO_2 + 2H_2O$
Rusting of iron	$2Fe + 3/2\ O_2 + 3H_2O$	$\rightarrow$	$2Fe(OH)_3$
Discharging of Daniel Cell	$Zn + Cu^{+2}$	$\rightarrow$	$Zn^{+2} + Cu$
Evaporation of water	$H_2O_{(l)}$	$\rightarrow$	$H_2O_{(g)}$

Flow of water from overhead tank to houses, photosynthesis, evaporation etc.

Some examples of non-spontaneous process

Charging of Daniel Cell	$Zn^{+2} + Cu$	$\rightarrow$	$Zn + Cu^{+2}$
Freezing of water	$H_2O_{(l)}$	$\rightarrow$	$H_2O_{(s)}$
Electrolysis of water	$2H_2O_{(l)}$	$\rightarrow$	$2H_{2(g)} + O_{2(g)}$

Lifting of water from well to overhead tank.

Compressing of a gas by applying pressure.

System and Surrounding:

- Universe is divided into two parts i.e. system and surrounding

    Universe = System + Surrounding

- The part of universe that is under consideration or observation is called a system.

- The remaining part of universe which is out side the system is called surrounding.

    e.g. analysis of water present in a glass is made, then water is system where as glass and any thing else in the universe is surrounding.

State of a System:

- A set of properties is called state of a system.
  e.g oxygen gas at 25ºC, 760 mmHg and having volume 300 ml is said to be in State-A. Let its temperature changed to 0 ºC, pressure changed to 700mmHg while volume changed to 298.4 ml, now the gas is said to be in State-B.

- Even if a single property changes we say the state of the system is changed.

State Function or State Properties:

"The properties which describe the state of a system"

or

"The properties whose change is independent of the path through which the change is brought and depends only upon the initial and final state of the system" are called state function or state properties.

are called state functions or state properties.

e.g. P, V, T, E (internal energy), H (enthalpy), S (entropy), n (mole) etc are state functions or state properties.
On other hand q (heat) and w (work) are path dependent properties so they are not state functions or state properties.

Internal Energy (E):

Sum of kinetic and potential energy of molecules of a system is called internal energy.

$$E = KE + PE$$

Enthalpy (H):

Sum of kinetic energy, potential energy and work is called enthalpy.

OR

Sum of internal energy and work is called enthalpy.

$$H = E + PV$$

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Entropy (S):

Disorderliness of molecules or particles of a system is called entropy.

Internal Energy and First Law of Thermodynamics:

First law of thermodynamics states:

## "Energy can neither be created nor destroyed"
Or
"Total energy of universe remains same"

It means when system give heat to surrounding or does work on surrounding then its internal energy decreases to same extent but total energy for universe remains same. Thus first law of thermodynamics can be written mathematically as

$$\Delta E = q - w \ldots\ldots\ldots\ldots\ldots (1)$$

This expression shows that internal energy is a state function.
Let the system is at 273K and is in State-A and it is heated to 298K now it is in State-B.
If we raise the temperature by heating the system or doing work by stirring the system or both heating as well as doing work by stirring, ΔE will change to same extent as evident by first law of thermodynamics, so internal energy is a state function.

Path-I (by heating)

State-A (273K) ———————→ State-B (298K)

Path-I (by heating)
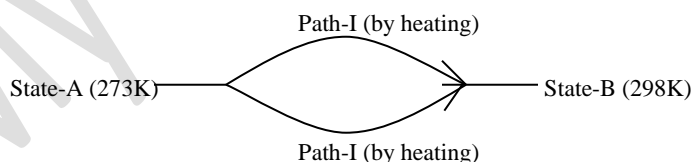
Signs:

q = **+ve** when surrounding gives heat to the system, it will increase internal energy of the system.

q = **-ve** when system gives heat to the surrounding, it will decrease internal energy of the system.

w = **+ve** when surrounding does work on the system, it will increase internal energy of the system.

w = **-ve** when system does work on the surrounding, it will increase internal energy of the system.

Work of expansion:

To derive an expression for work of expansion, consider a gas present in a cylinder fitted with freely movable piston.
Let the gas has volume V_1 and piston is at height h_1. Further suppose that gas expands to volume V_2 by pushing the piston to height h_2. In doing so gas (i.e system) did work on the piston (i.e surrounding) through a height Δh.
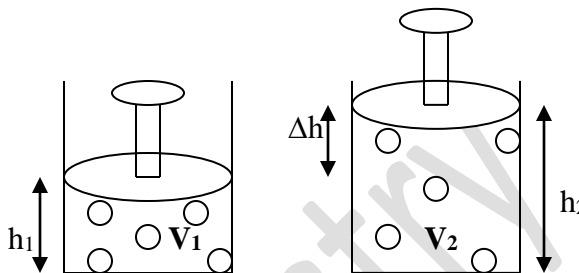
where $\quad\quad\quad\quad\quad\quad\quad\quad \Delta h = h_2 - h_1 \dots\dots\dots\dots\dots\dots\dots$ (2)

we know $\quad\quad\quad\quad\quad\quad\quad\quad$ w = force x distance = F x d …….. (3)

we also know $\quad\quad\quad\quad\quad\quad$ P = F/A

or $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ F = PA

and $\quad\quad\quad\quad\quad\quad\quad\quad\quad$ d = distance covered by piston covered by piston during work $= \Delta h$

Putting in eq.3, we get $\quad\quad\quad$ w = PA x Δh …………………... (4)

The volume changed during this work by ΔV

i.e $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \Delta V = V_2 - V_1 \dots\dots\dots\dots\dots\dots\dots$ (5)

we know $\quad\quad\quad\quad\quad\quad\quad\quad$ V = area x height = Ah

thus $\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $V_1 = Ah_1$ $\quad\quad$ "A" is area of cross section of piston and is constant

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $V_2 = Ah_2$

Putting in eq. 5 $\quad\quad\quad\quad\quad$ $\Delta V = Ah_2 - Ah_1$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $\Delta V = A(h_2 - h_1)$ ………………….. (6)

But $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $h_2 - h_1 = \Delta h$

So eq 6 becomes $\quad\quad\quad\quad\quad$ $\Delta V = A\Delta h$ ………………………… (7)

Comparing eq.7 with eq.4 we can write $\quad w = P\Delta V$

As this is work of expansion, which lowers internal energy of the system so negative sign will be used.

$$W = -P\Delta V \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Putting in eq.1 we get $\quad\boxed{\Delta E = q - P\Delta V} \ldots\ldots\ldots\ldots\ldots\ldots (9)$

This expression is workable form of First Law of Thermodynamics.

We can extend 1st law of thermodynamics to constant volume and constant pressure process.

(i) *First Law for Constant Volume process***:**

The process during which no change in volume occurs is called constant volume process.

The first law of thermodynamics for constant volume process can be written as

$$\Delta E = q_v - P\Delta V \ldots\ldots\ldots\ldots\ldots (1)$$

As during process no change in volume occurs

So $\quad\quad\quad\quad\quad \Delta V = 0$

And thus $\quad\quad\quad\quad P\Delta V = 0$

Thus eq.1 becomes $\quad\boxed{\Delta E = q_v} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$

Thus in constant volume process the heat which system exchanges with surrounding is equal to the change in internal energy of the system.

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(ii)　　*First Law for Constant Pressure process*:　　(*Enthalpy*)

The process during which no change in pressure occurs is called constant pressure process.

The first law of thermodynamics for constant pressure process can be written as

$$\Delta E = q_p - P\Delta V \quad \dots\dots\dots\dots\dots \text{(1)}$$

We know　　　　　　　$\Delta E = E_2 - E_1$

Also　　　　　　　　$\Delta V = V_2 - V_1$

So eq.1 becomes　　　$E_2 - E_1 = q_p - P(V_2 - V_1)$

Or　　　　　　　　　$E_2 - E_1 = q_p - PV_2 + PV_1$

On rearranging　　　　$E_2 + PV_2 - E1 - PV_1 = q_p$

Or　　　　　　　$(E_2 + PV_2) - (E1 + PV_1) = q_p \quad \dots.. \text{(2)}$

But we know　　　　　$H = E + PV$

So　　　　　　　　　$H_1 = E_1 + PV_1$

And　　　　　　　　$H_2 = E_2 + PV_2$

Therefore eq.2 can be written as　　$H_2 - H_1 = q_p$

Or　　　　　　$\boxed{\Delta H = q_p}\dots\dots\dots\dots\dots\dots \text{(3)}$

Thus in constant pressure process the heat which system exchanges with surrounding is equal to the change in enthalpy of the system.

- $\Delta E = \Delta H$ in following cases:

(i)　　When process is constant volume process then $\Delta E = \Delta H$.
(ii)

We know that　　$H = E + PV$

Multiplying both sides with Δ

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

As $\quad\quad\quad\quad\quad \Delta V = 0$

So $\quad\quad\quad\quad\quad \Delta H = \Delta E + P \times 0$

And therefore $\quad\quad \Delta H = \Delta E$

(iii) When system is solid or liquid then even in constant pressure process $\Delta E = \Delta H$. Reason is that in solid and liquid change in volume is negligible.

Standard State of a Substance:

The state in which a substance exists at room temperature and pressure is called its *standard state*. e.g. standard state of oxygen is gas, that of water is liquid while that of carbon is graphite.

Heat Capacity:

"*The amount of heat absorbed by a substance to raise the temperature by one degree (K or ^oC) is called heat capacity of the substance.*"

S.I unit for heat capacity is J K^{-1}.

Heat capacity of a substance is expressed in two ways.

(i) Specific Heat Capacity:

"*The amount of heat absorbed by one gram of a substance to raise the temperature by one degree (K or ^oC) is called specific heat capacity of the substance.*"

(ii) Molar Heat Capacity:

"*The amount of heat absorbed by one mole of a substance to raise the temperature by one degree (K or ^oC) is called molar heat capacity of the substance.*"

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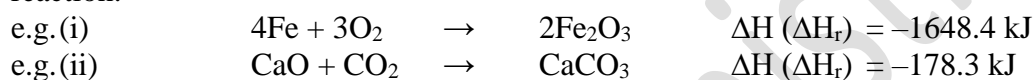
Calorimetry:

Some of important enthalpies are:

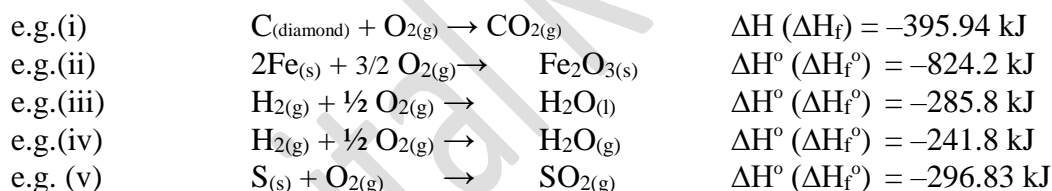Enthalpies are usually measured under room temperature and pressure.

(i)   **Heat or Enthalpy of Reaction** (ΔH_r):

"The heat released or absorbed or enthalpy change during a reaction for the number of moles as shown by balanced equation" is called heat of reaction or enthalpy of reaction.
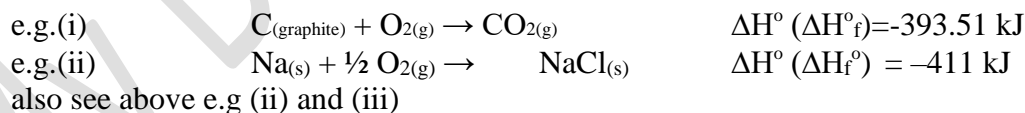
e.g.(i)	$4Fe + 3O_2$	$\rightarrow$	$2Fe_2O_3$	$\Delta H\,(\Delta H_r) = -1648.4$ kJ
e.g.(ii)	$CaO + CO_2$	$\rightarrow$	$CaCO_3$	$\Delta H\,(\Delta H_r) = -178.3$ kJ

(ii)   **Heat or Enthalpy of Formation** (ΔH_f):

"The heat released or absorbed or enthalpy change during the formation of one mole of a substance from its elements" is called heat of formation or enthalpy of formation.
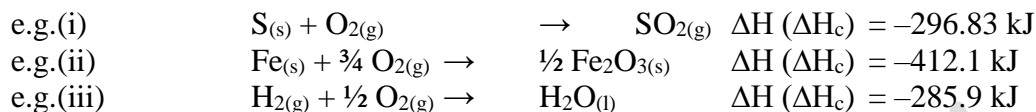
e.g.(i)	$C_{(diamond)} + O_{2(g)} \rightarrow CO_{2(g)}$	$\Delta H\,(\Delta H_f) = -395.94$ kJ
e.g.(ii)	$2Fe_{(s)} + 3/2\,O_{2(g)} \rightarrow Fe_2O_{3(s)}$	$\Delta H^o\,(\Delta H_f^o) = -824.2$ kJ
e.g.(iii)	$H_{2(g)} + \frac{1}{2}\,O_{2(g)} \rightarrow H_2O_{(l)}$	$\Delta H^o\,(\Delta H_f^o) = -285.8$ kJ
e.g.(iv)	$H_{2(g)} + \frac{1}{2}\,O_{2(g)} \rightarrow H_2O_{(g)}$	$\Delta H^o\,(\Delta H_f^o) = -241.8$ kJ
e.g. (v)	$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$	$\Delta H^o\,(\Delta H_f^o) = -296.83$ kJ

☞   "The heat released or absorbed or enthalpy change during the formation of one mole of a substance from its elements in their standard states" is called standard heat of formation or standard enthalpy of formation.

e.g.(i)	$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$	$\Delta H^o\,(\Delta H^o_f) = -393.51$ kJ
e.g.(ii)	$Na_{(s)} + \frac{1}{2}\,O_{2(g)} \rightarrow NaCl_{(s)}$	$\Delta H^o\,(\Delta H_f^o) = -411$ kJ

also see above e.g (ii) and (iii)

☞ *Heats of formation of elements in their standard states are always zero e.g. $C_{(graphite)}$, $S_{(rhombic)}$, $I_{2(s)}$, $O_{2(g)}$, $P_{(white)}$ etc.*

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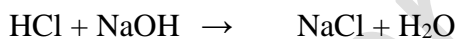Join Digital Kemistry Academy → WhatsApp number +92-3336753424 (only text for details)

(iii) *Heat or Enthalpy of Combustion* (ΔH_c):

"The heat released or enthalpy change during the combustion of one mole of a substance" is called heat of combustion or enthalpy of combustion.

e.g.(i) $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$ $\Delta H (\Delta H_c) = -296.83$ kJ
e.g.(ii) $Fe_{(s)} + \frac{3}{4} O_{2(g)} \rightarrow \frac{1}{2} Fe_2O_{3(s)}$ $\Delta H (\Delta H_c) = -412.1$ kJ
e.g.(iii) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta H (\Delta H_c) = -285.9$ kJ

(iv) *Heat or Enthalpy of Neutralization* (ΔH_n):

"The heat released or enthalpy change when one mole of H^+ ion from an acid reacts with one mole of OH^- ion from a base to produce water" is called heat of neutralization or enthalpy of neutralization.
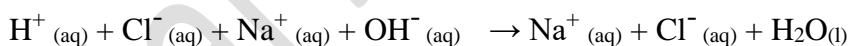
Consider a neutralization reaction between an acid and base
$$HCl + NaOH \rightarrow NaCl + H_2O$$
Acids and bases ionize in aqueous solutions

$$HCl + aq \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$
$$NaOH + aq \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

On mixing the two solutions

$$H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$$
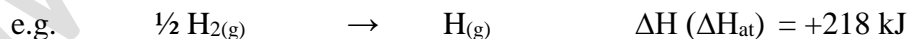
In the aqueous state, ions of salts remain uncombined. Thus neutralization reaction is actually reaction of hydrogen ions of acid and hydroxyl ions of base to produce water. Heat of neutralization of all strong acids and bases is same

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \qquad \Delta H (\Delta H_n) = -57.4 \text{ kJ}$$
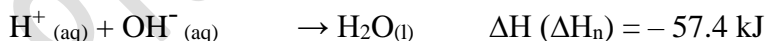
(v) *Heat or Enthalpy of Atomization* (ΔH_{at}):

"The heat absorbed or enthalpy change when one mole of gaseous atoms are produced from the element in its standard state" is called heat of atomization or enthalpy of atomization.

e.g. $\frac{1}{2} H_{2(g)} \rightarrow H_{(g)}$ $\Delta H (\Delta H_{at}) = +218$ kJ

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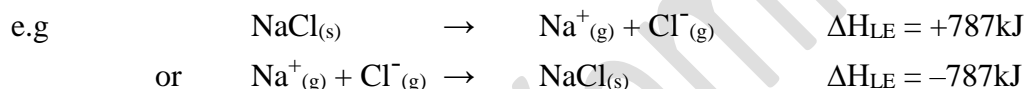(vi)   *Heat or Enthalpy of Solution* (ΔH_{soln}):

"The heat released or absorbed or enthalpy change when one mole of a substance is dissolved in so much solvent that further dilution causes no detectable heat change" is called heat of solution or enthalpy of solution.

e.g. $NH_4Cl_{(s)} + aq \quad \rightarrow \quad NH_4^+{}_{(aq)} + Cl^-{}_{(aq)} \quad \Delta H\ (\Delta H_{soln}) = +15.1$ kJ
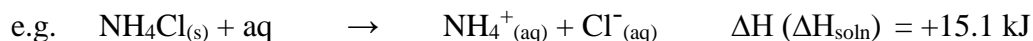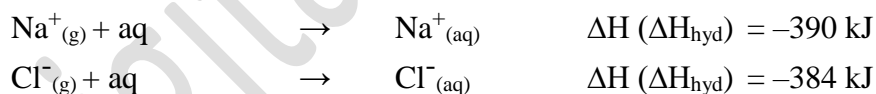
(vii)   *Lattice Energy* (ΔH_{LE}):

"The energy absorbed in breaking crystal lattice of one mole crystalline solid and to carry particles to infinite distance apart each other" is called lattice energy.

Or

"The energy released when one mole of crystalline solid is produced from its gaseous ions" is called lattice energy.

e.g $\qquad NaCl_{(s)} \qquad \rightarrow \qquad Na^+{}_{(g)} + Cl^-{}_{(g)} \qquad \Delta H_{LE} = +787$ kJ

$\qquad$ or $\quad Na^+{}_{(g)} + Cl^-{}_{(g)} \rightarrow \quad NaCl_{(s)} \qquad \Delta H_{LE} = -787$ kJ

(viii)   *Heat or Enthalpy of Hydration* (ΔH_{hyd}):

"The heat released or enthalpy change when one mole gaseous ion is dissolved in water to give an infinitely dilute solution" is called heat of hydration or enthalpy of hydration.

$\qquad Na^+{}_{(g)} + aq \qquad \rightarrow \qquad Na^+{}_{(aq)} \qquad \Delta H\ (\Delta H_{hyd}) = -390$ kJ

$\qquad Cl^-{}_{(g)} + aq \qquad \rightarrow \qquad Cl^-{}_{(aq)} \qquad \Delta H\ (\Delta H_{hyd}) = -384$ kJ

☞ By heats of hydration and lattice energy we can find heat of solution.
$\qquad \Delta H_{soln} = \Delta H_{LE} + \Delta H_{hyd}$

e.g. $\qquad NaCl_{(s)} + aq \quad \rightarrow \quad Na^+{}_{(aq)} + Cl^-{}_{(aq)} \qquad \Delta H_{soln} = ?$

$\qquad \Delta H_{soln\ (NaCl)} = \Delta H_{LE\ (NaCl)} + \Delta H_{hyd\ (Na^+)} + \Delta H_{hyd\ (Cl^-)}$
$\qquad \Delta H_{soln\ (NaCl)} = 787 + (-390) + (-384)$
$\qquad \Delta H_{soln\ (NaCl)} = 787 - 390 - 384$
$\qquad \Delta H_{soln\ (NaCl)} = +13$ kJ

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(ix)   *Heat or Enthalpy of Sublimation* (ΔH_{sub}):

"The heat absorbed or enthalpy change when one mole a solid substance directly changes to vapours at certain temperature" is called heat of sublimation or enthalpy of sublimation.

$$I_{2(s)} \quad \rightarrow \quad I_{2(g)} \qquad \Delta H\,(\Delta H_{sub}) = +62.3 \text{ kJ}$$
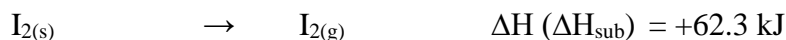
Measurements of Heats or Enthalpy Changes:

There are two types of methods available for measurements of heats or enthalpy changes of various process.

(A)   *Direct Calorimetry or Direct Method*:

Heats of reactions are directly measured by calorimeter.

There are two type of calorimeters i.e.
- ✓ simple calorimeter
- ✓ bomb calorimeter.

Reaction is carried out in the cup of calorimeter. The heat liberated is given to water present in the calorimeter and if reaction is endothermic then heat is taken from water due to which temperature of water rises or falls respectively and it is noted also mass of water is noted. Then by using formula
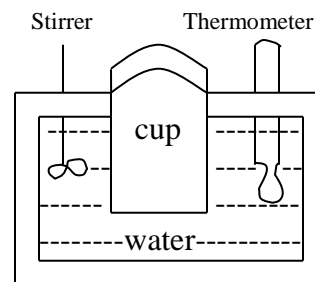
$q = mc\Delta t$ where q = heat

c = specific haet of water =4.2J/g or 1cal/g

Δt = rise or fall in temp of water

heat given to or taken from water is calculated.

Stirrer   Thermometer

cup

------water--------

Calorimeter

This is the heat involved in the reaction. The heat is then calculated for the number of moles as shown by balanced equation.

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Bomb Calorimeter:

It is specially designed for measuring heats of combustion. It consisits of a cylindrical steel vessel (bomb shaped).
A weighed mass of the substance is placed in platinum crucible inside the bomb. The lid is screwed on tightly and oxygen is filled at 20-25atm. The substance is ignited by electric coil placed on the sample. Rise in the temperature of water is noted and then heat is calculated.

Bomb calorimeter
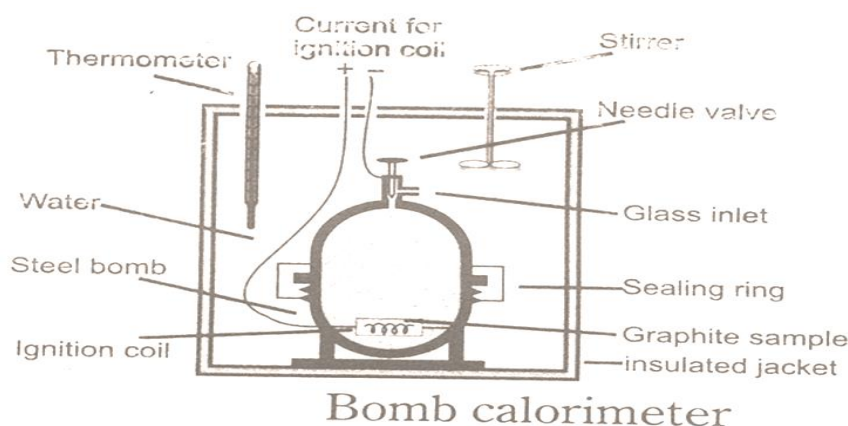
(B)   *Indirect Calorimetry or Indirect Methods*:

Several indirect methods are available to determine heats or enthalpies of reactions. A few are following.

(I)   **By Hess Law Method**:
Hess law states, "The heat of a reaction depends only upon the initial and final states of the system and is independent of the rout followed."

Or

"The heat released or absorbed or enthalpy change during a reaction is same whether reaction takes place in single step or in several steps"

This law is in accordance with law of conservation of energy. It means that sum of the heats involved in several steps is same as is the heat of single step.
Let a reactant-A changes directly to a product-D involving heat q. Alternatively by an another method A first changes to B, B then changes to C and C finally changes to D involving q_1, q_2 and q_3 heats respectively.
According to Hess law sum of the heats of three steps will be equal to the heat of single step reaction.

$$q = q_1 + q_2 + q_3$$
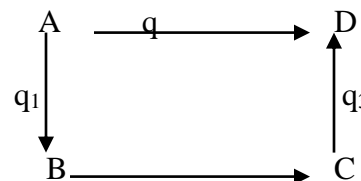
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q₂

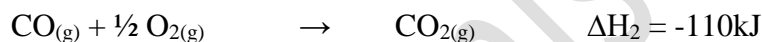e.g. Consider formation of carbon dioxide. CO_2 can be produced by two methods.

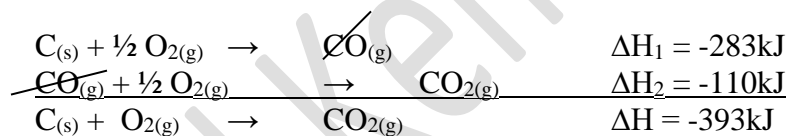(a) By burning carbon in excess of air CO_2 will be produced in single step.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H = -393kJ$$

(b) By burning carbon in limited supply of air CO is produced

$$C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H_1 = -283kJ$$

The CO on further burning produces CO_2

$$CO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_2 = -110kJ$$

Summation of two steps.

$$C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow \cancel{CO}_{(g)} \qquad \Delta H_1 = -283kJ$$
$$\cancel{CO}_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_2 = -110kJ$$
$$\overline{C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H = -393kJ}$$

The sum of heats of two steps gave same amount of heat as was the heat of single step reaction.

Thus Hess law can be applied to determine the heats of reactions whose heats cannot be determined directly by calorimeters. For such reactions we select reactions whose heats can be measured by calorimeters and whose sum gives required reaction. Then sum of their heats give the heat of required reaction.

(II) **By Heats of Formations**:

Heat of a reaction is always equal to the difference of total heats of formation of products and total heats of formations of reactants.

$$\Delta H = \sum H_{f(Products)} - \sum \Delta H_{f(Reactants)}$$

e.g. Consider the reaction

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = ?$$

Where $\Delta H_{f(CH_4)} = -74.81kJ$
$\Delta H_{f(CO_2)} = -393.51kJ$
$\Delta H_{f(H_2O)} = -285.5kJ$

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Then $\Delta H = [(\Delta H_{f(CO_2)}) + 2(\Delta H_{f(H_2O)})] - [(\Delta H_{f(CH_4)}) + 2(\Delta H_{f(O_2)})]$

Putting values $\Delta H = [(-393.51) + 2(-285.5)] - [(-74.81) + 2(0)]$

$\Delta H = -393.51 - 571 + 74.81 - 0$

$\Delta H = -889.7kJ$

(III) **By Bond Energies**:

Heat of a reaction is always equal to the difference of total heat absorbed in the breaking of older bonds and heat released in the formation of new bonds.

e.g. Consider the reaction $N_{2(g)} + 3 H_{2(g)} \rightarrow 2NH_{3(g)}$ $\Delta H = ?$

Where   Bond energy of $N \equiv N = 946kJ/mol$ bond

Bond energy of $H - H = 435kJ/mol$ bond

Bond energy of $N - H = 390kJ/mol$ bond

Then

ΔH = [Total energy absorbed during breaking of 1mole $N \equiv N$ bonds and 3 moles $H - H$ bonds] – [Total energy released in the formation of 6 moles $N - H$ bonds]

$$\Delta H = (+946) + 3(+435) + 6(-390)$$

$$\Delta H = +946 + 1305 - 2340$$
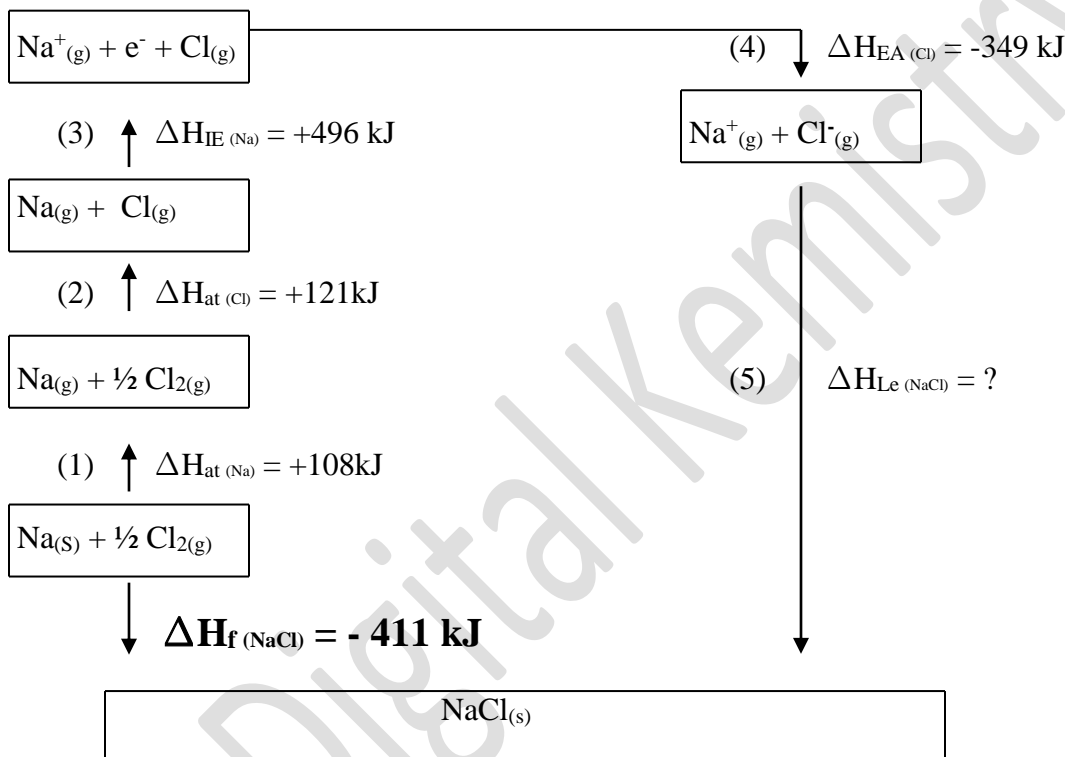
$$\Delta H = -89kJ$$

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Born Haber Cycle:

Born-Haber Cycle is a special application of Hess's law to binary ionic compounds.
It enables us to calculate their lattice energies.

e.g. Consider formation of NaCl. For NaCl formation Born-Haber Cycle can be written as

| $Na^+_{(g)} + e^- + Cl_{(g)}$ | (4) | $\Delta H_{EA\,(Cl)} = -349$ kJ |

(3) ↑ $\Delta H_{IE\,(Na)} = +496$ kJ

$Na^+_{(g)} + Cl^-_{(g)}$

$Na_{(g)} + Cl_{(g)}$

(2) ↑ $\Delta H_{at\,(Cl)} = +121$kJ

(5) $\Delta H_{Le\,(NaCl)} = ?$

$Na_{(g)} + ½ Cl_{2(g)}$

(1) ↑ $\Delta H_{at\,(Na)} = +108$kJ

$Na_{(S)} + ½ Cl_{2(g)}$

↓ $\Delta H_{f\,(NaCl)} = - 411$ kJ

$NaCl_{(s)}$

Applying Hess law to the formation reaction of NaCl

$$\Delta H_{f(NaCl)} = \Delta H_{at(Na)} + \Delta H_{at(Cl)} + \Delta H_{IE(Na)} + \Delta H_{EA(Cl)} + \Delta H_{Latt(NaCl)}$$
$$-411 = (+108) + (+121) + (+496) + (-349) + \Delta H_{Latt(NaCl)}$$
$$-411 = +108 + 121 + 496 - 349 + \Delta H_{Latt(NaCl)}$$
$$\Delta H_{Latt(NaCl)} = -411 - 108 - 121 - 496 + 349$$
$$\Delta H_{Latt(NaCl)} = -787 kJ$$