

Thermo Chemistry

1. Thermo-Chemistry

It is a branch of physical chemistry which deals with the study of thermal changes accompanying a physical or chemical transformation.

2. Law of Conservation of Energy :

"Total energy of the system and its surroundings remain constant". Although it can be transformed from one form to the other.

System and surroundings: The part of the universe chosen for thermodynamic study of called system. It is separated from the rest of the universe by a real or imaginary boundary.

The remaining portion of the universe, excluding the system is called **surroundings**.

3. SI Unit :

IUPAC convention follows SI unit.

- (i) Heat absorbed by the system (+q) = positive [SI and non – SI]
- (ii) Heat realised by the system (–q) = negative [SI and non–SI]
- (iii) Work done by the system on the surroundings (–w) = negative [SI]
- (iv) Work done on the system by the surroundings (+w) = positive [SI]

In SI unit work is expressed in Joule

$$1\text{J} = 10^7 \text{ erg} = 1 \text{ Nm} = 1 \text{ kgm}^2\text{s}^{-2}$$

Note : Usually SI unit is frequently followed

4. Expression for PV work :

All kinds of PV work is expressed as :

$$W = -P\Delta V$$

The above expression satisfy the sign conventions.

For expansion ΔV or $(V_2 - V_1)$ +ve and $W = -ve$

For compression ΔV or $(V_2 - V_1) = -ve$ and $W = +ve$

5. First law of thermodynamics (SI convention) :

First law of thermodynamics assumes the form :

$$\Delta E = q + w$$

For a system which involves only pressure volume work then :

$$\Delta E = q - P\Delta V \quad (\because W = -P\Delta V)$$

6. Type of Systems

(a) Isolated System – A system that cannot exchange mass and/or energy from the surroundings.

For example, ice, milk or any other liquid kept in a thermos flask.

(b) Closed system – It exchanges only energy from the surroundings.

For example, (i) water in closed bottle (boundaries of closed system act as conductor of heat), (ii) heating of CaCO_3 in sealed tube, etc.

(c) Open system – It exchanges energy and mass from the surroundings. For example, trees in forest, tea in an open cup, etc.

(d) Macro System – A very large number of molecules/atoms are present in this system. Properties of a macro system are called macro properties. For example, pressure, temperature, density, composition, viscosity, surface tension, colour, refractive index, etc.

(e) State of system – The system in which the values of macro properties are definite. It is said to be in definite state. Thus, the state of system is determined by its macro properties.

(f) State Functions – The properties of a system which depend only on initial and final states, and do not depend on its path. For example, free energy, enthalpy, internal energy, etc.

(g) Extensive Property – The property which depends on the amount of substance present in the system. For example, mass volume, heat capacity, entropy, enthalpy, free energy internal energy, etc.

(h) Intensive Property – These do not depend on the amount of substance present in the system. For example, temperature, density, viscosity, melting point, boiling point, surface tension, refractive index. etc.

7. Thermodynamic Process – The process by which a system gets changed from one state to the other state. Macro properties get changed in this process. These are of the following types.

(a) Isothermal Process – The process in which temperature of the system remains constant. In this process, the boundaries of the system are mobile. The energy released in the process is absorbed by the surroundings and the system takes the required energy back from the surroundings, while the temperature remains constant. Thus the change in temperature, $dT = 0$

Maximum work done in expansion of n moles of an ideal gas.

$$W_{\max} = -2.303 nRT \log \frac{V_2}{V_1}$$

where V_1 = Initial volume of the gas

V_2 = Final volume of the gas

(b) Adiabatic Process – In a closed system, heat is not exchanged by the surroundings, i.e. the system is in isolated state. In this process, temperature can increase and can decrease also. Change in heat (dQ) = 0

(c) Isobaric Process – This process takes place at constant pressure. Change in pressure (dp) = 0. For example. vaporisation of water, heating of water up to its boiling point at same atmospheric pressure

(d) Isochoric Process – The process which takes place at constant volume. Change in volume, (dV) = 0.

(e) Cyclic Process – The process in which a system proceeds via many intermediate steps and returns to the initial state. Change in internal energy (dE) = 0, change in enthalpy (dH) = 0

(f) Reversible Process – This process is slow and unreal. Its direction can be changed at any step. By this, the maximum work done by the system can be obtained.

(g) Irreversible Process – This process is fast. All the natural processes are of this type. In this, the work done is less than that in the reversible process.

$$W_{\text{Irreversible}} < W_{\text{Reversible}}$$

8. Thermodynamic Equilibrium

When macro properties of a system do not change with time, the system is said to be in equilibrium.

(a) Mechanical Equilibrium – When no work is done by one part of the system on its other part, it is said to be in a state of mechanical equilibrium. Pressure remains constant throughout the system.

(b) Thermal Equilibrium – Temperature remains constant throughout the system. No transfer of heat takes place from one part of the system to the other.

(c) Chemical Equilibrium – In this, composition of the system remains constant and definite.

9. Internal Energy –

1. The fixed amount of energy contained in a substance is called its internal energy
2. Internal energy is present in all the substances.
3. Quantitative Property – Internal energy depends on chemical nature, pressure, temperature and volume of the substance.
4. State Functions – Internal energy depends on the physical state of the system .
5. Internal energy is the total of all types of energy e.g., potential energy, kinetic energy, vibrational energy, rotational energy, etc.
6. Absolute value of internal energy cannot be determined. Only change in internal energy (ΔE) can be determined.

$$\Delta E = \text{Energy in final state} - \text{Energy in initial state.}$$

$$\Delta E = E_2 - E_1$$

$$\Delta E = \text{Energy of the products} - \text{Energy of reactants}$$

- * Internal energy is an extensive property.
- * In most stable form, internal energy of the system is regarded as zero.
- * Internal energy of one mole of a monoatomic gas at T Kelvin is $\frac{3}{2} RT$.

$\Delta E = -ve$ in exothermic reactions

$\Delta E = +ve$ in endothermic reactions

$$Q = E + W$$

10. First law of Thermodynamics

Energy can neither be produced nor destroyed, it can only be changed from one form to the other i.e.

[1] Total energy of an isolated system remains constant.

[2] Total energy of universe remains constant.

[3] Whenever some amount of any form of energy disappears, the same amount of energy of other form is produced.

Mathematical form –

Energy absorbed by a system

$$\Delta E = q + W$$

[1] For isothermic process

Energy change in system = heat given to system + work done on system

$$\Delta E = 0 \text{ as temperature is constant } \therefore 0 = q + W \text{ or } q = -W$$

[2] For isochoric process

$W = 0$ (System does not do any work)

$\Delta E = q + 0$ heat given to system at constant volume changes internal energy.

[3] For adiabatic process

$$Q = 0 \quad \Delta E = 0 + W \text{ or } \Delta E = W \text{ work done on system change internal energy}$$

[4] When a gas expands against a constant pressure, P, then

(a) The work done by this = $-P\Delta V$ ($\Delta V = V_2 - V_1$)

$$\Delta E = q - P\Delta V$$

Then, W = Litre atmosphere [1 litre atmosphere = 101.3 Joule]

(b) If a gas expands in vacuum, the work done, W = 0, because P = 0.

11. Heat Content or Enthalpy, H

$$\boxed{H = E + PV} \quad P = \text{External pressure}$$

At constant temperature and pressure

$$\boxed{\Delta H = \Delta E + P\Delta V} \quad \Delta E = \text{Change in internal energy}$$

$$P\Delta V = \Delta W = \text{Work done}$$

[1] Most of the chemical reactions occur at constant pressure (1 atmospheric) and in an open vessel .

[2] When $\Delta V = 0$ $\boxed{\Delta H = \Delta E}$

$\Delta H = -ve$, (reaction is exothermic)

$\Delta H = +ve$, (reaction is endothermic)

[3] Enthalpy of a system depends on physical state (solid, liquid and gas)

[4] H is a state function. Therefore, it depends only on initial and final states. Absolute value of enthalpy cannot be determined

(5) Enthalpy of monoatomic gas = $\frac{5}{2}RT$ per mole.

(6) Change in enthalpy of the products and reactants at 298 K and 1 atmospheric pressure is called standard molar enthalpy change.

Relationship between ΔH and ΔE .

[1] At constant pressure

$$\Delta H = \Delta E + P\Delta V, \text{ According to first law of thermodynamics}$$

$$\Delta E = Q + W$$

$$W = -P\Delta V$$

$$\Delta E = Q - P\Delta V$$

$$\Delta H = Q - P\Delta V + P\Delta V$$

$$\boxed{\Delta H = Q}$$

[2] For liquids and solids

$$\Delta V = 0 \quad W = 0$$

$$\boxed{\Delta H = \Delta E}$$

[3] For gaseous state

$$PV = nRT \quad P\Delta V = \Delta nRT$$

$$\boxed{\Delta H = \Delta E + (\Delta n)RT}$$

- (a) $\Delta n = 0$ $\Delta H = \Delta E$
 (b) $\Delta n = -ve$ $\Delta H < \Delta E$
 (c) $\Delta n = +ve$ $\Delta H > \Delta E$

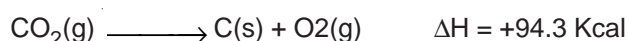
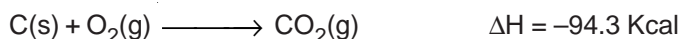
12. Law of Thermodynamics

It is study of heat change.

[1] Lavoisier and Laplace's Law

This law is based on the first law of thermodynamics.

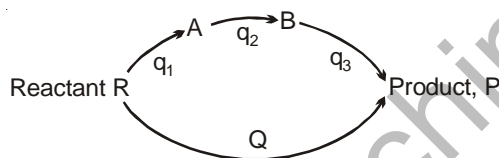
The heat released in the preparation of a compound from its constituent elements, is same as the amount of heat required to decompose that compound into its elements. For example,



[2] Hess's Law of Constant Heat Summation

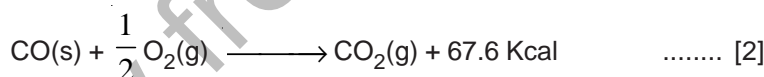
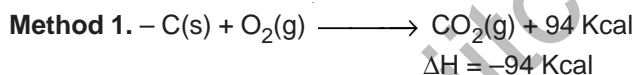
When a chemical reaction gets completed directly in one step or indirectly in two or more steps, the total energy change in the reaction remains same. i.e., the change does not depend on the path of a chemical reaction.

Reactant ,



$$Q = q_1 + q_2 + q_3$$

Example – Combustion of carbon



On summing up equations [1] and [2], $\Delta H = -94 \text{ Kcal}$

Applications – [1] Determination of heat of formation, heat of combustion, heat of transition, heat of reaction and bond energy.

13. Bond energy or Bond dissociation energy

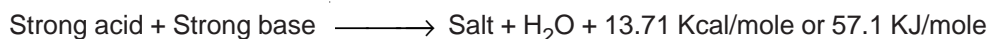
Average energy, required to break same type of 1 mole of bonds in gaseous state, is called bond energy. It is expressed in Kcal/mole or KJ/mole.

[1] Bond energy of same type of bonds is different in different compounds. For example. In CCl_4 , CH_3Cl , CH_2Cl_2 and $CHCl_3$, the values of C–Cl bond energy are different.

[2] Bond energy values of same type of bonds in the same compound are different. Therefore, average of bond energy values is taken into consideration. For example in CH_4 . C–H bond energy values are different.

[3] H–H bond energy 104.2 Kcal

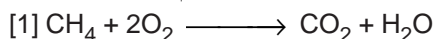
14. Heat of Neutralisation



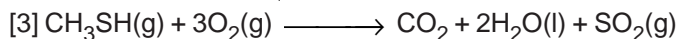
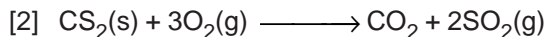
The value of heat of neutralisation is lower when acid and/or base are weak.

15. Heat of Combustion

Amount of heat released on total combustion of 1 mole substance at constant temperature (change in total heat) is called heat of combustion. Its value is always negative. For combustion of hydrocarbon.



$\Delta H = -210.8 \text{ Kcal/mole}$ (At 25°C and 1 atmospheric pressure)

**16. Heat of Reaction**

According to stoichiometry of balanced equation of a reaction. change in total heat on complete reaction of the reactants at constant temperature and pressure (or constant volume) is called heat of reaction of that reaction.

(a) At constant pressure

$$q_{(P)} = \Delta H = H_P(\text{Product}) - H_R(\text{Reactant})$$

(b) At constant volume

$$q_{(V)} = \Delta E = E_P(\text{Product}) - E_R(\text{Reactant})$$

17. Standard Heat of Reaction

Change in total heat (ΔH) at 25°C and 1 atmospheric pressure is called standard heat of reaction. Heat of reaction measured by Bomb calorimeter is ΔE .

Relation between QP and QV

$$\begin{aligned} \Delta H &= \Delta E + P\Delta V & q_{(P)} &= \Delta H \\ q_{(P)} &= q_{(V)} + P\Delta V & q_{(V)} &= \Delta E \\ PV &= nRT & P\Delta V &= \Delta nRT \end{aligned}$$

$$q_{(P)} = q_{(V)} + \Delta nRT$$

[1] R, $q_{(P)}$ and $q_{(V)}$ have same unit

$$R = 1.987 \text{ cal kelvin}^{-1} \text{ mol}^{-1}$$

$$R = 8.314 \text{ joule kelvin}^{-1} \text{ mol}^{-1}$$

[2] When $\Delta n = 0$

$$q_{(P)} = q_{(V)}$$



$$\Delta n = 0$$

Here, solids are not taken into consideration.

[3] For solids, liquids and solutions (all reactants and product)

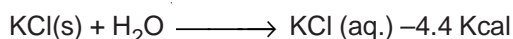
$$q_{(P)} = q_{(V)}$$

$$\Delta H = \Delta E$$

Example – Esterification, neutralisation

18. Heat of Solution

One mole of a substance is dissolved in so much amount of water that no change take place in heat on greater dilution. In this process, change in total heat is called heat of solution.



For KCl, $\Delta H = 4.4 \text{ Kcal}$ (Absorption)

Heat is liberated for MgSO_4 .

19. Integral Heat of Solution

Heat change on dissolving one mole of a substance in definite amount of solvent is called integral heat of solution.

20. Heat of Dilution

Difference of two integral heats is called heat of dilution.

21. Heat of Hydration

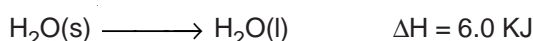
Heat released on complete hydration of one mole an anhydrous substance is called heat of hydration.

**22. Heat of Sublimation**

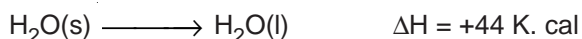
Heat used to change one mole of a solid substance into vapour state is called heat of sublimation

**23. Heat of Fusion**

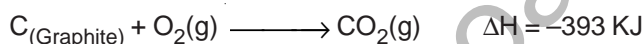
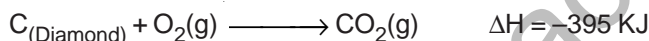
Amount of heat required to completely change one mole of a solid substance into liquid at its melting point, is called heat of fusion.

**24. Heat of Vaporisation**

Heat required to completely change one mole of a liquid into vapour at its boiling point, is called heat of vaporisation.

**25. Heat of Transition**

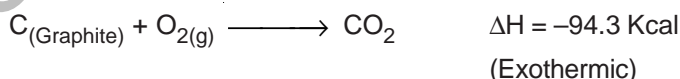
Heat change occurred in changing one mole of an allotrope of an element into its other allotrope, is called heat of transition



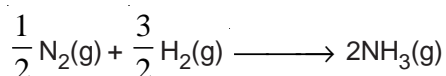
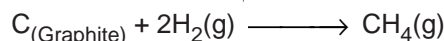
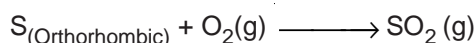
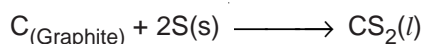
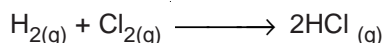
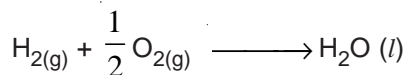
Therefore, heat of transition = 2KJ

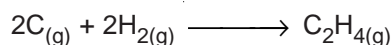
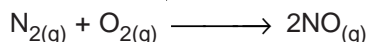
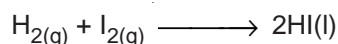
**26. Heat of Formation**

At a definite temperature, change in enthalpy (ΔH_f°) on formation of compound from standard state of its component elements is called standard heat of formation.



This is also the heat of combustion of graphite.

Exothermic

Endothermic

- * Heat of formation from standard state of an element is zero.
- * The form of an element or a compound, which is stable at 25°C and 1 atmospheric pressure, is regarded as standard state of that substance.
- * Standard state of carbon is graphite. Heat of formation of diamond is 1.89 KJ/mole.
- * Standard state of sulphur is orthorhombic.
- * Stability of a compound \propto Negative heat of formation

[1] Effect of Temperature on Heat of Reaction

According to Kirchoff's equation.

$$\text{Heat of reaction at temperature } T_1 = \Delta H_1$$

$$\text{Heat of reaction at temperature } T_2 = \Delta H_2$$

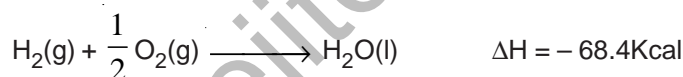
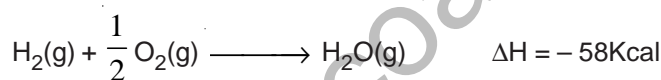
$$\text{At constant pressure, } \Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

$$\text{At constant volume, } \Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$$

$$\Delta E_2 \text{ and } \Delta E_1 \text{ are internal energy changes at temperatures } T_2 \text{ and } T_1$$

Molar heat of solution at constant pressure (ΔC_p) = Total heat capacity of the products – Total heat capacity of the reactants.

Heat required to heat 1 g of a gas to 1°C at constant pressure is called C_p .

[2] Effect of Physical State

Heat is liberated on condensation.

Heat of reaction also depends on allotropes.

[3] Effect of pressure and Volume

Heat of reaction

$$\text{At constant volume } q_v \quad P\Delta v = 0$$

$$\text{At constant pressure } q_p \quad W = P\Delta V$$

$$q_p = q_v + \Delta nRT$$

27. Second Law of Thermodynamics

Entropy of an isolated system increases and becomes stationary on reaching maximum i.e., stability is maximum at the state of maximum entropy.

[1] According to Clausius – Transfer of heat from a cold body to a hot body is not possible without doing some work.

[2] Entropy of a system increases in every spontaneous process or entropy of universe increases in every spontaneous process.

[3] It is not possible to convert the heat received from a source into an equivalent amount of work, unless some change is done in some other part of the system.

28. Entropy, S

It is a thermodynamic property and is a measure of disorderliness or randomness of a system, i.e., greater the disorder in a system, higher is the entropy of that system.

$$\boxed{\text{Solid} < \text{Liquid} < \text{Gas}}$$

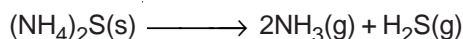
Entropy is a state function. It does not depend on path.

$$\Delta S = S_2 - S_1 = \frac{q(\text{reversible})}{T}$$

q = amount of heat (At temperature T) absorbed by the system in a reversible way.

Some Important points Related to Entropy

- [1] Entropy change, $\Delta S = S(\text{Final state}) - S(\text{Initial state})$
- [2] $\Delta S =$ Increase in entropy of positive system.
- [3] $\Delta S =$ Decrease in entropy of negative system.
- [4] When a solute gets dissolved in the solvent, the entropy increases.
- [5] When the number of gaseous products increases in a chemical reaction, the entropy also increases. For example.



- [6] $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{s})$ Entropy is decreasing.
- [7] For a reaction, change in entropy $\Delta S =$ Total of entropies of the products – Total of entropies of the reactants.
- [8] Unit of entropy is joule kelvin⁻¹ mole⁻¹.
- [9] At equilibrium, $\Delta S = 0$
- [10] Entropy change in an isothermic reversible expansion of a gas

$$\Delta S = 2.303 nR \log \frac{V_2}{V_1}$$

V_2 and V_1 are final and initial volumes of the gas.

Spontaneous Processes

This type of physical and chemical change occurs of its own under specific circumstances or on proper initiation
Examples –

- [1] Flow of liquids from higher to lower level.
- [2] Flow of gases from higher pressure to lower pressure.
- [3] Conduction of heat from hot body to the colder body
- [4] Flow of electric current from higher potential to lower potential.
- [5] Dissolution of sugar in water.
- [6] All naturally occurring processes.
- [7] Burning of coal and other fuels.

Some Important Points Related to Spontaneous Changes

- [1] These changes occur only in single direction. They do not occur in opposite direction by themselves. For example. water does not flow itself from lower to upper level.
- [2] Work can be done by a spontaneous change. For example, motion of a piston by expansion of gas, rotation of a wheel when water falls on it from some height, etc.
- [3] For a spontaneous change for an isolated system.

$$\Delta S = \text{Positive}$$

- [4] When it not anm isolated system

$$\Delta S_{(\text{total})} = \Delta S_{(\text{system})} + \Delta S_{(\text{surrounding})} > 0$$

- [5] Change in entropy of a system $\Delta S_{(\text{system})} = \frac{q(\text{Reversible})}{T}$

$$\Delta S_{(\text{Surroundings})} = \frac{q(\text{Reversible})}{T}$$

For a reversible process

$$\Delta S_{(\text{System})} + \Delta S_{(\text{Surroundings})} = \frac{q(\text{Reversible})}{T} + \frac{q(\text{Reversible})}{T} = 0$$

For nonreversible process

$$\Delta S_{(\text{Total})} = \frac{q(\text{Reversible})}{T} - \frac{q(\text{Reversible})}{T} > 0$$

[1] Adiabatic expansion

In adiabatic systems, $q = 0$ at each step. Therefore, $\Delta S = 0$. Thus, reversible adiabatic processes are called isentropic.

[2] Phase Transition – In phase transition process

$$\Delta S = S_2 - S_1 = \frac{q(\text{Reversible})}{T} = \frac{\Delta H}{T}$$

$$\Delta S(\text{Fusion}) = \frac{\Delta H(\text{Fusion})}{T} \quad (\text{Latent heat of fusion of solid})$$

T = Melting point of solid in kelvin

$$\Delta S(\text{Vaporisation}) = \frac{\Delta H(\text{Vaporisation})}{T}$$

where, $\Delta H(\text{Vaporisation})$ = Latent heat of vaporisation

T = Boiling point

It is difficult to find out the value of $\Delta S(\text{Surroundings})$. Therefore, there is no proper evidence in favour of entropic spontaneous change. Gibbs suggested the free energy step which is related only to the system. This is convenient.

29. Free Energy (G)

The available amount of energy during the process in the system which can be changed into maximum useful work, is called free energy of the system.

Thus, free energy change in the system (ΔG), is the measure of the capability of doing useful work by the system

$$G = H - TS \quad \text{Gibbs-Helmholtz equation}$$

$$H = E - PV$$

$$\Delta G = \Delta H - T\Delta S$$

If ΔG = Negative, then the reaction is spontaneous in forward direction

$\Delta G = 0$, at equilibrium

ΔG = Positive, then the reaction is nonspontaneous in backward direction.

30. Third Law of Thermodynamics, Entropy \propto Temperature

According to Nernst, entropy of an ideal crystalline substance is zero at absolute temperature

Absolute entropy of a pure substance can be calculated at different temperatures by this law. For this, the value of C_p (Heat capacity) is necessary.

Limitations of This Law

- [1] Entropy of glass-like substances is more than zero at 0 K.
- [2] Entropy of the solids, which are mixture of isotopes, is not zero at 0 K, e.g., $\text{Cl}_{2(s)}$
- [3] There is no ideal order in the crystals of NO, H_2O , CO, N_2O at 0 K. Therefore their entropy is not zero at 0K

31. Some Important Points

- [1] Capability of doing work is called energy.
- [2] Reactions in which heat is released on completion of the reaction, are called exothermic reactions.
- [3] Reactions in which heat is absorbed on completion of the reaction, are called endothermic reactions.
- [4] Old bonds break in a chemical reactions and new bonds are formed in which energy is released. Thus, there is change in energy of a system after the reaction.
- [5] The energy content of a substance is due to its molecular structure, temperature, pressure, mass and volume. This is called internal energy.
- [6] Total of the product of internal energy, pressure and volume of a substance is called enthalpy.
- [7] Difference of energy of the final and the initial state is called internal energy change.
- [8] Thermal chemical equation are represented by showing change in heat with chemical change.
- [9] Measure of disorder or randomness of a system is called entropy.
- [10] Heat released on neutralisation of one gram equivalent of an acid and one gram equivalent of a base, is called heat of neutralisation.
- [11] When the same changes is performed by different methods, the heat change in all of them will be same.
- [12] $\Delta G = \Delta H - T\Delta S$ shows relationship between enthalpy and entropy. When the value of free energy change is negative, the process is spontaneous and when it is positive, the process is nonspontaneous.
- [13] The energy produced by the combustion of petrol in an automobile engine is in the form of *heat and mechanical work*.
- [14] An open system involves exchange of both matter and energy with the surroundings a closed system involves only exchange of energy whereas an isolated system involves neither exchange of matter nor energy.
- [15] Internal energy is an extensive property i.e. depends upon the amount of the substance. It is a state function i.e. its value depends only on the state. Its absolute value cannot be determined.
- [16] $\Delta E = q_v$ i.e. internal energy change = heat evolved or absorbed at constant volume.
- [17] Enthalpy $H = E + PV$
- [18] Enthalpy change, $\Delta H = \Delta E + P\Delta V$
- [19] $\Delta H = q_p$ i.e. enthalpy change = heat evolved or absorbed at constant pressure.
- [20] The pollutants of the atmosphere are CO_2 , CO, oxides of nitrogen and sulphur and unburnt hydrocarbons.
- [21] An endothermic reaction which may be non-spontaneous at low temperature may become spontaneous at high temperature whereas an exothermic reaction which may be non-spontaneous at high temperature may become spontaneous at low temperature.
- [22] For hydrated salts like $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ etc. or for salts which do not form hydrates (like NaCl, KCl etc). the process of dissolution is endothermic.
- [23] $\Delta H_{\text{reaction}} = \text{S bond energies of reactants} - \text{S bond energies of products}$.
- [24] According to first law of thermodynamics (law of conservation of energy), $\Delta E = q + w$ or $q = \Delta E - w$.
- [25] ΔH is negative for exothermic reaction while it is positive for endothermic reactions.
- [26] Heat of formation of $\text{H}_2\text{O}(\ell)$ ($\Delta H_f^\circ = -285\text{kJ mol}^{-1}$) is greater than that of $\text{H}_2\text{O}(\text{g})$ ($\Delta H_f^\circ = -248.8\text{ kJ mol}^{-1}$) because the former includes heat of condensation of water vapour.

- (27) $q_p = q_v + P\Delta V = q_v + \Delta n_g RT$ where $\Delta n_g = (n_p - n_r)_{\text{gaseous}}$. Thus $q_p = q_v$ when
- the reaction is carried out in a closed vessel.
 - The reaction does not involve any gaseous reactant or product
 - $\Delta n_g = 0$ i.e. $n_p(g) = n_r(g)$
- (28) Standard enthalpy changes are measured at 298 K and 1 atmospheric pressure.
- (29) $\Delta H_{\text{reaction}}^{\circ} = \sum \Delta H_f^{\circ}(\text{products}) - \sum \Delta H_f^{\circ}(\text{reactants})$

32. Useful Conclusions :

Process 1. $\Delta H = -ve$
 $\Delta S = +ve$
 $\Delta G = \Delta H - T\Delta S = -ve$

Conclusion. The process is spontaneous at all temp.

Process 2. $\Delta H = +ve$

$\Delta S = -ve$
 $\Delta G = +ve$

Conclusion : The process is non-spontaneous at all temp.

Process 3. $\Delta H = -ve$

$\Delta G = -ve$

Conclusion : The process is non-spontaneous.

Process 4. $\Delta H = +ve$

$\Delta S = +ve$

$T = \text{low}; \Delta G = +ve$

Conclusion : The process is non-spontaneous

$T = \text{high} \quad \Delta G = -ve$

Conclusion : The process is spontaneous.

Further we have : $\Delta G^{\circ} = -2.303RT \log K$
 [K = equilibrium constant]

Third Law of Thermodynamics :

'At absolute zero temperature the entropy becomes zero in the case of perfectly crystalline substance'.

Formulae to evaluate ΔG

$$\Delta G = 2.303 nRT \log \frac{P_2}{P_1}, \Delta G = 2.303 nRT \log \frac{V_1}{V_2}$$

Composite equation representing first and second law of thermodynamics

$$\Delta E = q + w \quad \Delta S = \frac{q}{T}$$

$\therefore \Delta E = T\Delta S + w$

or $\Delta E = T\Delta S - PdV$

Solved Example

Ex.1 For a reaction at 25°C, enthalpy change ΔH and entropy change ΔS are -11.7×10^3 and 10^5 Joule per mole K^{-1} , respectively, the which of the following statements is true?

- [1] Spontaneous reaction [2] Nonspontaneous reaction
[3] Can be 1 as well as 2 [4] At equilibrium

Sol.
 $\Delta G = \Delta H - T\Delta S$
 $\Delta H = -11.7 \times 10^3 \text{ J mol}^{-1}$
 $\Delta S = -105 \text{ J mol}^{-1} \text{ K}^{-1}$
 $T = (25 + 273) = 298 \text{ K}$
 $\Delta G = (-11.7 \times 10^3) - 298 \times (-10^5)$
 $= +19.59 \text{ KJ mol}^{-1}$

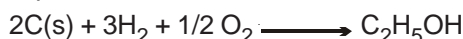
Therefore, ΔG is positive Reaction is not spontaneous.

Ex.2 Enthalpy of carbon, hydrogen and ethyl alcohol on combustion at 25°C are -94.0 , -68.4 and -327.0 kcal per mole, then the formation enthalpy of ethyl alcohol will be

- [1] -66.2 kcal/mol [2] 58.2 kcal [3] 60.2 kcal/mol [4] 60.4 kcal/mole

Sol. [1] $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$ $\Delta H = -68.4 \text{ kcal}$
 [2] $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$ $\Delta H = -94.0 \text{ kcal}$
 [3] $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$ $\Delta H = -327.0 \text{ kcal}$

Equation



Multiplying eq. 1 by 3 and eq. 2 by 2 and eq 3 by -1 , adding all the three would give enthalpy of formation of ethyl alcohol. $(3 \times -68.4) + (2 \times -94) - (-327) = -66.2 \text{ Kcal}$

Ex.3 The work of expansion for a system is 500 cal. The heat given to the system is 80 cal. The change in internal energy in the process will be -

- [1] 80 cal. [2] 500 cal. [3] -420 cal. [4] 420 cal.

Sol. $\Delta E = q + w$
 $80 + (-500) = -420 \text{ cal.}$

Ex.4 From the following thermochemical equations, find out the heat of ionisation Z for a weak acid HA-



- [1] $X + Y$ [2] $-(X + Y)$ [3] $X - Y$ [4] $(Y - X)$

Sol. Adding first and second equations :



Clearly: $Z + X = Y$

$$\therefore Z = [Y - X]$$

Ex.5 What is true for the reaction :



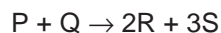
- [1] $\Delta H = \Delta E$ [2] $\Delta H > \Delta E$ [3] $\Delta H < \Delta E$ [4] None of these

Sol. $\Delta H = \Delta E + \Delta n RT$

$$\Delta n = 2 - 1 = 1$$

$$\therefore \Delta H > \Delta E$$

Ex.6 The gaseous endothermic reaction



at 27°C takes place spontaneously, because -

- [1] $\Delta H < 0; \Delta S < 0$ [2] $\Delta H > 0; \Delta S > 0$ [3] $\Delta H < 0; \Delta S > 0$ [4] $\Delta H > 0; \Delta S < 0$

Sol. For an endothermic reaction,

$$\Delta H = +ve$$

[less molecules \rightarrow more molecules], $\Delta S = +ve$

$$\therefore T\Delta S > \Delta H, \text{ and } \Delta G = -ve$$

Hence, the reaction occurs spontaneously,

Ex.7
$$\begin{aligned} \text{N}_2(\text{g}) + 2\text{O}_2 &\rightarrow 2\text{NO}_2(\text{g}) + X \text{ kJ} \\ 2\text{NO}(\text{g}) + \text{O}_2(\text{g}) &\rightarrow 2\text{NO}_2(\text{g}) + Y \text{ kJ} \end{aligned}$$

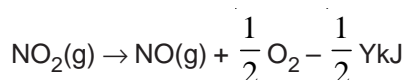
What is the heat of formation (ΔH_f) of NO –

- [1] $(2X - 2Y)$ [2] $X - Y$ [3] $\frac{1}{2}(Y - X)$ [4] $\frac{1}{2}(X - Y)$

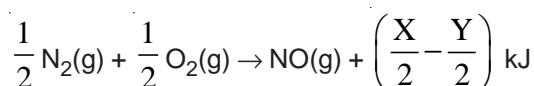
Sol. Dividing eqn. [1] by [2]:



On reversing eqn. [2] and dividing by 2



On adding:



$$\therefore (\Delta H_f) \text{ heat of formation} = \left(\frac{Y - X}{2} \right) \text{ kJ}$$

Ex.8 For the vaporisation of water: $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ [1 atm. pressure]

Given: $\Delta S = 120 \text{ JK}^{-1}$ and $\Delta H = +45.0 \text{ kJ}$.

Evaluate the temperature at which liquid water and water vapours are in equilibrium at 1 atm. pressure –

- [1] 273 K [2] 370 K [3] 373 K [4] 375 K

Sol. We know that: at equilibrium $\Delta G = 0$

$$\Delta G = \Delta H - T\Delta S$$

$$\therefore \Delta S = \frac{\Delta H}{T}$$

$$T = \frac{\Delta H}{\Delta S} = \frac{45.0 \times 10^3 \text{ J}}{120 \text{ JK}^{-1}} = 375 \text{ K}$$

Ex.9 The heat capacity of a bomb calorimeter is $500 \text{ J/}^\circ\text{C}$. In an experiment, in the combustion of 0.1 gm. methane, the temperature rise was by 2.0°C . What is the value of ΔE per mole?

- [1] 1 kJ [2] +160 kJ [3] -160 kJ [4] -1 kJ

Sol. For 2.0°C :

$$\begin{aligned} \text{Heat change} &= 2 \times 500 \text{ J} \\ &= 1000 \text{ J} \end{aligned}$$

\therefore For the combustion of 0.1 gm methane = 1000 J

$$\therefore \text{For the combustion of 16 gm methane} = \frac{1000}{0.1} \times 16 = 160000 \text{ J} = 160 \text{ kJ / mole}$$

(Heat of combustion is negative)

Ex.10 For a certain reaction the change in enthalpy and change in entropy are $40.63 \text{ kJ mol}^{-1}$ and 100 JK^{-1} . What is the value of ΔG at 27°C and indicate whether the reaction is possible or not?

- [1] $+10630 \text{ J mol}^{-1}$; possible [2] $+10630 \text{ J mol}^{-1}$ not possible
 [3] -7990 J mol^{-1} ; possible [4] $+7990 \text{ J mol}^{-1}$; possible

Sol. We know that :

$$\Delta G = \Delta H - T\Delta S$$

$$T = 27 + 273 = 300 \text{ K}$$

$$\Delta H = 40.63 \times 10^3 \text{ J mol}^{-1} = 40630 \text{ J mol}^{-1}$$

$$\Delta S = 100 \text{ JK}^{-1}$$

$$\Delta G = 40630 - 300 \times 100 = 40630 - 30000 = +10630$$

Positive value of ΔG indicates that the reaction is not possible.

Ex.11 The bond dissociation energies of methane and ethane are $360 \text{ kcal mol}^{-1}$ and $620 \text{ kcal mol}^{-1}$ respectively. The C–C bond energy in kcal mol^{-1} is –

- [1] 130 [2] 260 [3] 180 [4] 80

Sol. Methane contains four C–H bonds. Ethane contains six C–H bonds and one C–C bond.

\therefore Energy of four C–H bonds = 360 kcal

\therefore Energy of six C–H bonds = $\frac{360}{4} \times 6 = 540 \text{ kcal}$

For ethane

energy of six C–H bonds and one C–C bond = 620 kcal .

\therefore Energy of C–C bond = $620 - 540 \text{ kcal} = 80 \text{ kcal}$

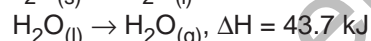
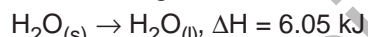
Ex.12 For the reaction $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$ $\Delta H_{298\text{K}} = -44.12 \text{ kcal}$

At 298 K , the enthalpy of formation of HCl is –

- [1] -44.12 [2] -22.06 [3] 44.12 [4] 22.06

Sol. Enthalpy of HCl will be half of -44.12 kcal . So its value is -22.06 kcal .

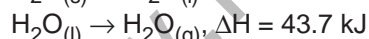
Ex.13 Consider the following data



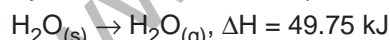
At 273 K , the sublimation energy of $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{g})$ is –

- [1] 43.7 kJ [2] 6.05 kJ [3] 49.75 kJ [4] 37.3 kJ

Sol. $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l}), \Delta H = 6.05 \text{ kJ}$



By addition of both this equation



Ex.14 The heat of formation of ICl $\Delta H(\text{ICl}) = 4.2 \text{ kcal mol}^{-1}$, $\Delta H(\text{Cl}) = 29.0 \text{ kcal mol}^{-1}$, $\Delta H(\text{I}) = 25.5 \text{ kcal mol}^{-1}$. What will be the bond energy of ICl?

- [1] 58.7 kcal [2] 50.3 kcal [3] 29.7 kcal [4] 33.2 kcal

Sol. $\Delta H = \Sigma \text{Bond energy (Reactants)} - \Sigma \text{Bond energy (Products)}$

$$4.2 = 29.0 + 25.5 - \text{Bond energy (I - Cl)}$$

Bond energy I – Cl = $29.0 + 25.5 - 4.2 = 50.3 \text{ kcal}$

Ex.15 For a spontaneous process the values of free energy and entropy change are respectively –

- [1] Postiove and negative [2] Negative and positive
 [3] Positive and positive [4] Negative and neative

Sol. In a spontaneous process, entropy increases and free energy decreases