Topic on Chemistry

CHEMICAL THERMODYNAMICS

Thermodynamics is the branch of science which deals with the energy changes accompanying all types of physical and chemical processes. The word 'thermodynamics' implies **flow of heat.**

Importance of thermodynamics—It is a fundamental subject of great importance in physical chemistry. Most of the important laws of physical chemistry like van't Hoff law of dilute solutions, distribution law, Raoult's law, law of chemical equilibrium, the phase rule and the laws of thermochemistry can be deduced from the laws of thermodynamics. It also helps to lay down the criteria for predicting feasibility or spontaneity of a process under a given set of conditions. It also helps to predict the yields of products.

Limitations—Laws of thermodynamics apply only to matter in bulk and to no individual atoms or molecules. In other words, the laws of thermodynamics apply to behaviour of assemblages of a vast number of molecules and not to individual molecules. It also does not tell anything about the rate at which a given process may proceed and gives no information about the mechanism or path taken by a process.

Terminology of Thermodynamics

1. System

A system is that part of the universe which is under thermodynamic study and the rest of universe is known as **surroundings**.

A system can be of three types.

(a) **Isolated system**—A system which can exchange neither energy nor matter with its surroundings.

(b) **Closed system**—A system which can exchange energy but not matter with its surroundings.

(c) **Open system**—A system which can exchange matter as well as energy with its surroundings.

2. Macroscopic properties

The properties associated with a macroscopic system (*i.e.*, consisting of large number of particles) are called macroscopic properties. These properties are pressure, volume, temperature, density, surface tension etc.

3. Thermodynamic equilibrium

A system in which the macroscopic properties do not undergo any change with time is said to be in thermodynamic equilibrium. It implies the existence of three kinds of equilibria in the system (a) Thermal equilibrium, (b) Mechanical equilibrium and (c) Chemical equilibrium.

4. Extensive and Intensive properties

Properties of a substance which depend on the quantity of matter (or amount of the substance) are called extensive properties. Examples—mass, volume, enthalpy, free energy, heat capacity etc. Properties which do not depend on the quantity of matter.are called intensive properties. Examples—pressure, temperature, surface tension, viscosity, specific heat etc.

5. State of a system

The conditions for existence of a particular system when its macroscopic properties have definite values. A system to be in a state must have definite values assigned to its macroscopic properties such as temperature, pressure, volume and composition. These four properties are called thermodynamic properties or parameters or state variables.

6. State functions

The thermodynamic parameters which depend only upon the initial and final states of the system and are independent of how the change is accomplished are called state functions. Examples—internal energy, enthalpy, entropy, pressure, temperature etc.

Thermodynamic processes and their types

The operation by which a system changes from one state to another is called a process. The following types of processes are known—

(a) **Isothermal**—Temperature of the system remains constant during each stage of the process.

(b) **Adiabatic**—Process in which no heat enters or leaves the system during any step of the process.

(c) **Isobaric**—Process in which the pressure of the system remains constant during each step of the process.

(d) **Isochoric**—Those processes in which the volume remains constant.

(e) **Cyclic**—When a process in a given state goes through a number of different steps and finally returns to its initial state.

Internal energy (E) and change in Internal energy (ΔE)

The total energy stored in a substance by virtue of its chemical nature is called its internal energy (E) or intrinsic energy. E is a state function *i.e.*, its value depends upon state of the substance but does not depend upon how the state is achieved. The various energies which contribute towards internal energy are translational energy of the molecule (E_t), rotational energy of the molecule (E_r), vibrational energy of the molecule (E_v), electronic energy (E_e), nuclear energy (E_n) and interaction energy of molecule (E_i)

$$E = E_t + E_r + E_v + E_e + E_n + E_i$$

The absolute value of internal energy can not be determined but the change in internal energy, which occurs during chemical reaction, can be determined by

$$\Delta E = \Sigma E_{products} - \Sigma E_{reactants}$$

For exothermic reactions ΔE is negative

because $\Sigma E_{reactants} > \Sigma E_{products}$

For endothermic reactions ΔE is positive,

because $\Sigma E_{products} > \Sigma E_{reactants}$

Zeroth law of thermodynamics

The law states that if two bodies X and Y are separately in thermal equilibrium with a third body, they all will be in thermal equilibrium with each other. This law introduces the concept of temperature. It is the underlying principle in the measurement of temperature.

First law of thermodynamics

This law was given by Meyer and Helmholtz in 1840. Energy can neither be created nor destroyed, however, it can be transformed from one form to another. This is also known as the **law of conservation of energy**. The law is based on the cumulative experience of ages that it is impossible to construct a perpetual motion machine *i.e.*, a machine which can produce energy without expenditure of energy.

For the mathematical expression, let us assume that a system having internal energy E_1 absorbs a certain amount of heat energy (q).

∴ Its internal energy $= q + E_1$

Let an amount of work w be done on it, so that its internal energy changes to E_2

∴ $\qquad E_2 = E_1 + q + w$

or, $\qquad E_2 - E_1 = q + w$

∴ $\qquad \boxed{\Delta E = q + w} \qquad \qquad ...(1)$

(Change in internal energy) = (Heat absorbed) + (Work done on the system)

When work is done by the system

$$\Delta E = q - w$$

Similarly q will be positive sign when heat is absorbed and negative sign when heat is evolved from the system.

For a cyclic process, where initial and final states are same,

$\qquad \qquad E_2 = E_1$

Hence, $\qquad \Delta E = 0$

and $\qquad \qquad q = w$

For the change in volume (ΔV) during the process at constant pressure P, the work is referred to as pressure–volume work and its expression is given as ($- P\Delta V$)

Thus $\qquad \qquad w = - P\Delta V$

∴ $\qquad \qquad \Delta E = q - P\Delta V \qquad ...(2)$

or, $\qquad \qquad q = \Delta E + P\Delta V$

If during the change, the volume remains constant, then no work is done

i.e., $\qquad \qquad P\Delta V = 0$

Hence, $\qquad \boxed{q_v = \Delta E}$

Thus, change in internal energy represents the heat change taking place during the process occurring at constant volume and constant temperature.

Enthalpy (H) and Enthalpy change (ΔH)

Enthalpy is the heat content of a system at constant temperature and pressure. It is the sum of internal energy and volume energy of a system.

Mathematically, $\quad H = E + PV$

Where PV = volume energy of a system.

If pressure is kept constant

∴ $\qquad$ then $\Delta H = \Delta E + P\Delta V$

The change in enthalpy may be expressed as—

$$\Delta H = H_{(products)} - H_{(reactants)}$$
$$= H_p - H_r$$

The enthalpy change of a reaction is equal to the heat absorbed or evolved during a reaction at constant temperature and constant pressure.

From first law of thermodynamics, we know that for expansion work

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

∴ $\qquad \qquad \Delta H = q - P\Delta V + P\Delta V$

∴ $\qquad \qquad \Delta H = q_{(p)} \qquad$ (Pressure being constant)


Remember

* For exothermic reactions
$$\Delta E \text{ or } \Delta H = -ve$$

* For endothermic reactions—
$$\Delta E \text{ or } \Delta H = +ve$$

* A process which is carried out so slowly that the system remains in equilibrium at every stage is called reversible process.

* Mechanical work is said to be done when there is a change in volume of the system at a constant temperature and pressure.

* The relation of unit mechanical work to thermal unit is called mechanical equivalent of heat. Its numerical value is 4.185×10^7 ergs = 4.185 joules. Thus, for expenditure of 4.185×10^7 ergs = 4.185 Joules of mechanical energy, one calorie of heat is produced. Hence,

$$1 \text{ calorie} > 1 \text{ joule} > 1 \text{ erg}$$

* The C. G. S. unit of mechanical energy is erg. It is defined as work done when a resistance of one dyne is moved through a distance of one cm.

* The C. G. S. unit of electrical energy is joule and
$$1 \text{ joule} = 10^7 \text{ ergs}$$

* The C. G. S. unit of thermal energy is calorie and
$$1 \text{ joule} = 0.2389 \text{ calorie}$$

* Heat change taking place at constant volume and constant temperature is represented by ΔE *i.e.*, **change in internal energy**.

* Heat change taking place at constant pressure and constant temperature is represented by ΔH, *i.e.* **change in enthalpy**.

Thus, enthalpy change (ΔH) represents, the heat change taking place during the process occurring at constant temperature and constant pressure.

Thermochemistry—A study of heat or energy changes accompanying a chemical reaction is termed as thermochemistry. An equation which indicates the amount of heat evolved or absorbed in the reaction process is called a thermochemical equation. It must essentially (a) be balanced, (b) give the value of ΔE or ΔH (c) mention the physical state of the reactants and products.

Heat of reaction—It is defined as "the amount of heat evolved or absorbed when the number of gram molecules of the substance as specified by the equation have completely reacted." For example—

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} + 393.5 \text{ kJ}$$
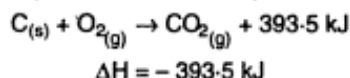
$$\Delta H = -393.5 \text{ kJ}$$

According to the equation when 1 gram atom (12 g) of solid carbon reacts with 1 mole (32 g) of oxygen gas to give 1 mole (44 g) of CO_2 at 25°C and at atmospheric pressure, 393.5 kJ (94380 calories) of heat is evolved. This is thus the heat of above reaction.

Heat of reaction at constant volume—Let us consider a chemical reaction taking place at constant temperature and constant volume. In such case $w = 0$ and hence, from first law (viz., $\Delta E = q - w$)

$$\Delta E = q_V$$

Suppose E_r and E_p are the internal energies of reactants and products respectively, then—

$$\Delta E = E_p - E_r$$

$$\Delta E = E_p - E_r = q_V$$

$$= \text{Heat of reaction at constant volume}$$

Thus the heat of reaction at constant volume and at a given temperature is given by the difference in the internal energies of the products and the reactants.

Heat of reaction at constant pressure—For the reaction at constant pressure and temperature

$$\Delta H = q_p$$

If H_p and H_r are the enthalpies of the products and reactants respectively, then

$$\Delta H = H_p - H_r$$

$$\Delta H = H_p - H_r = q_p$$

$$= \text{Heat of reaction at constant pressure}$$

Thus, the heat of reaction at constant pressure and at a given temperature is given by the difference in the enthalpies of the products and reactants.

Relation between heat of reaction at constant volume (ΔE) and constant pressure (ΔH)—

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

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

Δn = Difference in number of moles of gaseous products and gaseous reactants.

R = Gas constant, T = Temperature in kelvin.

If	$\Delta n = 0$;	$\Delta H = \Delta E$
If	$\Delta n = $ (Positive);	$\Delta H > \Delta E$
If	$\Delta n = $ (Negative);	$\Delta H < \Delta E$

Variation of heat of reaction with temperature—The variation of heat of reaction with temperature is given by Kirchoff's equation

$$\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1) \text{ and}$$

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

Where ΔC_v is difference in heat capacities of products and reactants at constant volume and ΔC_p is

difference in heat capacities of products and reactants at constant pressure. Heat of reaction depends on—

(i) Physical state and the amount of substance

(ii) Temperature

(iii) In the case of reactions involving gases whether the reaction is taking place at constant volume or at constant pressure.

Remember

- If $E_p > E_r$, reaction will be endothermic, ΔE will be positive.
- If $E_p < E_r$, reactions will be exothermic, ΔE will be negative.
- The value of ΔV is negligible in the reactions involving solids and liquids. Hence, for such reactions

$$P\Delta V = 0$$

and

$$\Delta H = \Delta E$$

That is heat of reaction at constant pressure is equal to that at constant volume

- $$\left(\frac{d\Delta H}{dt}\right)_p = \Delta C_p$$

and

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

are known as Kirchoff's equations which show variation of heat of reaction at constant pressure and constant volume respectively.

- Kirchoff's equation shows that change in heat of reaction at constant pressure or volume per degree change of temperature is shown by differences in heat capacities of products and reactants at constant pressure or volume.
- If molar heat capacities of products and reactants are same, then the heat of reaction is independent of temperature.
- The molar heat capacities of solids are almost equal to each other and hence heat of reactions involving solids are almost independent of temperature.

Types of heat of reactions

(1) Heat of formation—The quantity of heat evolved or absorbed when one mole of a compound is formed from its elements. It is expressed as ΔH_f .e.g.,

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}, \quad \Delta H_f = -68 \text{ k cal.}$$
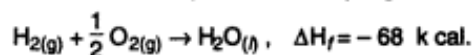
(2) Heat of combustion—The quantity of heat evolved when one mole of a substance is completely oxidised e. g.,

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$\Delta H = -213 \text{ k cal}$$
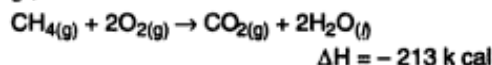
The heat of combustion is very useful in—

(a) Calculating the heat of formation which is otherwise not possible in many cases.

(b) Calculating the calorific value of fuels.

(c) Elucidating the structure of organic compounds.

(3) Heat of solution—The quantity of heat evolved or absorbed when one mole of a solute is dissolved completely in a large excess of water, so that the further dilution does not produce any heat change e. g.,

$$HCl_{(g)} + nH_2O \rightarrow HCl_{(aq)}, \quad \Delta H = -39.3 \text{ k cal.}$$

(4) Heat of neutralisation—The quantity of heat evolved when one equivalent (equivalent mass) of an acid is completely neutralised by one equivalent (equivalent mass) of a base in dilute solution e. g.,

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$
$$\Delta H = -13 \cdot 68 \text{ k cal.}$$
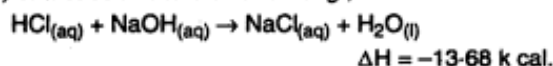
The heat of neutralisation of a strong acid and a strong base is always $- 13 \cdot 7$ k cal. On the basis of electrolytic dissociation theory, it has been clearly explained that this heat of neutralisation is merely the heat of formation of water from H^+ of an acid and OH^- of a base.

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}, \quad \Delta H = -13 \cdot 7 \text{ k cal}$$

The heat of neutralisation in case of a weak acid or a weak base is somewhat less than $- 13 \cdot 7$ k cal because some of the energy is used up in dissociating these weak electrolytes. The difference in the value gives the dissociation energy of the weak acid or a weak base.

The heat of neutralisation of CH_3COOH by NaOH is found to be $-13 \cdot 2$ k cal. The decrease in heat of neutralisation is due to the fact that some heat is utilised in dissociation of weak acid (CH_3COOH). Thus, the heat of dissociation (x) of acetic acid is—
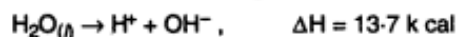
$$- 13 \cdot 7 + x = - 13 \cdot 2$$

or, $\quad\quad\quad\quad x = 0 \cdot 5 \text{ k cal.}$

Similarly, the heat of dissociation of weak base (NH_4OH) in its neutralisation by HCl is—

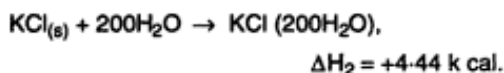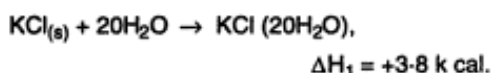$$13 \cdot 7 - 12 \cdot 3 = 1 \cdot 4 \text{ k cal.}$$

(The heat of neutralisation of NH_4OH by HCl is $- 12 \cdot 3$)

(5) Heat of dissociation or Ionisation—The quantity of heat absorbed when one mole of a substance completely dissociates into its ions. e. g.,

$$H_2O_{(l)} \rightarrow H^+ + OH^-, \quad \Delta H = 13 \cdot 7 \text{ k cal}$$

(6) Heat of dilution—The quantity of heat evolved or absorbed when solution containing one mole of a solute is diluted from one concentration to another.

$$KCl_{(s)} + 20H_2O \rightarrow KCl (20H_2O),$$
$$\Delta H_1 = +3 \cdot 8 \text{ k cal.}$$
$$KCl_{(s)} + 200H_2O \rightarrow KCl (200H_2O),$$
$$\Delta H_2 = +4 \cdot 44 \text{ k cal.}$$

$\therefore \quad$ Heat of dilution $= \Delta H_2 - \Delta H_1$
$$= 0 \cdot 64 \text{ k cal.}$$

(7) Heat of precipitation—The quantity of heat evolved in the precipitation of one mole of a sparingly soluble substance on mixing dilute solutions of suitable electrolytes e. g.,
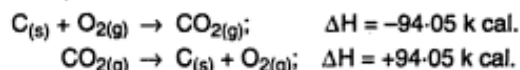
$$Ba^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \rightarrow BaSO_{4(s)}, \quad \Delta H = 4 \cdot 66 \text{ k cal.}$$

Laws of Thermochemistry

(1) Lavoisier and Laplace law—This law states that the amount of heat required to decompose a compound into its elements is always equal to the heat of formation of that compounds from its elements.

In other words the heat evolved in a particular reaction is equal to heat absorbed when reaction is reversed.

This thermochemical equation can be reversed only by changing the sign of heat evolved or absorbed.

For example—

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}; \quad\quad \Delta H = -94 \cdot 05 \text{ k cal.}$$
$$CO_{2(g)} \rightarrow C_{(s)} + O_{2(g)}; \quad \Delta H = +94 \cdot 05 \text{ k cal.}$$

(2) Hess's law of constant heat summation—It states that "the amount of heat evolved or absorbed in a chemical change is the same whether the process takes place in one step or in several steps". For e. g., A system changes from state 'A' to state 'B' in one step.

$$A \rightarrow B + Q$$
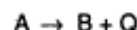
Now suppose the system changes from state A to B in three steps

$$A \rightarrow C + q_1$$
$$C \rightarrow D + q_2$$
$$D \rightarrow B + q_3$$
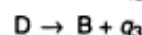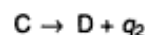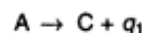
Then according to Hess's law

$$\boxed{Q = q_1 + q_2 + q_3}$$

Applications—(1) By using Hess's law, thermo-chemical equations may be multiplied, added, divided or subtracted just like ordinary algebraic equations.

(2) Hess's law helps us to calculate the heat of formation, heat of combustion of compounds.

(3) Hess's law is used in calculating the heat of transition, i.e., conversion of one allotropic form into another.

Bond Energy—It may be defined as the energy required to break a bond between two atoms, in one mole of a gaseous substance, forming gaseous atoms. For a diatomic molecule like H_2 that has only one bond, the dissociation energy of the molecule is identical to the bond energy. It may be noted that in molecules involving more than one bonds of the same type one takes an average value. e.g., in CH_4 there are 4 C—H bonds. The breaking of each of these C—H bonds is associated with a different enthalpy change. Hence C—H bond energy is taken as the average value. e.g.,

$$CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)}; \quad \Delta H = 398 \text{ k cal}$$
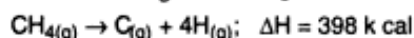
According to definition, the average bond energy of C—H bonds $\frac{398}{4} = 99 \cdot 5$ k cal.

Bond energies are used in the determination of enthalpies of reactions, enthalpies of formation of compounds and determination of resonance energy.

Limitations of first law : Need for the second law of thermodynamics—

(1) The first law states that during a process one form of energy can be changed into another form but the total amount of energy remains the same. However, it does not

predict whether the process in question can occur spontaneously or not and if so in which direction.

(2) The first law states that energy of one form can be converted into an equivalent amount of energy of another form. However, in experience it has been observed that although various forms of energy can be completely transformed into other; but heat energy cannot be completely converted into equivalent amount of work without producing some changes elsewhere.

Second law of thermodynamics—

Second law can be stated in various ways as—

(a) It is impossible to construct a machine working in cycles which can convert heat completely into an equivalent amount of work without producing any additional changes elsewhere (Planck's definition).

(b) It is impossible to construct a heat engine operating in cycles which can perform work at the expense of heat obtained from a thermal reservoir (Kelvin's statement)

(c) It is impossible for a self acting machine unaided by any external agency to transform heat from a colder body to a hotter body. (Clausius statement).

Although second law has been stated in a number of ways but all statements are modifications of the same fundamental concept **"work can always be converted into heat but the conversion of heat into work does not always takes place under all conditions."**

Carnot cycle or Carnot engine

In 1924, S. Carnot (a french engineer) observed that maximum conversion of heat into work occurs in a cyclic process in which all the necessary steps are carried out reversibly. Such a reversible cycle is called Carnot cycle and the engine working on the basis of this cycle is called Carnot engine or heat engine.

Efficiency of a heat engine is defined as the fraction of heat absorbed by the engine which it can convert into work.

It is expressed as—

$$\eta = \frac{q_2 - q_1}{q_2}$$

$$= \frac{T_2 - T_1}{T_2}$$

$$= \frac{w}{q_2}$$

η is efficiency, q_2 is heat absorbed by the engine at higher temperature equal to T_2 and q_1 is the heat evolved by the engine at lower temperature T_1. Since, $(T_2 - T_1)/T_2$ is always less than unity, the efficiency of a heat engine is always less than unity. In fact no heat engine has so far been constructed whose efficiency is equal to unity.

Entropy (S)—The concept of entropy was introduced by Clausius in 1854. It is a thermodynamic state quantity *i.e.*, It is a measure of the randomness or disorder of the molecules of the system. The change in entropy, ΔS for any process is given by the equation

$$\Delta S = S_{final} - S_{initial}$$

When $S_{final} > S_{initial}$, ΔS is positive.

Remember

- **Units of entropy change (ΔS)**

$$\Delta S = \frac{q}{T}, \text{ thus}$$

In C.G.S. units, $\Delta S = \dfrac{Calories}{Degrees} = cal. \, deg^{-1}$

In S. I. units, $\Delta S = \dfrac{Joules}{Degrees \, in \, Kelvin}$

$$= J. \, K^{-1}$$

- **An irreversible spontaneous** reaction is accompanied by an increase in the value of ΔS *i.e.*, for such a reaction, ΔS has a positive value.

$$\Delta S > \frac{q}{T}$$

or, $\qquad \Delta S > 0$

- A **non spontaneous** reaction is accompanied by a decrease in the value of ΔS *i.e.*, for such a reaction ΔS has a negative value.

- For a **reversible spontaneous** reaction ΔS is equal to zero *i.e.*,

$$\Delta S = \frac{q_{rev}}{T} = 0$$

- **When a solid melts—**

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{Melting \, temperature}$$

$$\Delta S_{vaporisation} = \frac{\Delta H_{vaporisation}}{Temperature \, of \, vaporisation}$$

- In general ΔS for any phase transition

$$= \frac{\Delta H_{transition}}{Transition \, temperature}$$

- All periodic machines working reversibly between the same temperatures of source and sink have same efficiency.

- If an isothermal change is carried out reversibly, it leads to maximum work of expansion. Therefore, reversible machine will give maximum efficiency.

- The fraction of heat absorbed by a machine which it can convert into work or other energy is called the efficiency of the machine.

- **First law**—The total amount of energy in nature is constant.

- **Second law**—The total amount of entropy in nature is increasing.

- Entropy always increases in the direction of spontaneous change.

- Entropy change in isothermal expansion of an ideal gas is given by—

$$\Delta S = nR \, ln \left(\frac{V_2}{V_1} \right)$$

- Entropy of mixing of ideal gases is given by—

$$\Delta S_{mix} = -(n_1 R \, ln \, N_1 + n_2 R \, ln \, N_2 \, ...)$$

where N_1 and N_2 are the mole fractions of gases and n_1 and n_2 are number of moles of gases.

We know that—

$$\Delta E = q - w; \, \Delta E = q - P\Delta V$$

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

$$\Delta S = \frac{q}{T} = \frac{(\Delta E + P\Delta V)}{T}$$

"A change in a system which is accompanied by an increase in entropy tends to be spontaneous."

When a system is allowed to change from one state to another state, the heat q, is absorbed or evolved during the change depending upon the way, the change is carried out.

Giving +ve sign to heat absorbed (q_1) and –ve sign to heat evolved (q_2) by a system, then for a reversible cycle—

$$+\frac{q_1}{T_1} = -\frac{q_2}{T_2}$$

or, $$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$$

Thus, for reversible cycle the summation of $\frac{q}{T}$ terms is equal to zero. Thus

$$\Sigma \frac{q}{T} = 0$$

For infinitesimal changes, equation is—

$$\Sigma \frac{dq}{T} = 0$$

Now, we know that dq and T are thermodynamic functions whose change measured by $\frac{dq}{T}$ is independent of path of change of system. This function is called entropy (S).

If S_A is the entropy in the initial state A and S_B is the entropy in the final state B, then the change in entropy, ΔS, is given by the equation

$$\Delta S = S_B - S_A$$
$$= \int_A^B \frac{dq}{T}$$

For each infinitesimally small change

$$dS = \frac{dq}{T}$$

At constant temperature for a finite change, dS becomes ΔS and dq becomes q

$$\therefore \qquad \Delta S = \frac{q}{T}$$

Like ΔH and ΔE, the entropy change (ΔS) is a definite quantity and it depends upon initial and final state of a system.

For an adiabatic change, $q = 0$ hence, $\Delta S = 0$. Such type of change is called **isoentropic** change.

Entropy is an extensive property and its value depends upon the amount of the substance involved.

Standard entropy (S°)—Standard entropy is the entropy of 1 mole of a substance in its pure state at 1 atm. pressure and 25° C.

Statement of second law of thermodynamics in terms of entropy change

It states that whenever a spontaneous process takes place, it is accompanied by an increase in the total energy of the universe, thus

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

The second law as stated above tells us that when an irreversible spontaneous process occurs, the entropy of the system and the surroundings increases.

In other words $\Delta S_{universe} > 0$.

When a reversible process occurs the entropy remains constant, $\Delta S_{universe} = 0$.

Since, the entire universe is undergoing spontaneous change, the second law can be most concisely stated as "the entropy of the system is constantly increasing".

Free energy (G) and work function (A)

Entropy change is considered in terms of other functions which can be determined more easily. Two such state functions are free energy and work function, represented by G and A respectively. These are defined by the equations,

$$A = E - TS \qquad \ldots(1)$$
and $$G = H - TS \qquad \ldots(2)$$

Where
A → Helmholtz work function
G → Gibb's free energy
E → Internal energy
H → Enthalpy
S → Entropy
T → Temperature

Since, E, H and S depend upon the state of a system, the functions A and G also depend upon the state of the system,

$$\therefore \qquad \Delta A = \Delta E - T\Delta S \qquad \ldots(3)$$
and $$\Delta G = \Delta H - T\Delta S \qquad \ldots(4)$$

If the study is carried out reversibly at constant temperature T, and that the heat absorbed is equal to q_{rev}. the increase in entropy

$$\Delta S = \frac{q_{rev}}{T}$$

Substituting it in equation (3), we get

$$\Delta A = \Delta E - q_{rev} \qquad \ldots(5)$$

From first law of thermodynamics ($\Delta E = q - w$) we have

$$-w_{rev} = \Delta E - q_{rev} \qquad \ldots(6)$$

Combining equations (5) and (6), we get

$$-\Delta A = w_{rev} \qquad \ldots(7)$$

As the process is carried out reversibly, w represents the maximum work. Thus decrease in the function ($-\Delta A$) gives the maximum work obtainable from a system during a given change. Thus, A is known as work function.

Free energy—At constant pressure, we know

$$\Delta H = \Delta E + P\Delta V$$
$$\Delta G = \Delta H - T\Delta S$$
$$\boxed{\Delta G = \Delta E + P\Delta V - T\Delta S}$$

or, $$\Delta G = \Delta A + P\Delta V \quad \text{(from equation 3)}$$
or, $$\Delta G = -w_{rev} + P\Delta V \text{ (from equation 7)}$$

or, $-\Delta G = w_{rev} - P\Delta V$

Thus, $-\Delta G$ gives the maximum work obtainable from a system other than that due to change of volume at constant temperature and pressure. The work other than that due to change of volume is called the **net work**.

Thus,   **net work** $= w_{rev} - P\Delta V = -\Delta G$

So, $-\Delta G$ is a measure of the maximum net work that can be obtained from a system at constant temperature and pressure. The function G, is due to Gibb's and is known as Gibb's free energy or simply free energy.

The free energy change (ΔG) for a chemical reaction is given by—

$$\Delta G = \Sigma(\Delta G_{products}) - \Sigma(\Delta G_{reactants})$$

ΔH	ΔS	ΔG = ΔH – TΔS	Remarks
(1) Negative	Positive	Negative	Reaction is spontaneous at all temperatures.
(2) Positive	Negative	Positive	Reaction is non-spontaneous at all temperatures.
(3) Negative	Negative	Negative at low Temperature	Spontaneous at low temperatures.
		Positive at high Temperature	Non-spontaneous at high temperatures.
(4) Positive	Positive	Positive at low Temperature	Non-spontaneous at low temperatures.
		Negative at high Temperature	Spontaneous at high temperatures.

> ### Remember
>
> Work function (A) and free energy (G) are extensive properties. For an isothermal process, these can be written as—
> $$\Delta A = \Delta E - T\Delta S \quad \ldots(i)$$
> $$\Delta G = \Delta H - T\Delta S \quad \ldots(ii)$$
> Substraction (i) from (iii)
> $$\Delta G - \Delta A = \Delta H - \Delta E$$
> If ΔH is measured at constant pressure—
> Then $\Delta H - \Delta E = P\Delta V$
> Therefore, $\Delta G = \Delta A + P\Delta V$
> 'A' is known as Helmholtz function and 'G' is known as Gibb's function.
>
> Gibb's and Helmholtz equations
> (1) $\Delta A - \Delta E = T\left(\frac{\delta(\Delta A)}{\delta T}\right)_v$
> (2) $\Delta G - \Delta H = T\left(\frac{\delta(\Delta G)}{\delta T}\right)_p$
> Gibb's equation—
> $$\Delta G = \Delta H - T\Delta S$$

For a system at equilibrium, $(\Delta G)_{T, P} = 0$.

All spontaneous processes taking place at constant temperature and pressure are accompanied by a decrease in free energy i.e., ΔG is negative. A process is thermodynamically not feasible when ΔG is positive. Thus, depending on the sign of ΔH and $T\Delta S$, the following four cases may be studied.

Relation between the standard free energy change ($\Delta G°$) and equilibrium constant (K) of a reaction—

$$\Delta G° = -RT \ln K$$
or, $\Delta G° = -2.303\ RT \log K$
If R is taken as $8.314\ JK^{-1}\ mol^{-1}$
$$\Delta G° = -2.303 \times 8.314\ T \log K$$
$$= -19.147\ T \log K$$

Third law of thermodynamics—This law helps in determining the absolute values of entropy of various substances. For a crystalline substance at 0 K, there is perfect order, consequently, the disorder or entropy of substance at absolute zero is zero. This law was propounded by Nernst in 1906. It states as—

"At absolute zero temperature, the entropy of perfectly crystalline substance is zero."

It may be stated in a number of other ways—

"At any pressure, the entropy of any crystalline solid in thermodynamic equilibrium at absolute zero is always zero."

"It is rather impossible to reduce the temperature of any system to absolute zero by any process."

As the absolute temperature reaches zero, increase in entropy for isothermal process in crystalline state approaches zero as the limit.

IMPORTANT PROBLEMS WITH SOLUTION

1. In a certain process, 678 J of heat is absorbed by a system while 290 J of work is done on the system. What is the change in internal energy for the process ?

Solution :
$$q = +678\ J$$
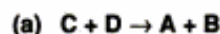Since, work is done on the system, w has a positive value
$$w = +290\ J$$
$\therefore$ $\Delta E = q + w = 678 + 290 = 968\ J$

2. Given the following information
$$A + B \rightarrow C + D, \quad \Delta H° = -10.0\ k\ cal$$
$$C + D \rightarrow E, \quad \Delta H° = 15.0\ k\ cal$$

Calculate $\Delta H°$ for each of the following reactions :

(a) $C + D \rightarrow A + B$

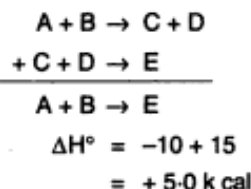(b) $2C + 2D \rightarrow 2A + 2B$

(c) $A + B \rightarrow E$

Solution :

(a) Since, the reaction is the reverse of the first given so the sign of $\Delta H°$ becomes positive + 10·0 k cal.

(b) Since there are twice the number of moles of each reactant, the value of $\Delta H°$ will also be doubled.

$$\therefore \quad \Delta H° = 20\text{·}0 \text{ k cal}$$

(c) Adding the two equations given

$$A + B \rightarrow C + D$$
$$\underline{+ C + D \rightarrow E}$$
$$A + B \rightarrow E$$
$$\Delta H° = -10 + 15$$
$$= +5\text{·}0 \text{ k cal}$$

3. The reaction of cyanamide $NH_2CN_{(s)}$ with oxygen was run in a bomb calorimeter, and ΔE was found to be −742·7 kJ/mol of $NH_2CN_{(s)}$ at 298 K. Calculate ΔH_{298} for the reaction.

$$NH_2CN_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}$$
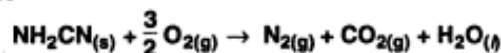
Solution :

The number of moles of gaseous reactant (O_2) is $\frac{3}{2}$, the number of moles of gaseous products $(N_2 + CO_2)$ is 2.

$$\Delta H = \Delta E + P\Delta V$$
$$= \Delta E + \Delta nRT$$
$$\Delta n = 2 - \frac{3}{2} = \frac{1}{2}$$
$$\Delta H = -742\text{·}7 \text{ kJ} + (0\text{·}500 \text{ mol}) (8\text{·}314 \text{ J/mol. K})$$
$$(298 \text{ K})$$
$$= -742\text{·}7 \text{ kJ} + 1240 \text{ J} \quad (\therefore 1240 \text{ J} = 1\text{·}240 \text{ kJ})$$
$$= -741\text{·}46 \text{ kJ}$$

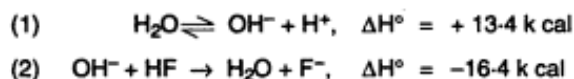**4.** What is the enthalpy change when 1·00 g of water is frozen at 0°C ? ΔH_{fusion} = 1·435 k cal/mol

Solution :

Freezing is just the reverse of melting, hence, the enthalpy change must be − 1·435 k cal/mol

$$\Delta H = -\frac{1435 \text{ cal/mol}}{18\text{·}0 \text{ g/mol}}$$
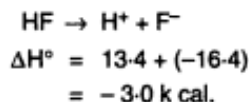$$= -79\text{·}7 \text{ cal/g}$$

$\therefore$ 79·7 cal of heat is liberated when 1·00 g of water is frozen at 0°C and 1·00 atm. pressure.

5. The heat released on neutralisation of CsOH with all strong acids is 13·4 k cal/mole. The heat released on neutralization of CsOH with HF(weak acid) is 16·4 k cal/mole. Calculate $\Delta H°$ of ionization of HF in water.

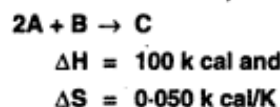## Solution :

(1) $\quad H_2O \rightleftharpoons OH^- + H^+, \quad \Delta H° = +13\text{·}4 \text{ k cal}$

(2) $\quad OH^- + HF \rightarrow H_2O + F^-, \quad \Delta H° = -16\text{·}4 \text{ k cal}$

Adding two equations

$$HF \rightarrow H^+ + F^-$$
$$\Delta H° = 13\text{·}4 + (-16\text{·}4)$$
$$= -3\text{·}0 \text{ k cal.}$$

6. For the reaction at 298 K,

$$2A + B \rightarrow C$$
$$\Delta H = 100 \text{ k cal and}$$
$$\Delta S = 0\text{·}050 \text{ k cal/K}$$

Assuming ΔH and ΔS to be constant over the temperature range, at what temperature will the reaction become spontaneous ?

Solution :

The reaction will just be spontaneous when

$$\Delta G = 0$$
$$\Delta G = \Delta H - T\Delta S = 0$$
$$\Delta H = T\Delta S$$
$$\therefore \quad T = \frac{\Delta H}{\Delta S}$$
$$= \frac{100 \text{ k cal}}{0\text{·}050 \text{ k cal/K}}$$
$$= 2000 \text{ K}$$

7. What is the standard free energy change for the melting of 3·0 mol of water at 0°C ? Determine the entropy change for this process. Is the entropy greater for the liquid than that of the solid ? ΔH_{fusion} = 1·435 k cal/mol

Solution :

$\Delta G°$ is 0 for this reversible process

$$\Delta G = \Delta H - T\Delta S = 0$$
$$\Delta S = \frac{\Delta H}{T}$$
$$= \frac{+1435 \text{ cal/mol}}{273 \text{ K}}$$
$$= 5\text{·}26 \text{ cal/mol. K}$$
$$(5\text{·}26 \text{ cal/mol. K}) (3\text{·}0 \text{ mol}) = 15\text{·}78 \text{ cal/K}^.$$

The entropy is greater for the liquid as seen by the positive sign of ΔS. The melting of a solid into liquid results into increase in randomness or increase in entropy.

8. $\Delta G°_f$ for the formation of $HI_{(g)}$ from its gaseous elements is −10·10 kJ/mol at 500 K when the partial pressure of HI is 10·0 atm, and that of I_2 is 0·001 atm. What must the partial pressure of hydrogen be at this temperature to reduce the magnitude of ΔG for the reaction to 0 ?

Solution :

$$\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightarrow HI, \quad \Delta G° = -10\text{·}10 \text{ kJ at 500 K}$$
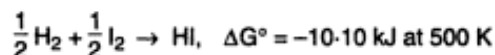
When $\Delta G = 0$, the reaction is at equilibrium

$$-\Delta G° = RT \ln K$$
$$= 2\text{·}303 \, RT \log K$$
$$\log K = \frac{-\Delta G°}{2\text{·}303 \, RT}$$

$$= \frac{+10 \cdot 10 \times 10^3 \text{ J}}{(2 \cdot 303)(8 \cdot 31 \text{ J/K})(500 \text{ K})}$$

$$= 1 \cdot 055$$

$$K = 11 \cdot 36 = \frac{P^{(HI)}}{[P^{(H_2)}]^{1/2}[P^{(I_2)}]^{1/2}}$$

$$= \frac{10 \cdot 0}{(10^{-3})^{1/2}[P^{(H_2)}]^{1/2}}$$

$$P^{(H_2)} = \frac{100}{(10^{-3})(11 \cdot 36)^2}$$

$$= 775 \text{ atm.}$$

9. Calculate the entropy change when 1 mole of an ideal gas expands reversibly from an initial volume of 2 litres to a final volume of 20 litres at 25°C.

Solution :

We know that $\Delta S = nR \ln \dfrac{V_2}{V_1}$

$$= 2 \cdot 303 \, nR \log \frac{20}{2}$$

$$= 2 \cdot 303 \times 1 \times 8 \cdot 314 \times 1$$

$$= 19 \cdot 15 \text{ J/mol.K}$$

10. An athlete is given 100 g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilises 50 per cent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would have to perspire. The enthalpy of evaporation of water is 44 kJ/mole.
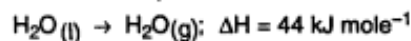
Solution :

Net amount of energy given to athlete = 1560 kJ

Energy lost in an event $= \dfrac{1560 \times 50}{100}$

$$= 780 \text{ kJ}$$

Energy left out = 1560 − 780 kJ = 780 kJ

Now, consider the evaporation of water

$$H_2O_{(l)} \rightarrow H_2O_{(g)}; \ \Delta H = 44 \text{ kJ mole}^{-1}$$

Thus, for consumption of 44 kJ of energy the amount of water evaporated = 18 g.

∴ For consumption of 780 kJ of energy the amount of water to be evaporated

$$= \frac{18}{44} \times 780 \text{ g}$$

$$= 319 \cdot 09 \text{ g}$$

CHEMICAL THERMODYNAMICS

Topic on Chemistry

Introduction

- The word thermodynamics implies **flow of heat**. Thermodynamics deals with energy in its various forms and their interconversion. Thus the branch of science dealing with quantitative relationship between different forms of energy is known as **thermodynamics**.
- The branch of science which deals with energy changes during chemical reactions is called **chemical energetics** and which deals with heat changes is called **thermochemistry**.
- The chemical processes release stored energy as heat or work or both. These quantities are linked through **first law of thermodynamics**. How much heat can be converted into useful work is governed by second **law of thermodynamics**.
- The importance of thermodynamic lies in the fact that it provides explanation of **macroscopic** (bulk) properties of matter, specially the thermal properties consistent with our **microscopic views** of material world made up of atoms and molecules.

Basic Concepts in Thermodynamics

Thermodynamic scale of temperature

- It is based on **absolute zero** of temperature and the **triple point** of water (0.58 torr and 0.01°C) at which water ice, water and water vapour all exist in equilibrium.
- The basic S.I. unit of temperature is **Kelvin (K)**. One Kelvin is $\frac{1}{273.16}$ of the triple point of water (273.16 K). This scale is called the *thermodynamic temperature scale*. It has its zero point as the lowest possible temperature. Thus −273.16°C temperature is absolute zero (−273.16 + 273.16 = 0 K) on Kelvin scale.

Zeroth Law of Thermodynamics

- When two objects at different temperatures are brought in thermal contact, they exchange heat with each other until they reach a state of thermal equilibrium.
- These ideas are expressed in the form of **law of temperature** or **thermal equilibrium**, which is also known as **zeroth law of thermodynamics**.
- This law can be summarised in the following ways :
  (i) Two objects at different temperature in thermal contact with each other tend to move towards the same temperature.
  (ii) Two objects in thermal equilibrium with third one are in the thermal equilibrium with each other.

System

- The **thermodynamics system** refers to any part of the real world under study. Everything that is not the part of the system and can interact with it is called **surroundings**.
- A system and surroundings are always separated by boundaries (real or imaginary) across which matter and energy may be exchanged.
- The surroundings can affect the system by the transfer of matter and energy.
- **Isolated system**—If it cannot exchange matter and energy with surroundings *e.g.*, coffee in a thermos flask.
- **Closed system**—A system is said to be closed if it can exchange energy (heat or work) with surrounding. For example coffee in a closed steel flask.
- **Open system**—It can exchange both matter and energy with surrounding *e.g.*, a tumbler of coffee.

State of a Macroscopic System

- The state of thermodynamic system is described by its measurable or macroscopic properties.
- The state of a gas can be described by quoting its pressure (P), volume (V), temperature (T) and amount (*n*) etc. The variables like P, V, T are called **state variables** or **state functions** because their values depend only on the state of the system and not on how it is reached.
- State functions are very useful because change in their values depends only on the **initial** and **final state** of a system and not on how change is carried out.
- A system in state of **thermodynamic equilibrium** is one in which the macroscopic properties do not change with time.
- The **initial state** of a system refers to the starting state of a system in equilibrium, prior to interaction with surroundings.
- In **final state** the system attain equilibrium after interaction with surroundings. The interaction with surroundings means transfer of matter or energy or both.
- The laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state.
- As in a **chemical equilibrium**, the concentration of reactants and products does not change with time, the macroscopic properties of system like P, T, V etc. do not change with time in **thermodynamic equilibrium**.

Thermodynamic Processes

- When a thermodynamic system undergoes a change of state, we say it has undergone a **process**. The process may be accompanied by an exchange of matter and energy between the system and surroundings.

- The term **process** means change in at least one of the state variables of the system.
- The path of a process consists of the series of **thermodynamic states** through which the system passes from initial state to final state.
- There are certain processes in which a particular state variable (thermodynamic properties of the system) remains unchanged. Such processes are given special names. For example :
  - **Isothermal process**—When temperature of the system remains constant during the change.
  - **Adiabatic process**—When system does not exchange heat with surroundings.
  - **Reversible process**—When a change is carried out so slowly that the system and surroundings are always in equilibrium such states are called **quasi-equilibrium** state.
  - The process in which P and V are kept constant are called **isobaric** and **isochoric** processes respectively.

First Law of Thermodynamics

- This is the law of **conservation of energy**. It can be stated in the following statements—
  - The energy can neither be created nor destroyed, although it can be changed from one form to another.
  - The total energy of the universe is constant.
  - The energy of a system that is isolated from surroundings, i.e., in case of isolated system, is always constant.
- First law provides useful information about energy changes in chemical reactions. Before arriving to the mathematical form of this law, it is worthwhile to know about **internal energy** and the effect of **heat** and **work** on it.
- **Heat**—Heat is the form of energy. Although two have same units, but they are not synonymous. Heat is transferred from one system to another as a result of temperature difference and basically it is energy on move.
- **Internal energy**—The energy of thermodynamic system under given condition is called internal energy. Following points be kept in mind regarding internal energy—
  - Internal energy is made up of kinetic and potential energy of the constituent particles. The kinetic energy arises due to the motion of particles and potential energy due to different kinds of interactions between particles.
  - The kinetic energy is the function of temperature. Internal energy changes when heat is transferred from system to surrounding or vice-versa.
  - According to first law of thermodynamics, the internal energy, denoted as U, for an isolated system is always constant. First law does not provide any way to measure absolute value of internal energy, however, it only provides ways to measure the **change of internal energy, ΔU**, i.e., the difference between internal energies of initial and final states.

- The internal energy of a system depends upon state of the system and not upon how the system attains that state. The internal energy is, therefore, a **state function**.
- The internal energy of a system can be changed in two ways—
  - (i) Either by allowing heat to flow into system or out of system.
  - (ii) By work done on the system or by the system.
- Let us consider a system whose internal energy is U_1 and if the system is given 'q' amount of heat, the internal energy of system increases to $U_1 + q$. If work (W) is now done on the system the internal energy in the final state of the system U_2 is given as—

$$\boxed{U_2 = U_1 + q + W \text{ or } U_2 - U_1 = q + W \text{ or } \Delta U = q + W}$$

This statement which relates internal energy, work and heat is called the statement of **first law of thermodynamics**.

- The values of 'q' and 'W' depend upon the way the processes are carried out and not on initial and final state. Hence individually they are not **state functions**.
- $q + W \, (= \Delta U)$ does not depend upon how the change is brought about and hence independent of path. However, the net change in internal energy, i.e., $q + W$, depends only on initial and final states and hence, is a **state function**.
- When a system undergoes a change in which internal energy of the system remains constant, i.e., $\Delta U = 0$, then $- W = q$. This means that work (W) done by the system equals the heat (q) absorbed by the system.
- A mechanical work is performed when a system changes its volume against external pressure. This kind of work is specially important in systems which contain gases.
- In certain reactions involving gases volume changes occur at constant atmospheric pressure. If a system expands during the reaction, there will be a **pressure-volume work**. If pressure, P is constant and the volume changes from V_i to V_f, the work done by the system is given as

$$\boxed{W = - P\,(V_f - V_i) = - P\,\Delta V}$$

- Above equation is applicable for expansion as well as compression of a gas—
  - (a) When gas expands $(V_f - V_i) > 0$ and $- P\Delta V$ is a negative quantity, the system does work on its surroundings, so 'W' is negative
  - (b) When gas is compressed, $(V_f - V_i) < 0$ and $-P\Delta V$ is a positive quantity, surroundings do work on the system, so 'W' is positive.
- Now if we substitute $P\Delta V$ for 'W', we get,

$$\boxed{\Delta U = q - P\Delta V} \text{ ; Pressure is constant.} \quad …(A)$$

$$\boxed{\Delta U = q_v} \text{ ; Volume is constant, i.e., } \Delta V = 0. \quad …(B)$$

● Equation (B) shows that one can determine ΔU by measuring the heat absorbed at constant volume. For doing so, the reaction must be carried out in a closed, rigid container with constant volume. This is achieved in a **Bomb calorimeter**.

Sign Convention for 'q' and 'W'

● When heat is absorbed by the system, q is positive, i.e., $q > 0$

● When heat is evolved by the system, q is negative, i.e., $q < 0$

● When work is done on the system, W is positive, i.e., $W > 0$

● When work is done by the system, W is negative, i.e., $W < 0$

Enthalpy

● For a process or a chemical reaction carried out at constant volume, the heat absorbed or evolved is equal to corresponding change in internal energy (ΔU).

● In chemistry, most of the chemical reactions are carried out at constant pressure, i.e., at atmospheric pressure. In order to measure heat change at constant pressure, it is useful to define a new state function called **enthalpy (H)** as

$$H = U + PV$$

● The change in enthalpy (ΔH) is given as :

$$\Delta H = \Delta U + \Delta(PV)$$

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

When change takes place at constant pressure, i.e., $\Delta P = 0$, then $\Delta H = \Delta U + P\Delta V$

As we know that $\Delta U = q - P\Delta V$; at constant pressure, then

$\Delta H = q_P$ (at constant pressure), 'q_P' is heat absorbed at constant pressure.

● Enthalpy change (ΔH) can be directly measured using **coffee-cup calorimeter** and when we measure heat change (q_P) at constant pressure we actually measure change in enthalpy (ΔH).

● Relation between heat of reaction at constant volume (ΔU) and heat of reaction at constant pressure (ΔH)

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

$$\Delta H = \Delta U + \Delta n \, RT$$

(Δn = difference of number of moles of products and reactants for gaseous reactions)

If $\qquad \Delta n = 0$ then $\Delta H = \Delta U$

If $\qquad \Delta n > 0$ then $\Delta H > \Delta U$

If $\qquad \Delta n < 0$ then $\Delta H < \Delta U$

Heat Capacity of a System

● Heat capacity of a system is quantity of heat required to raise the temperature of the system by one degree Celsius or one kelvin.

● If the mass of system is 1 gm, the heat capacity is called **specific heat** of the system. If mass is 1 mole as is generally the case in physical chemistry, then heat capacity is termed as **molar heat** capacity.

$$C_{(T_2T_1)} = \frac{q}{T_2 - T_1}$$

As heat capacity varies with temperature, hence true molar heat capacity is defined by the differential equation

$$C = \frac{dq}{dt}$$

● As the heat capacity of a system, specially a gaseous system determined at **constant volume** is different from determined at **constant pressure**. In former W = 0 as there is no change in volume. Hence from the first law of thermodynamics

$$\Delta U = q_V$$

$$C_{V(T_2T_1)} = \left(\frac{q}{T_2 - T_1}\right)_V$$

$$= \left(\frac{\Delta U}{T_2 - T_1}\right)_V$$

Key Points

● The variation of heat of a reaction with temperature is given by **Kirchhoff's equations**

$\Delta U_2 - \Delta U_1 = \Delta C_V (T_2 - T_1)$, at constant volume

$\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$, at constant pressure,

or $\quad \left(\frac{d\,\Delta U}{dt}\right)_V = \Delta C_V$ and $\left(\frac{d\,\Delta H}{dt}\right)_P = \Delta C_P$

● If molar heat capacities of products and reactants are same, then the **heat of a reaction** is independent of temperature.

● The molar heat capacities of solids are almost constant and hence the **heat of reactions** involving solids are almost independent of temperature.

● For an ideal gas the internal energy (U) depends on temperature. Hence if temperature is constant (isothermal process), the internal energy remains constant and hence, $\Delta U = 0$.

We know that $\Delta H = \Delta U + \Delta n\,RT$ and since for isothermal process ΔT as well ΔU are equal to zero and hence, $\Delta H = 0$

● **Calculation of W and q for isothermal process.** According to first law, $\Delta U = q + W$. Now $\Delta U = 0$ and hence $W = -q$. It means work is done at the expanse of heat absorbed.

● For an **adiabatic expansion** $q = 0$, i.e., heat is neither allowed to enter or leave the system and hence $\Delta U = 0 + W$, i.e., $W = \Delta U$, during such expansion work is done by system on surroundings 'W' is $-ve$ and consequently ΔU is also $-ve$, i.e., decrease in internal energy and fall in temperature.

● During **adiabatic compression** 'W' is $+ve$ and ΔU will also be $+ve$ consequently rise in temperature. Since work is done on the system by surroundings, the work is stored in the system in the form of increase in energy.

● At constant pressure, there is change in volume and some work is done by the system and hence

$$C_{P(T_2 T_1)} = \left(\frac{q}{T_2 - T_1}\right)_P$$

$$= \left(\frac{\Delta H}{T_2 - T_1}\right)_P$$

● $C_P - C_V$ = work done by one mole of the gas in expansion when heated through 1°C at constant pressure. The work done by one mole of an **ideal gas** in expansion at constant pressure when heated by 1°C is equal to R, *i.e.*, 1·987 cal or 8·314 J.
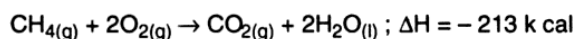
$$\boxed{C_P - C_V = R}$$

Kinds of Heat of Reactions

● **Heat of formation**—The quantity of heat evolved or absorbed when one mole of a compound is formed from its elements. For example :

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)} ; \Delta H_f = -68 \text{ k cal}$$
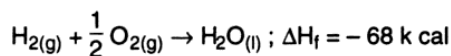
● **Heat of combustion**—The quantity of heat evolved when one mole of substance is completely oxidised. For example :

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} ; \Delta H = -213 \text{ k cal}$$

● **Heat of solution**—The quantity of heat evolved or absorbed when one mole of a **solute** is dissolved completely in large excess of solvent, so that further dilution does not produce any heat change. For example :

$$HCl_{(g)} + nH_2O_{(l)} \rightarrow HCl_{(aq)} ; \Delta H = -39·3 \text{ k cal}$$
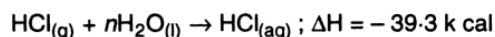
● **Heat of neutralisation**—The quantity of heat evolved when one equivalent of an acid is completely neutralised by one equivalent of base in dilute solution

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} ;$$

$$\Delta H = -13·68 \text{ k cal}$$
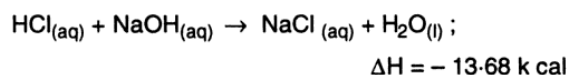
Actually heat of neutralisation is merely the heat of formation of water from H^+ and OH^- ions *i.e.*,

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} ; \Delta H = -13·7 \text{ k cal}$$
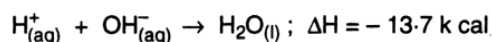
| Note |—The heat of neutralisation of weak acid or weak base is somewhat less than 13·7 k cal because some energy is used up to dissociate these weak electrolytes.

➡ The heat of neutralisation of CH_3COOH by NaOH is found to be −13·2 k cal. Some heat is utilised in dissociation of weak acid (CH_3COOH). Thus, the heat of dissociation of CH_3COOH is given as

$$-13·7 + x = -13·2 \text{ k cal}$$

$$x = 0·5 \text{ k cal}$$

➡ Similarly the heat of dissociation (x) for weak base NH_4OH can be calculated by determining the heat of neutralisation of NH_4OH by HCl (− 12·3 k cal)
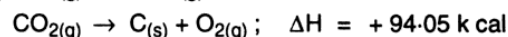
$$-13·7 + x = -12·3 \text{ k cal}$$

$$x = 1·4 \text{ k cal}$$

Laws of Thermochemistry

● **Lavoisier and Laplace law**—The amount of heat required to decompose a compound into its elements is always equal to the heat of formation of that compound from its elements.

● This law can also be stated as : The heat evolved in a particular reaction is equal to heat absorbed when reaction is reversed. Thus, the thermochemical equation can be reversed only by changing the sign of heat evolved or absorbed. For example :

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} ; \quad \Delta H = -94·05 \text{ k cal}$$

$$CO_{2(g)} \rightarrow C_{(s)} + O_{2(g)} ; \quad \Delta H = +94·05 \text{ k cal}$$

● **Hess's law of constant heat summation**—The amount of heat evolved or absorbed in a chemical change is always same whether the process takes place in one step or in several steps. If a system changes from A to B in single step

$$A \rightarrow B ; \Delta H = Q$$
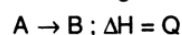
Now if same system changes from A to B in three steps
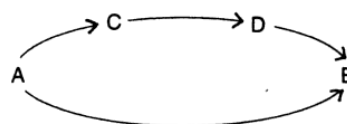
then : $A \rightarrow C ; \Delta H = q_1$

$$C \rightarrow D ; \Delta H = q_2$$

$$D \rightarrow B ; \Delta H = q_3$$

Thus according to Hess's law

$$\boxed{Q = q_1 + q_2 + q_3 \dots}$$

● **Application of Hess's law**—Following are important applications—

(a) Thermochemical equations may be multiplied, added, divided or subtracted just like algebraic equations.

(b) Hess's law helps in calculating heat of formation and heat of combustion of compounds.

(c) Hess's law is used in calculating the heat of transition.

● **Bond energy**—In molecules involving more than one bond of same type, average value is taken as bond energy. For example CH_4 has four C—H bonds and each bond is associated with different enthalpy change and hence C—H bond energy is taken as average value.

$$CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)} ; \Delta H = 398 \text{ k cal}$$
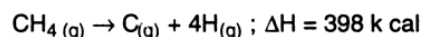
Hence, C—H bond energy $= \dfrac{398}{4} = 99·5$ k cal

Bond energy finds use in calculation of enthalpies of reactions, enthalpies of formation of compounds and resonance energy.

● **Limitations of first law of thermodynamics**—The first law stands fully verified because no transformation has been observed which violates the principle of conservation of energy.

However, it is also observed that all the processes have natural direction, *i.e.*, a direction in which they take place **spontaneously.**

First law fails to explain as to why these reactions take place spontaneously in one direction but not in other.

Closer-Look

● We always find that hot tea in a cup spontaneously cools down by losing heat to surroundings. The first law is obeyed as energy is lost by system.

● The first law will also be obeyed in the reverse process where surrounding loses energy and system gains it. If such a process takes place spontaneously, we will have an amusing situation where a cup of tea at room temperature becomes hot on its own.

● In short, the cooling of a hot body in a room proceeds spontaneously in one direction but not in the other though both the directions are allowed by the first law.

● A cup of tea at room temperature can be made hot by heating but this is not a spontaneous process because an outside agency (burner) has to be used.

● The direction of spontaneous process can be understood by the concept of **entropy** introduced by **second law of thermodynamics**.

Second Law of Thermodynamics

Following are important statements of second law of thermodynamics—

➡ It is impossible to construct a machine working in cycles which can convert heat completely into equivalent amount of work without inflicting any additional change elsewhere (**Planck's** definition).

➡ It is impossible to construct a heat engine operating in cycles which can produce work at the expense of heat obtained from thermal reservoir (**Kelvin** definition).

➡ It is impossible for self acting machine unaided by any external agency to transform heat from colder body to hotter body, (**Clausius** definition).

➡ Work can always be converted into heat but conversion of heat into work does not always take place in all conditions.

● **Carnot cycle or Carnot engine**—In 1924 S. Carnot (a French engineer) observed that maximum conversion of heat into work occurs in a cyclic process in which all steps are carried out reversibly. Such a cyclic process is called **Carnot cycle** and engine working on this basis is called **Carnot engine.**

● Efficiency of a heat engine is defined as the fraction (η) of heat absorbed by the engine which it can convert into work,

$$\eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} = \frac{W}{q_2}$$

q_2 = heat absorbed at temperature T_2 and q_1 is heat evolved at lower temperature T_1. Since $\frac{T_2 - T_1}{T_2}$ is less than unity and hence efficiency of engine is always

less than unity. In fact no heat engine has so far been constructed whose efficiency is equal to unity.

● **Entropy and Spontaneity**—The direction of a spontaneous process and the fact that it eventually reaches equilibrium, can be understood on the basis of entropy concept introduced through second law of thermodynamics.

● **Entropy (S)** like **internal energy** and **enthalpy**, is a state function. When state of a system changes, entropy also changes. The change in entropy (ΔS) is defined as :

$\Delta S = \frac{q_{rev}}{T}$ (Here q_{rev} means heat is being supplied isothermally and reversibly)

If 'q' is expressed in joule (J) and temperature in Kelvin (K), the entropy change (ΔS) is given as **JK^{-1}**.

● Entropy (S) is a measure of randomness or disorder in the system. For a given substance, **solid state** has lowest entropy and **gaseous state** is of highest entropy and the **liquid state** intermediate between two.

● In an **isolated system** there is no exchange of heat or matter between system and surroundings. Therefore, for a spontaneous process in an isolated system, the change in entropy (ΔS) is positive. Spreading of ink droplet in a beaker filled with water and mixing of two gases are examples of isolated systems.

Key Points

● An **irreversible spontaneous reaction** is accompanied by an increase in the value of ΔS, *i.e.*, for such a reaction ΔS has a +ve value.

$$\Delta S > \frac{q}{T} \quad \text{or} \quad \Delta S > 0.$$

● A **non-spontaneous reaction** is accompanied by a decrease in value of ΔS, *i.e.*, ΔS has −ve value ($\Delta S < 0$).

● For a **reversible spontaneous reaction** ΔS is equal to zero. ($\Delta S = 0$).

● When a solid melts then

$$\Delta S_{Fusion} = \frac{\Delta H_{Fusion}}{\text{Melting temperature}}$$

● When a liquid vaporises then

$$\Delta S_{Vap} = \frac{\Delta H_{Vap}}{\text{Temp. of vaporisation}}$$

● In general ΔS for any phase transition can be represented as

$$\Delta S_{Transition} = \frac{\Delta H_{Transition}}{\text{Temperature of transition}}$$

● Work done by expansion is given by the product of P^{ext} ΔV. If P^{ext} is only infinitesimally smaller than pressure of gas (P), then expansion is *reversible* and maximum work is done by gas.

● If external pressure (P^{ext}) is smaller than gas pressure (P) expansion is rapid, *i.e.*, *irreversible* and work done for same amount of expansion will be much smaller.

● If external pressure is zero (gas expands in vacuum), the work done will be zero.

- When a system is not isolated e.g., a cup of tea, we have to consider entropy changes of system and surroundings. Thus

$$\Delta S_{(Total)} = \Delta S_{(system)} + \Delta S_{(surroundings)}$$

For a process to be spontaneous $\Delta S_{(Total)}$ must be positive, i.e.,

$$\Delta S_{Total} = \Delta S_{(system)} + \Delta S_{(surroundings)} > 0.$$

- When a system is in equilibrium, the entropy is maximum. The mathematical condition for entropy (S) to be maximum is that change in entropy (ΔS) is zero.

$$\Delta S = 0 \text{ (at equilibrium)}$$

All the spontaneous chemical reactions proceed until an equilibrium is attained. Once equilibrium is attained the concentration of reactants and products do not change.

- **Entropy** is an extensive property as its value depends upon amount of substance involved. Entropy change (ΔS) depends upon initial and final state of a system.

- **Standard entropy** is the entropy of 1 mole of a substance in pure state at 1 atm. pressure and 25°C.

- Since entire universe is undergoing spontaneous change, the second law can be most concisely stated as : **The entropy of the universe is constantly increasing.**

ΔH	ΔS	ΔG	Remark about reaction
(a) Negative	Positive	Negative	Spontaneous at all temperatures
(b) Positive	Negative	Positive	Non-spontaneous at all temperatures
(c) Negative	Negative	Negative at low temp.	Spontaneous
		Positive at high temp.	Non-spontaneous
(d) Positive	Positive	Positive at low temp.	Non-spontaneous
		Negative at high temp.	Spontaneous

- Relation between standard free energy ($\Delta G°$) and equilibrium constant (K) of a reaction is as :

$$\boxed{\Delta G° = - RT \ln K \text{ or } \Delta G° = - 2.303 \, RT \log K}$$

- **Free energy (G) and work function (A)**

$$A = U - TS \quad \text{and} \quad G = H - TS$$
$$\Delta A = \Delta U - T\Delta S \quad \text{and} \quad \Delta G = \Delta H - T\Delta S$$

When the study is carried out reversibly at **constant T** and the heat absorbed is q_{rev}, then $\Delta S = \dfrac{q_{rev}}{T}$ or

$$T\Delta S = q_{rev}$$

$$\therefore \quad \boxed{\Delta A = \Delta U - q_{rev}}$$

From first law of thermodynamics ($\Delta U = q + W$) we have :

$$W_{rev} = \Delta U - q_{rev}$$

If during the change under consideration, work is done by the system, it will carry a negative sign so that

$$- W_{rev} = \Delta U - q_{rev}$$

$$\therefore \quad \Delta A = - W_{rev}$$
$$\text{or} \quad - \Delta A = W_{rev}$$

As the process is carried out reversibly, W represents the maximum work. Thus, decrease in function ($-\Delta A$) gives maximum work obtained from a system during a given change. Thus 'A' is known as work function.

- At **constant-pressure** we know $\Delta H = \Delta U + P\Delta V$.

$$\Delta G = \Delta H - T\Delta S$$
$$\Delta G = \Delta U + P\Delta V - T\Delta S$$
$$\text{or,} \quad \Delta G = \Delta A + P\Delta V$$
$$\text{or,} \quad \Delta G = - W_{rev} + P\Delta V \text{ or}$$
$$\boxed{- \Delta G = W_{rev} - P\Delta V}$$

- $-\Delta G$ gives maximum work obtainable from a system other than pressure-volume work at constant T and P. The work other than pressure-volume work (PΔV) is called **network**. Thus

$$\boxed{\text{Net work} = W_{rev} - P\Delta V = - \Delta G}$$

- In case of **galvanic cell**, free energy change (ΔG) is related to electrical work done in the cell. If E is the e.m.f. of the cell and 'n' mole of electrons are involved, the electrical work will be equal to nFE, where F is Faraday constant.

$$\Delta G = - nF \, E_{cell}$$

- **Standard free energy of formation** ($\Delta G_f°$) of a compound is defined as the change in free energy when 1 mole of the compound is formed from its constituent elements in their standard state

$$\Delta G°_f = \Sigma \Delta G_f° \text{ (Products)} - \Sigma \Delta G_f° \text{ (Reactants)}$$

- A reaction which is accompanied by decrease of free energy i.e., ΔG is –ve, is called **exergonic reaction**. Thus all spontaneous processes are exergonic. Similarly which are accompanied by increase in free energy i.e., ΔG is +ve, are **endergonic reactions**. Thus all non-spontaneous processes are endergonic.

Third Law of Thermodynamics

- At absolute zero temperature, the entropy of a perfectly crystalline solid is taken as zero.

- This law was first formulated by Nernst in 1906.

Points to Remember

- **Joule and Thomson effect**—When a real gas is allowed to expand adiabatically from a region of high pressure to lower one through a fine aperture, it accompanies by cooling, except H_2 and He which get warm up. During this process enthalpy remains constant, it is, therefore, called **iso-enthalpic** process.

- Actual change in temp. on expansion of a gas is expressed in terms of Joule-Thomson coefficient (μ), defined as :

$$\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_H}$$

Thus, μ is the temp. change in degrees produced by a drop of one atm. pressure when a gas expands under constant enthalpy.

- For cooling, μ = +ve (as ∂T as well ∂P are –ve)

  For heating, μ = –ve (∂T is +ve and ∂P is –ve)

  For neither cooling nor heating, μ = 0 (∂T = 0 for any value of ∂P)

- The temp. at which a real gas shows no cooling or heating effect on adiabatic expansion (μ = 0) is called **inversion temperature**. Below this gas shows cooling effect and above it heating effect.

- Most of the real gases have inversion temp. above room temp. H_2 and He both have inversion temperatures –80°C and –240°C respectively. This is the reason that they show heating effect at room temperature during adiabatic expansion.

- For ideal gases, μ = 0 at any temperature.

  Applications of First Law of Thermodynamics :

- For isochoric process (V is constant) ΔV = 0. Hence, $\Delta U = q + P\Delta V$ becomes

  $$\boxed{\Delta U = q_v}$$

- For a isobaric process (P is constant),

  $$\boxed{\Delta U = q_P - P\Delta V \text{ or } q_P = \Delta U + P\Delta V = \Delta H}$$

- For isothermal process (T is constant), for ideal gas $\Delta U = 0$. Under this condition,

  $$\boxed{W_{exp} = -2{\cdot}303\, n\, RT \log \frac{V_2}{V_1} = -2{\cdot}303\, n\, RT \log \frac{P_1}{P_2}}$$

- For adiabatic process, $q = 0$ and hence $\Delta U = W$

  but $\dfrac{\Delta U}{\Delta T} = C_v$

- $\therefore \Delta U = C_v\, \Delta T$

  $$\boxed{\text{Total work, } W = n\, C_v\, (T_2 - T_1)}$$

- Contrary to the expectations (i) when a rubber band is stretched, entropy decreases because the macromolecules get uncoiled and hence, arranged in more ordered manner, i.e., the randomness decreases. (ii) When an egg is boiled hard, entropy increases because denaturation occurs resulting into a change in protein from helical to random coiled form.

IMPORTANT NUMERICAL PROBLEMS

Q. 1. The heat of combustion of $CH_{4\,(g)}$ at constant volume at 298·2 K is found to be – 885389 J/mol. What will be the enthalpy change ?

Solution :

$$CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{(l)}\,;$$
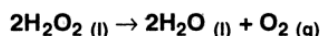$$\Delta E = -885389 \text{ J/mole}$$
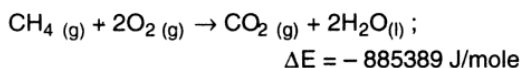
$$\Delta n = 1 - (1 + 2) = -2$$

$$\Delta H = \Delta U + \Delta n\, RT$$
$$= -885389 \text{ J mol}^{-1} + (-2)$$
$$[8{\cdot}3143 \text{ J mol}^{-1}\, K^{-1}] \times (298{\cdot}2\, K)$$
$$= -890{\cdot}348 \text{ k J mol}^{-1}$$

Q. 2. Calculate enthalpy change for the reaction. Is it endothermic or exothermic ?

$$2H_2O_{2\,(l)} \rightarrow 2H_2O_{(l)} + O_{2\,(g)}$$

Given : $\Delta H°_f (H_2O_{2(l)}) = -188 \text{ kJ mol}^{-1}$

$$\Delta H°_f (H_2O_{(l)}) = -286 \text{ kJ mol}^{-1}$$

$$\Delta H°_f (O_{2(g)}) = 0$$

Solution :

$$\Delta H° = \Sigma \Delta H°_f \text{ (Products)} - \Sigma \Delta H°_f \text{ (Reactants)}$$

$$\therefore \Delta H° = 2(-286) \text{ kJ mol}^{-1} + 0 - 2(-188) \text{ kJ mol}^{-1}$$
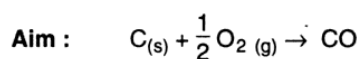
$$= -196 \text{ kJ mol}^{-1}$$

It is an exothermic reaction as $\Delta H°$ has negative value.

Q. 3. The enthalpies of combustion of carbon and carbon monoxide are –390 kJ mol^{-1} and –278 kJ mol^{-1} respectively. What will be the enthalpy of formation of carbon monoxide ?

Solution :

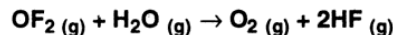**Given : (i)** $C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}\,; \Delta H = -390 \text{ kJ}$

(ii) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2\,(g)}\,; \Delta H = -278 \text{ kJ}$

Aim : $\qquad C_{(s)} + \frac{1}{2}O_{2\,(g)} \rightarrow CO$

Equation (i) – (ii) gives

$$\Delta H = -390 - (-278) = -112 \text{ kJ}$$

Q. 4. Calculate standard enthalpy change ($\Delta H°$) and standard internal energy change ($\Delta U°$) for the reaction at 298K.

$$OF_{2\,(g)} + H_2O_{(g)} \rightarrow O_{2\,(g)} + 2HF_{(g)}$$

Given : Standard enthalpies of formation of various compounds as :

$$OF_{2\,(g)} = +23{\cdot}0 \text{ kJ mol}^{-1}$$
$$H_2O_{(g)} = -241{\cdot}8 \text{ kJ mol}^{-1}$$
$$HF_{(g)} = -268{\cdot}6 \text{ kJ mol}^{-1}$$

Solution :

$$\Delta H° = \Sigma \Delta H°_f \text{ (Products)} - \Sigma \Delta H°_f \text{ (Reactants)}$$
$$= 2(-268{\cdot}6 \text{ kJ mol}^{-1}) - \{(+23{\cdot}0 \text{ kJ mol}^{-1}) + (-241{\cdot}8 \text{ kJ mol}^{-1})\}$$
$$= -318{\cdot}4 \text{ kJ mol}^{-1}$$

$$\Delta U° = \Delta H° - \Delta n\, RT$$
$$= -318{\cdot}4 \text{ kJ} - (1 \text{ mol})[8{\cdot}31 \text{ kJ/K mol}](298K)$$
$$= -318{\cdot}4kJ - 2476 \text{ J}$$
$$= -318{\cdot}4 \text{ kJ} - 2{\cdot}5 \text{ kJ} = -320{\cdot}9 \text{ kJ mol}^{-1}$$

Q. 5. The enthalpy change for the transition of liquid H_2O to steam is 40·8 kJ mol^{-1} at 273 K. What will be entropy change for the process ?

Solution :

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{40{\cdot}8 \times 1000 \text{ J mol}^{-1}}{273\, K}$$
$$= 109 \text{ J mol}^{-1}\, K^{-1}$$