

Dnyansagar Coaching Classes, A'nagar

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CHEMICAL THERMODYNAMICS AND ENERGETICS

☞ **Thermodynamics :**

The branch of science which deals with the study of quantitative relationship between heat and other forms of energy is called thermodynamics.

➤ **Chemical thermodynamics :**

The branch of thermodynamics which deals with the study of energy changes taking place during chemical transformations called chemical thermodynamics.

➤ **Limitations of thermodynamics:**

- i) Thermodynamics is applicable to macroscopic systems only i.e the systems having matter in bulk. It is not applicable to microscopic systems such as atoms, molecules etc.
- ii) It deals only with the initial and final states of the system and not with rate of the reaction or mechanism of the process.
- iii) It does not deal with the internal structure of atoms or molecules.

➤ **System :**

The specific portion of the universe which is under thermodynamic consideration is called system.

e.g. Solution in a breaker, gas in a container. In chemistry, generally system is a chemical reaction.

➤ **Surroundings :**

The portion of the universe other than the system is called surroundings.

➤ **Boundary :**

The real or imaginary surface which separates the system and surroundings is called boundary.

Exchange of matter or energy or both between the system and surroundings takes place through boundary.

➤ **Open system :**

The system which can exchange both energy and matter with the surroundings is called open system.

Example:

Reaction between metallic zinc and dil H_2SO_4 carried out in beaker.



In this case, both energy (heat) and matter (H_2 gas) are given to the surroundings.

➤ **Closed system :**

The system which can exchange only energy but not matter with the surroundings is called closed system. e.g. Reaction between metallic zinc and dil. H_2SO_4 carried out in a perfectly closed vessel.

Example:



In this case, only energy (heat) but not matter is exchanged with the surroundings.

➤ **Isolated system :**

The system which can exchange neither energy nor matter with the surrounding is called isolated system.

Example:

Reaction between metallic zinc and dil. H_2SO_4 carried out in a thermos flask.



In this case, neither energy nor matter is exchanged with the surroundings.

➤ **Homogeneous system :**

The system which is completely uniform throughout i.e. consists of only one phase is called homogeneous system.

It has same chemical composition throughout.

Example:

Mixture of gases, true solution, pure solid etc.

➤ **Heterogeneous system :**

The system which is not uniform throughout i.e. consists of two or more phases is called heterogeneous system.

It has not same chemical composition throughout.

Example:

. Mixture of two immiscible liquids like oil and water, mixture of two or more solids, ice in contact with water etc.

➤ **Extensive properties :**

The properties of system which depend upon the quantity of matter present in the system are called extensive properties.

e.g. Mass, area, volume, work, energy, enthalpy etc.

➤ **Intensive properties :**

The properties of system which do not depend upon the quantity of matter present in the system are called intensive properties.

They depend upon nature of the substance and its composition.

Example:

Pressure, temperature, melting and boiling

points, density, viscosity, surface tension, refractive index etc.

➤ **State of system :**

i) A known set of certain macroscopic properties like pressure, temperature, volume, composition etc. which describes a system completely is called state of a system.

ii) If one or more of these properties are changed, state of the system also changes.

	State A		State B
Pressure -	P_1	Change of state	P_2
Temperature -	T_1		T_2
Volume -	V_1		V_2
No. of moles-	n_1		n_2

iii) Since state of a system changes due to the change in these macroscopic properties, they are also called state variables, state functions or thermodynamic functions.

☞ **State function (Thermodynamic function):**

i) The property whose value depends only upon the initial and final states of the system and not on the path or way by which the change is carried out is called state function.

ii) Consider a system in initial state A having pressure P_1 and volume V_1 . Let the system is changed to final state B having pressure P_2 and volume V_2 .

iii) It is found that the change in pressure ΔP , ΔV , are independent of the path. Hence pressure and volume are state functions.

Some other state functions are internal energy, enthalpy.

☞ **Thermodynamic equilibrium :**

i) A system is said to be in thermodynamic equilibrium if its macroscopic properties like pressure, temperature, volume etc. do not change with time.

ii) A system is in thermodynamic equilibrium if there exist three equilibria simultaneously.

These are -

- **Thermal equilibrium** : A system is said to be in thermal equilibrium if temperature of the system does not change with time.
- **Chemical equilibrium** : A system is said to be in chemical equilibrium if chemical composition of the system does not change with time.
- **Mechanical equilibrium** : A system is said to be in mechanical equilibrium if no mechanical work is done by one part of the system on the other part.
In mechanical equilibrium, particles from the system do not pass into the surroundings and vice-versa. This is possible only if pressure of the system remains constant throughout.
- **Process** : The path or operation by which a system changes from one state to another state is called a process.
- **Isothermal process** :
 - i) The process in which temperature of the system remains constant throughout is called isothermal process.
e.g. Boiling of water, fusion of ice etc.
 - ii) During isothermal process, to keep temperature constant heat is absorbed or liberated by the system.
 - iii) Since in an isothermal process temperature remains constant ($\Delta T = 0$), internal energy of the system also remains constant ($\Delta E = 0$)
 - iv) For an exothermic reaction to be isothermal, heat liberated is given to the surroundings. Hence temperature of the system does not increase.
For an endothermic reaction to be isothermal, required heat is supplied by the surroundings. Hence temperature of the system does not decrease.

➤ **Adiabatic process** :

- i) The process in which heat is neither absorbed nor evolved by the system is called adiabatic process.
e.g. Chemical reaction carried out in a thermos flask.
- ii) Since in adiabatic process heat is neither absorbed nor evolved, temperature and hence internal energy of the system changes. But enthalpy of the system remains constant ($\Delta H = 0$).
- iii) For an exothermic reaction to be adiabatic, heat evolved remains within the system and hence temperature of the system increases. For an endothermic reaction to be adiabatic required heat is supplied by the system and hence temperature of the system decreases.

➤ **Reversible process** :

- i) The process in which driving force is infinitesimally greater than the opposing force and whose direction can be reversed by an infinitesimal increase in the opposing force is called reversible process.
e.g. Isothermal reversible expansion of an ideal gas.
 - ii) Reversible process is a non-spontaneous process.
 - iii) It is an infinitesimally slow process.
 - iv) It takes infinite time for its completion.
 - v) In it system is always in pressure-temperature equilibrium with the surroundings.
 - vi) In it maximum work is obtained.
 - vii) It is an imaginary and theoretical process.
- **Irreversible process** :
- i) The process in which driving force is greater than the opposing force by large magnitude and whose direction cannot be reversed by an infinitesimal increase in the opposing force is called irreversible process.

e.g.. All natural processes are irreversible processes. Flow of heat from hot body to cold body, flow of water from higher level to lower level etc.

- ii) It is a spontaneous process and proceeds in a definite direction.
- iii) It is a faster process.
- iv) It takes finite time for its completion.
- v) In this process equilibrium is attained only after the completion of process.
- vi) In it maximum work cannot be obtained.
- vii) It is a real process.

➤ **Isobaric process :**

- i) The process in which pressure of the system remains constant throughout is called isobaric process.

$$\therefore \Delta P = 0$$

e.g. Reaction carried out in an open vessel.

➤ **Isochoric process :**

- i) The process in which volume of the system remains constant throughout is called isochoric process.

$$\therefore \Delta V = 0$$

e.g. Reaction carried out in a closed vessel.

7) **Cyclic process :**

The process in which system undergoes a series of operations but again returns to its initial state is called a cyclic process.

Thus in a cyclic process, initial and final states are same.

$$\therefore \Delta P = 0$$

☞ **Nature of work and heat :**

- i) On the basis of first law of thermodynamics, energy is classified into two types - heat energy and work energy.
- ii) Heat is the form of energy which transfers from one body to another due to tempera-

ture difference.

The energy which transfers in all other ways, except temperature difference, is called work energy.

e.g. Mechanical energy, electrical energy etc.

- iii) Since all other forms of energy get easily converted into heat, energy and energy changes are measured in terms of heat only.
- iv) Therefore heat and work are equivalent and they have same units.

✍ **Note : Units of Work and heat :**

1) **Litre - Atmosphere :**

It is the work done when volume of system changes by one litre against a constant pressure of one atmosphere. It is represented by lit-atm or $\text{dm}^3\text{-atm}$.

2) **Erg : (c.g.s.):** It is the work done when a force of one dyne acts through a distance of one centimeter.

3) **Calorie :** It is the work done when a force of one newton acts through a distance of one meter.

Interconversion of units -

1) **1 lit-atm** = 24.22 cal.

$$= 101.34\text{J}$$

$$= 101.34 \times 10^7 \text{ ergs}$$

2) **1 erg** = 1×10^{-7} Joules

$$= 0.239 \times 10^{-7} \text{ cal}$$

$$= 9.868 \times 10^{-10} \text{ lit. - atm}$$

3) **1 Joule** = 1×10^7 ergs.

$$= 0.239 \text{ cal}$$

$$= 9.868 \times 10^{-3} \text{ lit-atm}$$

4) **1 calorie** = 4.184 Joules

$$= 4.184 \times 10^7 \text{ ergs}$$

$$= 4.129 \times 10^{-2} \text{ lit-atm}$$

☞ **Pressure - volume (PV) type of work:**

The work done due to the expansion or contraction of a against the constant opposing pressure is called pressure-volume type of work.

$$W_{\max} = 2.303 nRT \log_{10} \left(\frac{V_2}{V_1} \right)$$

$$W_{\max} = 2.303 nRT \log_{10} \left(\frac{P_1}{P_2} \right)$$

where P_1 is the initial pressure and P_2 is the final pressure of the gas.

This is the expression for maximum work done in an isothermal reversible process.

➤ **Different forms:**

- Energy can neither be created nor destroyed, though it can be converted from one form to another.
- Whenever a quantity of one form of energy disappears, an equivalent amount of energy of another form makes its appearance.
- Total energy of an isolated system always remains constant.
- Total energy of the universe always remains constant.
- Total energy of system and its surroundings always remains constant.
- It is impossible for any machine to produce work without consuming energy. Such a machine is called **perpetual motion machine**.

➤ **Corollary :**

Joule put forth the concept of mechanical equivalent of heat. It is corollary of the first law of thermodynamics.

It is stated as "Mechanical energy or work can be quantitatively converted into heat energy".

➤ **Einstein's equation :**

According to Einstein, mass and energy are interconvertible. They are related by the equation,

$$E = mc^2$$

where 'E' is energy produced in J, 'm' is quantity of mass destructed in kg and 'c' is velocity of light in m/s.

➤ **Modified form of first law of thermodynamics on the basis of Einstein's equation.**

According to Einstein, mass and energy are equivalent.

Hence the first law of thermodynamics is modified as, "The total mass and energy of an isolated system always remain constant".

$$\left[\begin{array}{c} \text{Heat} \\ \text{absorbed} \end{array} \right] = \left[\begin{array}{c} \text{change in} \\ \text{internal energy} \end{array} \right] + [\text{work done}]$$

$$\therefore q = E_2 - E_1 + W$$

$$\therefore q = \Delta E + W$$

This is the required expression.

✍ **Note : Expression of first law of thermodynamics for different processes.**

i) **For pressure-volume type of work,**

$$W = P \Delta V,$$

$$\therefore q = \Delta E + P \Delta V$$

ii) **For an adiabatic process, $q = 0$**

$$\therefore 0 = \Delta E + W$$

$$\therefore W = -\Delta E$$

iii) **For an isothermal process,**

$$\Delta E = 0$$

$$\therefore q = W$$

(Therefore according to thermodynamics, work and heat are equivalent)

iv) **For an isochoric process, $\Delta V = 0$**

$$\therefore q = \Delta E$$

➤ **Sign conventions :**

1) **For q (Heat) :**

- i) If heat is absorbed by the system, 'q' is positive. (+q)
- ii) If heat is evolved by the system, 'q' is negative. (-q)

2) **For ΔE (Internal energy change) :**

- i) If internal energy of the system increases i.e. $E_2 > E_1$, ΔE is positive (+ ΔE).
- ii) If internal energy of the system decreases, i.e. $E_2 < E_1$, ΔE is negative (- ΔE).

3) **For W (Work) :**

- i) If work is done by the system on the surroundings (work of expansion), W is positive (+W).
- ii) If work is done on the system by the surroundings (work of compression), W is negative (-W).

➤ **Enthalpy :**

- i) Heat absorbed or evolved in a chemical reaction at constant pressure can be conveniently expressed in terms of a new thermodynamic function called enthalpy or heat content of a system.
- ii) The total energy content of a system, including pressure - volume type of energy is called enthalpy of system.

Mathematically, $H = E + PV$

where,

H = Enthalpy,

E = Internal energy,

P = Pressure and

V = Volume

- iii) Since E, P and V are state functions, enthalpy is also a state function. Absolute value of enthalpy cannot be calculated, but change in enthalpy (ΔH) can be calculated.

$$\Delta H = H_2 - H_1$$

where, H_1 and H_2 are the enthalpies in initial

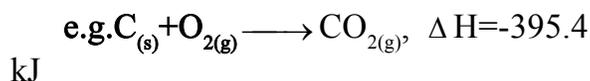
and final states respectively.

☞ **Thermochemistry.**

The branch of chemistry which deals with the study of heat changes taking place during chemical reactions is called thermochemistry.

➤ **Exothermic reaction :**

A chemical reaction in which heat is evolved is called an exothermic reaction,



In this reaction

- i) Heat is evolved.
- ii) Enthalpy of reaction is greater than the enthalpy of products.
- iii) Change in enthalpy is negative (- ΔH).
- iv) Products are more stable than the reactants.

➤ **Endothermic reaction :**

A chemical reaction in which heat is absorbed is called an endothermic reaction.



In this reaction,

- i) Heat is absorbed.
- ii) Enthalpy of products is greater than the enthalpy of reactants.
- iii) Change in enthalpy is positive (+ ΔH).
- iv) Reactants are more stable than the products.

☞ **Thermochemical equation :**

The chemical equation which indicates the amount of heat absorbed or evolved in a chemical reaction is called a thermochemical equation.

➤ **Example and interpretation :**



This equation indicates that when one mole of solid carbon ($12 \times 10^{-3} \text{ kg}$) combines with one mole of oxygen gas ($32 \times 10^{-3} \text{ kg}$) to form one mole of carbon dioxide gas ($44 \times 10^{-3} \text{ kg}$)

at constant pressure, 395.4kJ of heat is evolved.

1) Heat of reaction or heat of reaction at constant pressure (ΔH).

It is defined as, "The difference between enthalpies of the products and reactants when the number of moles of the reactants indicated by chemical equation have completely reacted at given temperature and constant pressure".

$$\therefore \Delta H = \sum H_{\text{products}} - \sum H_{\text{reactants}}$$

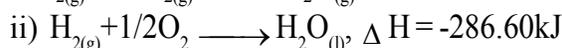
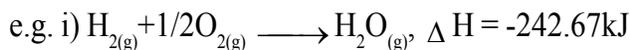
2) Heat of reaction at constant volume (ΔE):

It is defined as, "The change in enthalpy when the number of moles of the reactants indicated by chemical equation have completely reacted at given temperature and constant volume".

☞ Factors affecting heat of reaction :

1) Physical state :

Heat of reaction depends upon the physical states of the reactants and products.



2) Temperature :

Heat of reaction depends upon the temperature of the reactants and products.

e.g. i) At 298 K :



ii) At 348 K :



3) Condition of reaction :

For the reactions involving only solids or liquids, heat of reaction is nearly the same whether the reaction is carried out at constant pressure or at constant volume.

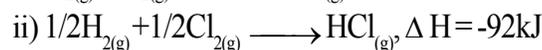
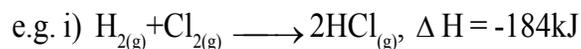
i.e. $\Delta H = \Delta E$

But for the reactions involving gases, ΔH

and ΔE are related by the equation. $\Delta H = \Delta E + \Delta nRT$

4) Amount of substances :

It also depends upon amounts of the substances involved in the reaction.



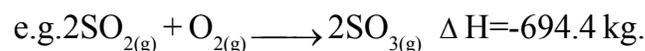
A chemical equation which in deceits the amount of heat evolved or absorbed during the chemical reaction in addition to the quantities of reactants or products.

We can write thermochemical equation by two ways.

A) Heat effect can be written as one of term along with the products.

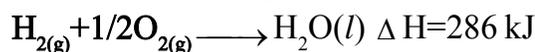


B) Heat evolved or absorbed can be expressed in terms of ΔH .

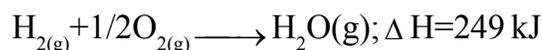


☞ Note :

In this thermochemical equation we must mention the physical status of various reactants & products while writing thermochemical equations because change of state is also accompanied by the enthalpy charges. e.g. When 1 mol of hydrogen react with 1/2 mol of oxygen gas to the produce 1 mol of liquid water, 286 kg of heat is produced.



On the other hand, it 1 mol of water nippers is produced instead of 1 mol of liquid water, the value of ΔH will be different.

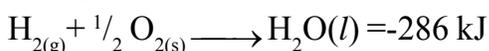


i) The coefficients of various substances of chemical equation represents the number of their respect +ve moles. In thermodynamics interpretational of an equation, we never interpret the coefficients as number of mol-

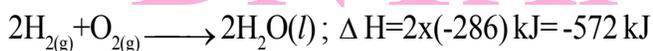
ecules. Hence, it is acceptable to write coefficient in fractions whenever necessary.

ii) The value of ΔH in a thermochemical equation corresponds to the enthalpy change taking places when a specified number of moles of various reactants & products (as it indicated by the coefficients of the various substances in the chemical equation), are involved in the reaction.

iii) In case of the coefficients in the reaction or chemical equation are multiplied or divided by some integer, the ΔH value must also be multiplied or divided by the same integer.



If the whole equation is multiplied by Q, the ΔH for the new thermochemical equation is as :



4) When a chemical equation is reversed, the magnitude of ΔH remains same, however, its sign is reversed. For example, if ΔH is +ve for forward reactions, it would be negative for the reverse reaction

➤ **Heat of formation (ΔH_f) :**

i) Heat of formation of a compound is defined as “The enthalpy change when one mole of the compound is formed from its elements in their standard states”.

ii) e.g. $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$, $\Delta H = -395.4 \text{ kJ}$
It means 395.4 kJ heat is evolved when one mole of CO_2 gas is formed from its constituent elements i.e. solid carbon and oxygen gas.

➤ **Heat of combustion : (ΔH_c) :**

i) Heat of combustion of a substance defined as “The enthalpy change when one mole of the substance is completely burnt in excess of oxygen”.

ii) e.g. $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$, $\Delta H = -395.4 \text{ kJ}$
It means 395.4 kJ heat is evolved when one mole of solid carbon is completely burnt in excess of oxygen.

➤ **Heat of neutralization (ΔH_n) :**

i) Heat of neutralization is defined as “The enthalpy change when one gram-equivalent of an acid is completely neutralized by one gram-equivalent of a base in dilute solution”.

ii) e.g. $HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O(l)$, $\Delta H = -57.3 \text{ kJ}$
It means 57.3 kJ heat is evolved when one gram equivalent of HCl is completely neutralized by one gram equivalent of NaOH.

➤ **Heat of solution :**

i) Heat of solution of a substance is defined as “The enthalpy change when one mole of the substance is dissolved completely in such a large excess of solvent that further dilution does not produce any change in enthalpy.”

ii) e.g. $KCl_{(s)} + aq \longrightarrow KCl_{(aq)}$, $\Delta H = +18.46 \text{ kJ}$
It means 18.4 kJ heat is absorbed when one mole of solid KCl is completely dissolved in excess

➤ **Heat capacity :**

i) “The quantity of heat in calories required to raise the temperature of system through one degree under the given condition is called heat capacity.

ii) Thus heat capacity is the rate of change of heat with respect to temperature.

$$\therefore C = \frac{q}{T_2 - T_1} \quad \text{or} \quad C = \frac{dq}{dT}$$

where dq is the quantity of heat required to realize the temperature of the system through dT.

iii) As it depends upon the quantity of matter, it is an extensive property.

➤ **Molar heat capacity :**

i) The quantity of heat required to raise the

temperature of one mole of a substance through one degree is called molar heat capacity of the substance.

$$\therefore C = \frac{dq}{dT}$$

where,

dq = small amount of heat absorbed.

dT = small increase in temperature.

ii) It is an intensive property.

➤ **Molar heat capacity at constant pressure (C_p):** The quantity of heat required to raise the temperature of one mole of a gas through one degree at constant pressure.

$$\therefore C_p = \left(\frac{dH}{dT} \right)_p$$

where dH is a very small change in enthalpy due to a very small change in temperature dT .

iii) Thus the molar heat capacity at constant pressure is the rate of change of enthalpy with respect to temperature.

➤ **Molar heat capacity at constant volume (C_v):** The quantity of heat required to raise the temperature of one mole of a gas through one degree at constant volume is called molar heat capacity at constant volume.

$$\therefore C_v = \left(\frac{dE}{dT} \right)_v$$

where, dE is a very small change in internal energy due to a very small change

☞ **Note:**

C_p is greater than C_v by the work done when one mole of a gas is heated through one degree.

☞ **Kirchoff's law :**

The rate of change of heat of reaction with respect to temperature is equal to the difference between the molar heat capacities of the products and reactants at constant pressure.

☞ **Application :**

- i) Kirchoff's equation is used to calculate the heat of reaction at one temperature, if its value at any other temperature and ΔC_p are known.
- ii) It can also be used to calculate the molar heat capacity of a substance.

✂ **Note :**

1) Similarly, Kirchoff's eqⁿ for constant volume is,

$$i) \left(\frac{d\Delta E}{dT} \right)_v = \Delta C_v$$

$$ii) \Delta E_2 = \Delta E_1 + \Delta CV (T_2 - T_1)$$

$$iii) \Delta CV = \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1}$$

2) Kirchoff's equation gives the effect of temperature on heat of reaction

➤ **Internal energy :**

- i) Every substance possesses a certain amount of energy called internal or intrinsic energy. As it depends upon the quantity, it is an extensive property.
- ii) It is defined as, "The sum total of all forms of energies associated with the matter in a system".
It is mainly due to kinetic and potential energy.
- iii) Kinetic energy is due to the translational, vibrational and rotational motions of the molecules in the system, whereas potential energy is due to the bonding between the molecules and between the atoms in the molecules.
 $\therefore E = \text{Kinetic energy} + \text{Potential energy}$
 $= E_{\text{trans}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{intermole}} + E_{\text{intramole}}$
- iv) The absolute value of internal energy cannot be calculated but the change in internal energy can be calculated.

$$\Delta E = E_2 - E_1$$

$$= \Delta E_{\text{trans}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}} + \Delta E_{\text{intermole}} + E_{\text{intramole}}$$

where E_1 and E_2 are the internal energies of the system in the initial and final states respectively.

- v) The change in internal energy depends only upon the initial and final states of the system and not upon the path.

➤ **Internal energy change for a cyclic process :**

- i) Cyclic process is a process in which system undergoes a series of operations and again returns to its initial state.

- ii) Thus in a cyclic process, initial and final states are same,

$$\text{i.e. } E_1 = E_2.$$

∴ Change in internal energy is,

$$\Delta E = E_2 - E_1 \\ = 0$$

Thus the change in internal energy for a cyclic process is zero.

➤ **Kinetic energy :**

The energy possessed by a system due to different types of motions of molecules present in the system is called kinetic (or thermal) energy.

It depends upon external factor like temperature. Hence it is also defined as, "The energy of a system which depends upon external factor like temperature".

It is of three types.

➤ **Translational energy (E_{trans}) :**

- i) Molecules in liquids and gases are always in a state of motion along straight line paths in random directions.

- ii) The energy possessed by molecules due to such motion is called translational energy.

- iii) Solids do not have translational energy because molecules in solids do not have translational motion.

- iv) Monoatomic gases have only translational

energy.

➤ **Vibrational energy (E_{vib}) :**

- i) Atoms in molecules vibrate with respect to each other. These vibrations are due to

- a) Stretching and compression in case of linear diatomic molecules and,

- b) Bending in case of polyatomic molecules.

- ii) The energy possessed by molecules due to vibrations of the atoms is called vibrational energy.

- iii) Monoatomic molecules do not possess vibrational energy.

➤ **Rotational energy (E_{rot}) :**

- i) Diatomic and polyatomic molecules rotate about the axes perpendicular to the line joining the nuclei and passing through the center of gravity.

- ii) The energy possessed by molecules due to the rotation about their axes is called rotational energy.

- iii) Solids and monoatomic molecules do not possess rotational energy.

➤ **Potential energy :**

The energy possessed by a system due to bonding between the molecules and between the atoms in the molecules is called potential (or bonding) energy.

It does not depend upon external factor like temperature. Hence it is also defined as, "the energy of a system which is independent of external factor like temperature".

It is of two types.

1) **Intermolecular or intramole energy ($E_{\text{Intermole}}$) :**

- i) In solids and liquids, molecules are held together by weak binding forces called Van de Waals' forces.

- ii) The energy required to separate molecules from each other is called intermolecular energy.

iii) In gases, binding forces between the molecules are negligible. Hence gases do not possess intermolecular energy.

➤ **Intramolecular or Intramole energy ($E_{\text{intermole}}$):**

i) Atoms in molecules are held together by strong binding forces called chemical bonds.

ii) The energy required to break molecules into the constituent atoms is called intramolecular energy.

iii) Monoatomic molecules do not possess intramolecular energy.

☞ **Hess's law :** This law was stated by a Russian chemist H. Hess in 1840. It is based upon the law of conservation of energy.

➤ **Statement :** The change in enthalpy during a chemical reaction is independent of the path between the initial and final states.

The total amount of heat absorbed or evolved during a chemical reaction is same whether the reaction takes place in one step or in many steps.

➤ **Explanation :**

i) Consider conversion of substance A to D by two different paths.

Path - I



Path - II



ii) According to Hess's law,

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

$$\therefore -Q = (-Q_1) + (-Q_2) + (-Q_3)$$

$$\therefore -Q = -Q^1 \text{ (say)}$$

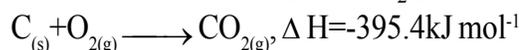
iii) If the values of $-Q$ and $-Q^1$ are not exactly the same, then some amount of energy is either created or destroyed. But this is contrary to the first law of thermodynamics.

$$\therefore -Q = -Q$$

iv) Graphical representation of Hess's law:

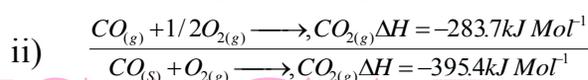
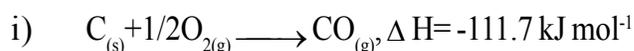
Consider the formation of CO_2 gas by two different paths.

Path- I : Carbon in solid state is burnt in excess of oxygen to give CO_2 gas.



Path - II :

Carbon in solid state is burnt in limited supply of oxygen to give first CO gas, which is then burnt in excess of oxygen to give CO_2 gas.



Thus the heat of formation of CO_2 gas by both the paths is same. This proves the Hess's law.

➤ **Applications of Hess's law :**

i) Using Hess's law thermochemical equations can be added, subtracted or multiplied like algebraic equations.

ii) To calculate the heats of reactions which do not take place extremely slowly.

iii) To calculate the heats of formation which take place extremely slowly.

iv) To calculate the heats of reactions which take place fastly.

v) To calculate the heat of reaction from the heats of formation of the compounds which cannot be formed directly from their elements.

vi) To calculate heat of reaction from the heats of formation of reactants and products.

vii) To calculate the calorific values of foods and fuels.

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