

Thermodyna



As the values of energy required to break the chemical bonds and the energy evolved in the chemical bond formation during the above reactions are not the same, either the energy is absorbed or the energy is evolved.

When fuel like methane is combusted, then, at the end of certain chemical reactions the energy stored by its molecule is liberated as chemical energy. Like combustion of cooking gas and coal energy liberated in the air, when fuel is combusted in engine, the use of chemical energy is made in mechanical work; in a galvanic cell like dry cell energy is obtained in the same way. In the similar way, energy can be obtained with the help of interactions under certain conditions, from the different forms of energy. They can be transformed from one form to the other. The study of all these forms of energy is called thermodynamics. The laws of thermodynamics are concerned with the transformations of energy. They are associated with molecules in large proportion associated with macroscopic systems and a few molecules present in microscopic systems are not related to how the reaction occurs and with what rate. Thus, thermodynamics is independent of study of chemical kinetics. It depends on the energy transformation between initial state and final state. Laws of thermodynamics apply only when a system is in equilibrium or move from one equilibrium state to another equilibrium state. The macro factors like temperature, pressure etc. are unable to change the system in equilibrium with time. We shall try to obtain answers for some of the important questions with the help of thermodynamics.

It is important in chemistry to get answers to the following questions :

(i) Will the reaction occur between certain substances in definite conditions ?

(ii) If the reaction between these substances is possible, to what extent (proportion) will it occur ?

If the answers to these two questions can be obtained theoretically, the work of the chemist will be easier. We know that both graphite and diamond are the allotropes of carbon. Can graphite be transformed into diamond ? The answer to

this question, when examined from theoretical point of view is found to be positive. So the scientists got inspiration to transform graphite into diamond and now-a-days artificial diamonds are prepared and produced in a similar way. The science which can answer the chemical problems is called chemical thermodynamics.

In chemical thermodynamics, the changes in energy associated with physical and chemical reactions have been studied. This whole study is based on four basic laws. These four laws are known as the zeroth, the first, the second and the third law of thermodynamics. These laws are the conclusions obtained from the available experimental results. Not a single chemical reaction till present time is found to be the exception to these laws. Here, before we study the laws of thermodynamics, it is necessary to understand its background.

3.2 Basic Concepts of Thermodynamics

We are interested in the chemical reactions and energy exchange. For this, we shall discuss the basic concepts of thermodynamics.

3.2.1 System and Surrounding : An extremely small part of the universe which is separated from the remaining part of universe by a definite boundary and on which we note the observations of the experiments carried out by external changes is called system. The remaining part of the universe excluding the system is called surrounding. Surrounding means the part of the universe except the system. The system and the surrounding together makes the formation of universe viz. whether there is any reaction of hydrochloric acid (HCl) with washing soda (Na_2CO_3) ? We add few drops of hydrochloric acid on washing soda by taking it into a testtube and observe whether the reaction occurs or not. Here, the mixture of washing soda and hydrochloric acid is a system. Testtube is not included in the system. Testtube is the borderline of the system while the remaining universe which is in contact with system is surrounding of the system.

Types of the system : There are three types of systems depending on the exchange of energy and matter between system and surrounding. (i) Open system (ii) Closed system (iii) Isolated system.

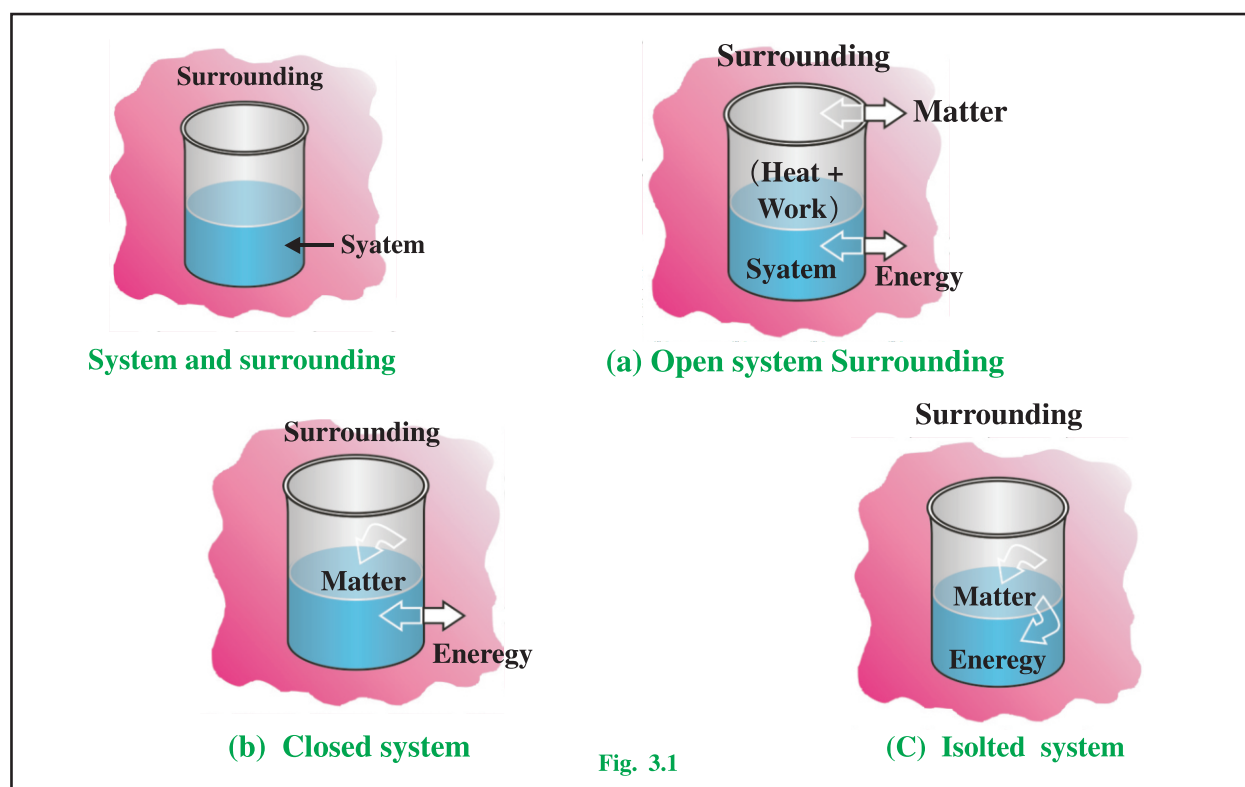
(i) Open system : The system in which the energy and the matter can go on its own from system to the surrounding or enter from surrounding to the system is called open system viz. If we place an ice cube in a saucer, it melts on its own absorbing heat from atmosphere and the water from saucer enters the atmosphere through evaporation. Hence, the ice cube placed in the open vessel saucer and the water in the saucer is an open system. Similarly a flame of the burner is also an open system.

(ii) Closed system : The system which can exchange energy on its own with surrounding but the exchange of matter on its own is not possible, is called a closed system.

of good quality provides its example at a particular moment, but after sometime, it provides the example of the closed system. Hence, it is difficult to find an example of an absolute isolated system.

3.2.2 Process : The conversion of state of system from one to another is called a process. During this conversion, if the temperature of the system does not change that is temperature remains constant, then, the process is called **Isothermal process** that is the system gain energy from the surrounding or releare the energy to the surrounding.

During the change in the system, if the system does not lose heat or does not



viz. The cold or hot water poured in the bottle and closed with a cork. The vessel in which this system is present must be energy conductor. The cooker used in household purposes is the closed system.

(iii) Isolated system : The system which is not able to exchange energy and matter on its own with surrounding is called an isolated system. In fact, formation of isolated system is not possible but the thermos flask of very good quality is the example of isolated system. The hot tea poured in a thermos flask

receive heat, then the process is called **Adiabatic process**.

If the system contains gaseous materials and the pressure of the system remains constant during the change, then that process is called **Isobaric process**.

3.2.3 Extensive and Intensive properties : Some properties of the substance depend on the quantity of the matter. These properties are known as **Extensive properties**. The mass of a substance, volume, enthalpy of formation, entropy, free energy, elevation in boiling points, depression in freezing point etc. are such

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3.2.7 Enthalpy (H) : The total amount of energy obtained from internal energy (U) of substance and energy obtained by product of pressure (P) and volume (V) is called enthalpy (H).

$$H = U + PV$$

If any reaction is carried out in an open vessel, then the reaction system is in direct contact with the atmosphere and so the pressure of constant atmosphere applies. Thus, any chemical reaction, when carried out at constant pressure, then the change in its energy is called enthalpy change (ΔH)

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

when H_p is enthalpy of products and H_r is enthalpy of reactants.

Thus, enthalpy is the change in heat at constant pressure.

3.3 Zeroth Law of Thermodynamics

When two diathermic (thermal conductor) substances at different temperatures come in contact with each other, then heat conducts on its own from the substance having higher temperature to substance having lower temperature. This conduction of heat continues till the temperatures of both the substances do not remain the same. When the temperatures of the two substances become the same, the conduction of heat does not take place in them. This condition (state) is called **thermal equilibrium**. Thus the procedure to obtain thermal equilibrium of any two diathermic substances is called **zeroth law of thermodynamics**.

When any person suffers from fever, the temperature of his body is measured by a thermometer. The thermometer comes in contact with the body of that person, the heat from human body enters into the mercury of the thermometer and the volume of the mercury increases. When the temperature of the body and the temperature of mercury become equal, the increase in the volume of mercury stops. Hence, it can be said that the temperature of the body and that of the mercury in the thermometer is the same. This condition (state) is known as thermal equilibrium. From the reading on the thermometer, fever can be measured.

3.4 First Law of Thermodynamics

The first law of thermodynamics, in fact, is the law of conservation of energy. This law can be expressed in different forms. **(i) The total quantity of energy in the universe is constant. (ii) Energy can neither be created nor can be destroyed but transformation of one form into another form can be possible.**

The change in internal energy of the system can be brought by two methods. (i) By adding heat to the system or removing the heat from the system. (ii) By working on the system or working by the system.

Here, heat and work are on one side while energy on the other. It is necessary to understand the important difference between these two.

The heat and work indicate the process, which is not a state function, while energy is the property associated with any equilibrium and it is state function.

3.4.1 Symbolic equation of the First law of thermodynamics : Suppose, the internal energy of any system, at a definite equilibrium state is U_1 . If this system after undergoing a reaction attains a new equilibrium state having internal energy U_2 , then, the heat absorbed by the system or heat lost by the system during this reaction is q . Now, if the work done (W) is on the system or the work done by the system is W , then according to First law of thermodynamics :

$$U_2 = U_1 + q + W \quad \text{OR}$$

$$U_2 - U_1 = q + W$$

Now, writing change in energy

$$U_2 - U_1 = \Delta U$$

$$\Delta U = q + W$$

This equation is the symbolic form of the First law of thermodynamics.

3.4.2 Mathematical form of the First law of thermodynamics : In the symbolic equation of the First law of thermodynamics, when it is used for the calculation, then, generally, (+) positive and (–) negative signs are connected with q and W .

- (i) If heat is lost during process in the system, the value of q is negative (–) or the value of exothermic reaction is always negative (–).
- (ii) If heat is added during the process in the system, the value of q is positive (+) or the value of q for endothermic reaction is always positive (+).
- (iii) If the work is done on the system, then the value of W is always positive (+).
- (iv) If the work is done by the system, then the value of W is always taken negative (–).

If the internal energy of the system during any process remains constant then $\Delta U = 0$. i.e., $q + W = 0$ or $q = -W$. This indicates that the total heat absorbed by system during the process is completely used up in the work.

Internal energy is the state function. If the system follows any path during change from one state to another, even then the value of ΔU does not change, but q and W are not being state functions, their values do not depend upon how one form of the system changes into the other.

Example 1 : A system receives 224 Joule heat and does work of 156 Joule. Calculate the change in the internal energy.

Solution : System receives the heat

$$\therefore q = 224 \text{ Joule}$$

Work done by the system

$$\therefore W = -156$$

According to First law of thermodynamics

$$\Delta U = q + W$$

$$\Delta U = 224 - 156 = 68 \text{ Joule}$$

3.4.3 Work and the First law of thermodynamics : It is necessary to have information about work before we understand the applications of the First law thermodynamics. When can we say that work is done ? When on any substance, force is applied at a point where it is applicable and the point moves in the direction of the force applied, then it is said that work is done.

In chemistry mainly two types of works are observed :

(i) Electrical work and (ii) Mechanical work.

Electrical work is important in the reaction between ions in the system. The mechanical work is important in which, during the reactions there is change in volume in presence of external pressure. The systems which possess gaseous state, for them, mainly, mechanical work is more important. If gaseous substances are associated with the chemical reaction, then there is change in volumes in most of the reactions under constant external pressure. If the volume of this type of system increases during reaction, then work is done by the system and if the volume decreases, then work is done on the system.

If the initial volume of the system is V_1 and the final volume is V_2 and the external pressure P applied on the system is constant, then, the work done by the system due to change in volume can be shown by the following equation :

$$\begin{aligned} W &= P(V_2 - V_1) \\ &= P\Delta V \end{aligned}$$

Hence, if the work done during the reaction is only of PV type $q = q_p$ and if the work is done by the system, then $W = -P\Delta V$.

According to symbolic equation of First law of thermodynamics,

$$\Delta U = q + W$$

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

But, if there is no change in the volume of the system during chemical reaction, $\Delta V = 0$. Hence, $\Delta U = q_v$. Thus, in the reactions occurring at constant volume, the value of change in internal energy of the system is equal to the heat received by the system or heat lost by the system at constant volume.

Example 2 : At one bar pressure, the volume of a gas is 0.6 litre. If the gas receives 122 Joules of heat at one atmosphere pressure, the volume becomes 2 litres, then calculate its internal energy. (1 litre bar = 101.32 Joule)

Solution : Pressure $P = 1$ bar

Initial volume of gas $V_1 = 0.6$ litre

Final volume of gas $V_2 = 2$ litre

$$\begin{aligned} \Delta V &= V_2 - V_1 \\ &= 2.0 - 0.6 = 1.4 \text{ litre} \end{aligned}$$

Now, $W = P \Delta V$

$$W = 1 \times 1.4 = 1.4 \text{ litre bar}$$

But 1 litre bar = 101.32 joule

$$\therefore W = 1.4 \times 101.32 = 141.85 \text{ joule}$$

Here, the work is done by the system

$$\therefore W = - 141.85 \text{ joule}$$

The heat obtained by the system

$$q = 122 \text{ joule}$$

According to First law of thermodynamics

$$\Delta U = q + W$$

$$= 122 - 141.85 = - 19.85 \text{ joule}$$

3.4.4 Enthalpy and First Law of Thermodynamics : Generally, the chemical reactions occur in open vessels at constant pressure. A new state function has to be defined for change in energy occurring in this type of process. This new state function is called enthalpy (H). The relation between enthalpy (H) and internal energy (U) is shown by the following equation :

$$H = U + PV$$

Hence, if there is a change in state of a system, the change in its enthalpy can be shown by the following equation.

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

If the reaction occurs at constant pressure, then $\Delta P = 0$. Hence

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

But, according to symbolic equation of the First law of thermodynamics, if the reaction occurs at constant pressure, then work done by the system is only of PV type and so $q = q_p$ and $W = - P\Delta V$.

$$\therefore \Delta U = q_p - P\Delta V$$

Hence, the equation,

$$\Delta H = \Delta U + P\Delta V \text{ will be as follows.}$$

$$\Delta H = (q_p - P\Delta V) + P\Delta V$$

$$\therefore \Delta H = q_p$$

Thus, the change in enthalpy of the system in which chemical reactions occur, at constant pressure is equal to the value of the heat gained or lost by the system.

Hence, it is apparent that at constant temperature and constant pressure, the enthalpy of the substance is constant.

Reaction	Change in internal energy	Change in enthalpy
Exothermic	$\Delta U = -Ve$	$\Delta H = -Ve$
Endothermic	$\Delta U = +Ve$	$\Delta H = +Ve$

3.4.5 Mole and First Law of Thermodynamics : If the number of gaseous molecules of the reactants is changing because of chemical reaction and the reaction is occurring at constant pressure, then the volume of the system changes.

Suppose, the volume of the system has n_1 moles of gaseous reactants at constant pressure P and constant temperature T. Now, if under constant pressure and constant temperature the volume of n_2 moles of gaseous products, becomes V_2 , then according to ideal gas equation,

$$PV = nRT$$

$$PV_1 = n_1RT \text{ and } PV_2 = n_2RT$$

$$PV_2 - PV_1 = n_2RT - n_1RT$$

$$P(V_2 - V_1) = (n_2 - n_1) RT$$

$$P\Delta V = \Delta n_g RT$$

Here, Δn_g shows the difference between total number of moles of gaseous products and the total number of moles of gaseous reactants. Now, according to the equation showing relation between change in internal energy and change in enthalpy,

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

$$\Delta H = \Delta U + \Delta n_g RT \quad \text{OR}$$

$$\Delta U = \Delta H - \Delta n_g RT$$

If the total number of moles of gaseous reactants and gaseous products is same, then the difference will be zero;

$$\Delta n_g = 0 \text{ and so } \Delta H = \Delta U$$

If the total number of moles of gaseous reactants is more than the total number of moles of gaseous products;

$$\Delta n_g < 0, \text{ and hence, } \Delta H < \Delta U$$

If the total number of moles of gaseous products is less than the total number of moles of gaseous reagents $\Delta n_g > 0$, and hence, $\Delta H > \Delta U$

If, $\Delta n_g \neq 0$, then $\Delta H \neq \Delta U$

Example 3 : The specific volumes of ice and water are 1.089 and 1.0 ml gm^{-1} at 273 K temperature. The molar heat of fusion (melting) of ice is 6.025 kJ mole^{-1} at 273 K temperature and 1 bar pressure. If 90 gram ice melts at 273 K temperature and 1 bar pressure, water is produced at that temperature, then, calculate the values of ΔH and ΔU for the process. (1 litre bar = 101.32 Joule)

Solution :

$$\begin{aligned} \therefore \text{Moles of ice} &= \frac{\text{Weight of ice}}{\text{Molecular mass of ice}} \\ &= \frac{90 \text{ gram}}{18 \text{ gram mole}^{-1}} \\ &= 5 \text{ moles} \end{aligned}$$

When 1 mole of ice melts at standard pressure 6.025 kilojoule heat is absorbed.

$$\begin{aligned} \therefore \text{When 5 moles of ice melts} \\ &= 5 \text{ mole} \times 6.025 \text{ kilojoule mole}^{-1} \\ &= 30.125 \text{ kilojoule} \\ &= 30125 \text{ Joule heat will be absorbed.} \end{aligned}$$

At, constant pressure,

$$\therefore \Delta H = q_p = 30125 \text{ Joule}$$

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

$$= \Delta U + P(V_2 - V_1)$$

$$\therefore \Delta U = \Delta H - P(V_2 - V_1) = q_v$$

Here, $V_1 = \text{Volume of ice};$

$V_2 = \text{Volume of water}$

Volume of 1 gram ice = 1.089 millilitre

$$\therefore \text{Volume of 90 gram ice } (V_1)$$

$$= 90 \times 1.089 = 98 \text{ millilitre}$$

Volume of 1 gram water = 1 millilitre

$$\therefore \text{Volume of 90 gram water } (V_2)$$

$$= 90 \times 1 = 90 \text{ millilitre}$$

Here the change in volume of the system

$$\Delta V = V_2 - V_1$$

$$= 90 - 98 = -8 \text{ millilitre}$$

$$= -0.008 \text{ litre}$$

$$P(V_2 - V_1) = 1 \times -0.008$$

$$= -0.008 \text{ litre bar}$$

Now, 1 litre bar = 101.32 joule

$$\therefore -0.008 \text{ litre bar}$$

$$= 101.32 \text{ joule} \times (-0.008) = (-0.81) \text{ joule}$$

According to the above equation

$$\Delta U = q_v = \Delta H - P(V_2 - V_1)$$

$$= 30125 - (-0.81)$$

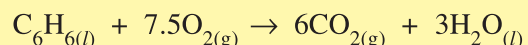
$$= 30125 + 0.81 \text{ Joule (0.81 joule is}$$

negligible in comparison to 30125)

$$\therefore \Delta U = 30125 \text{ joule}$$

Example 4 : The heat associated with combustion of liquid benzene, at constant volume is $-3268 \text{ kilojoule mole}^{-1}$. Calculate the change in enthalpy, when this reaction occurs at 300 K temperature ($R = 8.314 \text{ joule mole}^{-1} \text{ kelvin}^{-1}$)

Equation :



Solution : Here, the change in heat at constant volume,

$$q_v = \Delta U = -3268 \text{ kilojoule mole}^{-1}$$

$$\begin{aligned} \Delta n_g &= (\text{Total number of moles of gaseous} \\ &\quad \text{products}) - (\text{Total number of moles} \\ &\quad \text{of gaseous reactants}) \end{aligned}$$

$$= 6 - 7.5 = -1.5 \text{ mole}$$

$$T = 300 \text{ K, } R = 8.314 \text{ Joule}$$

$$= 8.314 \times 10^{-3} \text{ kilo joule mole}^{-1} \text{ kelvin}^{-1}$$

Now, according to the equation

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

$$\begin{aligned} \therefore \Delta H &= -3268 + (-1.5 \times 8.314 \times 10^{-3} \times 300) \\ &= -3268 - 3.74 = -3271.74 \text{ kJmole}^{-1} \end{aligned}$$

Example 5 : 1 mole of an ideal gas is filled in a cylinder at 300 K temperature and 10 bar pressure. This gas leaks in atmosphere due to leakage in the valve of the cylinder, then (What work should be done in the diffusion of gas under this condition ?) calculate the values of ΔH and ΔU for this process. (1 litre bar = 101.32 joule) (Take $R = 0.082$)

expansion or contraction of
 at temperature takes place,
 by and the enthalpy of the

$\Delta U = 0$ and $\Delta H =$
 the gas $w = P$
 change in volume
 of the moles of
 expansion will

nR
 $1 \times 8.314 \times 2 \times 30$
 pa $2 \times 30 = 2.46$
 liter expansion V

$1 \times 8.314 \times 32 \times 30$
 ans on 24.2

(1)

2.46×22.14

the gas $W = P$

$14 = 2.14$ litre

$r = 10.32$ joule

$2.46 = 243.23$ joule

is done by

Calculate the ΔH of
 following reaction
 314 joule)

(e) $\Delta H = 1.314$ kilojoule

Solution
 $\Delta H = n_p \times 314$
 $2 - 1 = 1$
 $\Delta H = 30 \times 314$
 $= 9420$ joule
 $= 9.42 \times 10^3$ joule

also cannot be obtained from the First law of thermodynamics. This point can become clear from the following examples of physical change.

(i) If an ice-cube is kept in a saucer, at room temperature, it melts by absorbing heat from atmosphere and the heat absorbed by the ice becomes equal to the heat lost by the atmosphere. This process occur on its own and obeys the first law. In the reaction opposite to this, if the water in the saucer loses heat and changes into ice, then again the First law of thermodynamics will be obeyed, but this does not occur on its own.

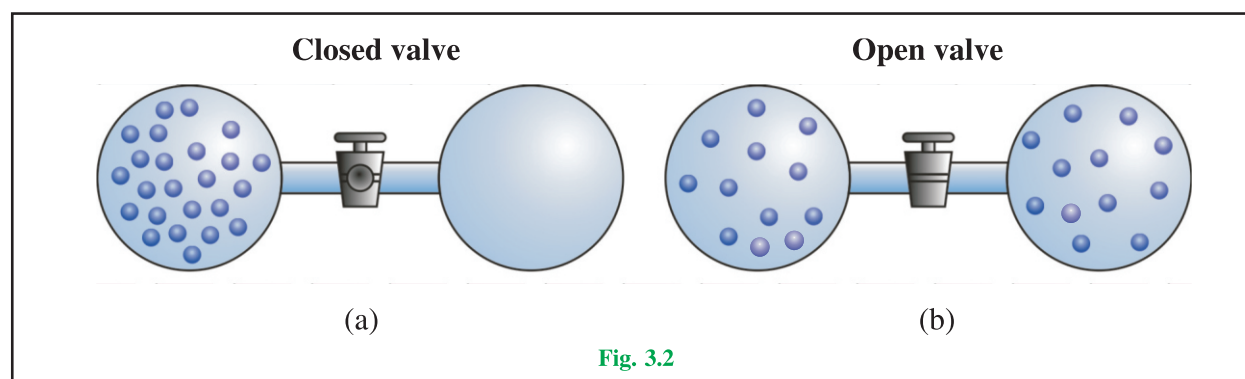


Fig. 3.2

Similarly, the hot tea kept in saucer gets cold on its own, but if the cold tea becomes hot on its own, then the First law is obeyed. But, here also, this reaction is not possible on its own.

(ii) As shown in the Figure 3.2, if one bulb filled with gas is connected with an evacuated bulb and on opening the valve in the tube connecting the two bulbs, the gas from one bulb will diffuse into the second bulb till the pressure of both the bulbs is not same. This reaction occurs on its own. This system also follows the First law of thermodynamics. Now, if the gas in one of the bulbs diffuses into the second bulb and attains its original state, then prodction of vacuum in the other bulb can be imagined. In this also, the First law is obeyed but this does not occur on its own.

(iii) If a drop of ink is dropped in a beaker containing water, the drop of the ink diffuses on its own throughout the water in the beaker and the solution becomes coloured. Is it possible to have reaction opposite to this ? Is the first law obeyed ?

Now, for the experience of chemical change we take the following example :

On mixing equal volumes and equal concentrations of hydrochloric acid (HCl) and

sodium hydroxide (NaOH), neutralisation reaction will occur on its own and sodium chloride and water will be produced. 56 kilojoule mole⁻¹ energy is released in this exothermic reaction. This reaction occurs on its own, but by dissolving sodium chloride in water and supplying 56 k Joule mole⁻¹ heat to it, sodium hydroxide (NaOH) and hydrochloric acid (HCl) cannot be obtained by reverse reaction on its own. Thus, in this chemical reaction, the First law is obeyed but reverse reaction does not occur on its own.

Thus, the prediction for any reaction to occur on its own cannot be done on the basis of the

First law of thermodynamics. To get this information, the Second law of thermodynamics is useful.

3.5 Heat Capacity

Enthalpy is the state function only for measuring the changes in heat of the system at constant pressure. This state is not useful for determining changes in energy at constant volume. Hence, a new function becomes necessary to explain the relation between temperature and changes in heat at constant pressure or at constant volume. This new function is called heat capacity. It is not a state function.

The quantity of heat required for increase in temperature by 1 °C of any substance is called heat capacity (C) of that substance.

If the temperature of the substance is increased by 1 °C at constant volume, the heat capacity is expressed as C_v , and if the temperature of the substance is increased by 1 °C at constant pressure, the heat capacity can be expressed as C_p . There is no much difference in heat capacities C_p and C_v of liquid and solid substances, but in gaseous substances, this difference is observed to a greater extent.

When the initial temperature T_1 of a sample of gaseous substance is changed to temperature T_2 , then the relation between heat (q), heat capacity (C) and difference in temperature ($T_2 - T_1$) is shown by the following equation.

$$q = C \times (T_2 - T_1) \quad (T_2 - T_1) = \Delta T$$

$$C = \frac{q}{\Delta T}$$

$$\therefore \text{Heat Capacity} = \frac{\text{Absorbed heat}}{\text{Difference in temperature}}$$

The unit of heat capacity is joule kelvin⁻¹.

The heat capacity is proportional to the quantity of the substance and so it is an extensive property. Hence, sometimes specific heat capacity and molar heat capacity are used in chemistry.

Specific Heat Capacity : The quantity of heat required for increase of temperature of 1 gram substance by 1°C is called specific heat capacity.

\therefore Specific heat capacity =

$$\frac{\text{Absorbed heat}}{\left(\text{Difference in temperature}\right) \times \left(\text{Weight of substance in gram}\right)}$$

The unit of specific heat capacity is joule kelvin⁻¹ gram⁻¹.

Molar Heat Capacity : The quantity of heat required for increase of temperature of 1 mole substance by 1°C is called molar heat capacity.

\therefore Molar heat capacity =

$$\frac{\text{Absorbed heat}}{\left(\text{Difference in temperature}\right) \times (\text{mole})}$$

The unit of molar heat capacity is joule kelvin⁻¹ mole⁻¹.

3.5.1 Relation between C_p and C_v : The heat capacity (C_p) for the temperature change at constant pressure.

$$C_p = \frac{q_p}{\Delta T} \quad \text{and } q_p = C_p \times \Delta T = \Delta H$$

The heat capacity (C_v) for temperature change at constant volume

$$C_v = \frac{q_v}{\Delta T} \quad \text{and } q_v = C_v \times \Delta T = \Delta U$$

As studied earlier, for 1 mole ideal gas,

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

$$PV = nRT$$

Hence, for 1 mole $PV = RT$

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

$$\Delta H = \Delta U + R\Delta T$$

Putting the value of ΔH and ΔU

$$C_p \Delta T = C_v \Delta T + R\Delta T$$

$$\therefore C_p = \frac{(C_v + R)\Delta T}{\Delta T}$$

$$\therefore C_p = C_v + R$$

$$\therefore C_p - C_v = R$$

Similarly the ratio of C_p and C_v i.e. C_p/C_v will be constant which can be expressed as γ (gamma).

$$\therefore C_p / C_v = \gamma \text{ (gamma)}$$

where γ is a constant. The value of γ for ideal gas is 1.4.

3.5.2 Enthalpy of reaction : When a chemical reaction occurs at constant pressure and constant temperature, the change in heat is called enthalpy change ΔH or heat of reaction.

To understand the characteristics of the reaction, scientist in practice express heat as standard enthalpy change (ΔH^0). For this, it is necessary to know the standard enthalpy of the elements and compounds. In scientific practice, 1 bar pressure and 298 K temperature are considered as standard states. The element or compound whose solid, liquid or gaseous form is stable at 1 bar pressure and 298 K temperature, it is called a standard state.

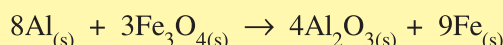
Solid elements sodium, copper, silver etc. are accepted as standard states. The gaseous elements like H, N, O and Cl are taken in the form of their diatomic molecules H_2 , N_2 , O_2 and Cl_2 respectively as standard state. The elements which are available in allotropic forms, their most stable allotrope is considered as standard state, viz., graphite allotrope for carbon and rhombic sulphur allotrope in standard state. The enthalpy of the compound in standard state is mentioned as standard enthalpy H^0 .

The value of standard enthalpy (H^0) of any element is considered as zero. Starting from the standard forms of the reactants and bringing the

products obtained at the end of chemical reaction in standard state, the value of total change in the enthalpy during the reaction is called standard enthalpy change of the reaction (ΔH^0). This standard enthalpy change is called "Heat of reaction". Its value is expressed in kilojoule.

Example 7 : In the following reaction, the standard enthalpies of $\text{Al}_2\text{O}_{3(s)}$ and $\text{Fe}_3\text{O}_{4(s)}$ are -1669.4 kilojoule mole^{-1} and -1117 kilojoule mole^{-1} respectively. What is the enthalpy change of the reaction ?

Reaction :



Solution :

$$\Delta H^0 = (\text{Total enthalpy of products}) - (\text{Total enthalpy of reactants})$$

$$\Delta H^0 = (4 \times \Delta H^0_{\text{Al}_2\text{O}_3} + 9 \times \Delta H^0_{\text{Fe}}) - (8 \times \Delta H^0_{\text{Al}} + 3 \times \Delta H^0_{\text{Fe}_3\text{O}_4})$$

$$\therefore \Delta H^0 = [4(-1669.4) + 9(0)] - [8(0) + 3(-1117)]$$

The enthalpy of elements Al and Fe are taken to be equal to zero as they are in elemental forms.

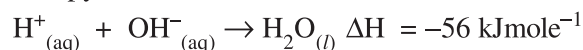
$$\begin{aligned} \therefore \Delta H^0 &= -6677.6 - (-3351) \\ &= -6677.6 + 3351 \\ &= -3326.6 \text{ kilojoule} \end{aligned}$$

\therefore Enthalpy of reaction = -3326.6 kilojoule

Enthalpy of Neutralisation : The experimental results show that when 1 mole dilute aqueous solutions of strong acids HCl, H_2SO_4 or HNO_3 are neutralised by 1 mole dilute aqueous solutions of strong bases like NaOH or KOH one mole of salt and one mole water are formed, with 56 kilojoule heat is produced which is known as enthalpy of neutralisation. In short, when one equivalent weight of any strong base in its dilute solution neutralises one equivalent weight of any strong acid in its dilute solution, the heat produced is called enthalpy of neutralisation. The standard enthalpy of neutralisation is constant equal to 56 kilojoule mole^{-1} .

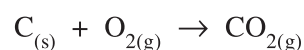
In neutralisation experiment dilute solutions are used so that acid and base are completely dissociated. In neutralisation reaction between acid and base the net reaction is the formation of $\text{H}_2\text{O}_{(l)}$ by reaction of $\text{H}^+_{(aq)}$ of the acid and $\text{OH}^-_{(aq)}$ of the base. Hence, standard enthalpy change in the reaction between these two ions is called standard enthalpy of neutralisation. Thus,

in neutralisation of any strong acid with any strong base, the net reaction being same, the value of enthalpy of neutralisation remains constant.



Enthalpy of Formation $\Delta_f H^0$: When one mole of compound is formed under standard conditions from elemental state of constituent elements, thermal changes is called standard enthalpy of formation $\Delta_f H^0$.

Generally, the value of enthalpy of formation of stable compounds is negative (-ve) but in certain stable compounds the value of heat of formation is positive (+ve).



$$\Delta_f H^0 = -393.5 \text{ kilojoulemole}^{-1}$$

In the formation of carbon dioxide (CO_2) by combustion of carbon, the standard enthalpy change will be

$$\Delta_f H^0 = -393.5 \text{ kilojoulemole}^{-1}$$

$$\Delta_f H^0 = H_p^0 - H_r^0$$

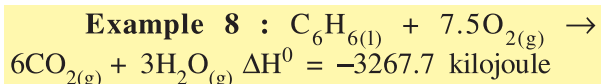
$$\begin{aligned} \Delta_f H^0 &= (\text{Total standard enthalpy of products}) \\ &\quad - (\text{Total standard enthalpy of reactants.}) \\ &= (\text{standard enthalpy of } \text{CO}_{2(g)}) - \\ &\quad (\text{standard enthalpy of } \text{C}_{(s)} \text{ and } \text{O}_{2(g)}) \end{aligned}$$

Here, $\text{C}_{(s)}$ and $\text{O}_{2(g)}$, elements are in standard state and so their enthalpies are considered as zero.

$$\begin{aligned} \therefore \Delta_f H^0 &= (\text{standard enthalpy of } \text{CO}_{2(g)}) \\ &= \Delta_f H^0_{\text{CO}_2} = \text{enthalpy of formation} \end{aligned}$$

\therefore enthalpy of formation $\Delta_f H_{\text{CO}_2} = -339.5$ kilojoulemole $^{-1}$

In this reaction the value ΔH^0 is negative (-ve) and so the reaction is exothermic. Thus, the total enthalpy of the products, is less than the total enthalpy of the reactants.



In this reaction, the standard enthalpy of formation of $\text{CO}_{2(g)}$ and $\text{H}_2\text{O}_{(l)}$ are -393.5 and -285.85 kilojoule mole^{-1} respectively. Calculate the standard enthalpy of formation of benzene.

Solution :

$$\Delta H^0 = (\sum \text{enthalpy of formation of products}) - (\sum \text{enthalpy of formation of reactants.})$$

$$\begin{aligned} \therefore \Delta H^0 &= (6 \times \Delta_f H^0_{\text{CO}_2} + 3 \times \Delta_f H^0_{\text{H}_2\text{O}}) - \\ &\quad (\Delta_f H^0_{\text{C}_6\text{H}_6} + 7.5 \Delta_f H^0_{\text{O}_2}) \end{aligned}$$

$$-3267.7 = [6(-393.5) + 3(-285.85)] -$$

$$[(\Delta_f H^0_{C_6H_6} + 7.5\Delta_f H^0_{O_2})]$$

The standard enthalpy of formation of element O_2 is zero

$$-3267.7 = [-2361 + (-857.55)] - [\Delta_f H^0_{C_6H_6}]$$

$$-3267.7 = -3218.55 - \Delta_f H^0_{C_6H_6}$$

$$\Delta_f H^0_{C_6H_6} = 49.15 \text{ kilojoule mole}^{-1}$$

The standard enthalpy of formation of benzene = 49.15 kilojoule mole⁻¹

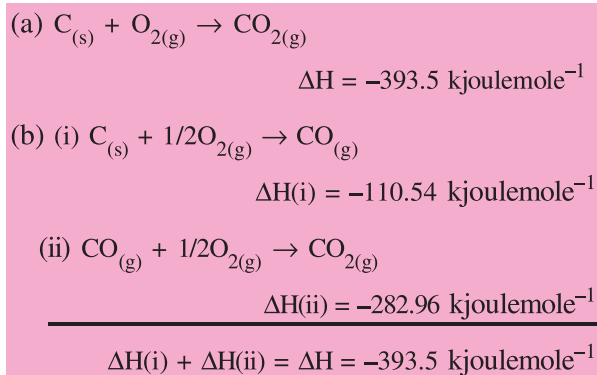
Enthalpy of Combustion : The heat evolved during the complete combustion of one mole of organic compound at constant pressure in presence of oxygen is called the enthalpy of combustion.

Mostly by the combustion of organic compounds carbon dioxide and water are formed as products. So, if its enthalpy of formation and enthalpy of combustion are known, the enthalpy of formation of organic compound can be calculated. In this case, enthalpy of combustion is one type of enthalpy of formation.

Thus, on the basis of enthalpy of combustion, change in enthalpy between different allotropes of some elements can be determined. The value of enthalpy between different allotropes of carbon graphite and diamond can be determined from the values of this enthalpy of combustion.

according to Hess's law. The enthalpy evolved or absorbed during different chemical reactions like enthalpy of formation, enthalpy of combustion, enthalpy of neutralisation etc. can be determined on the basis of Hess's law. The utility of Hess's law can be understood from the following example :

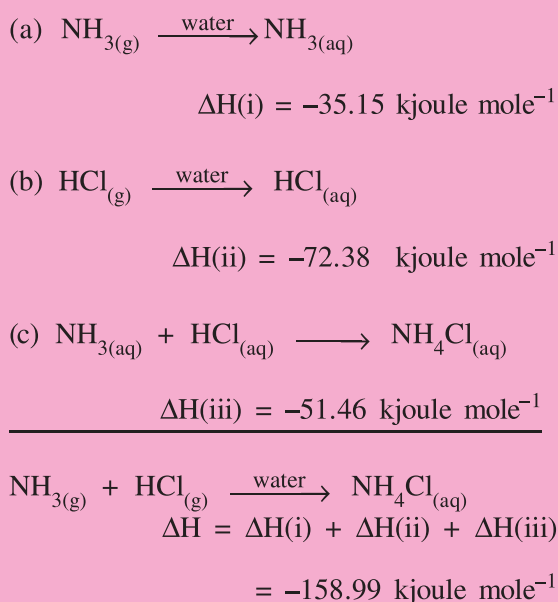
Illustration (a) : Carbon dioxide is formed by chemical reaction between carbon and oxygen. This reaction can occur in the following two steps.



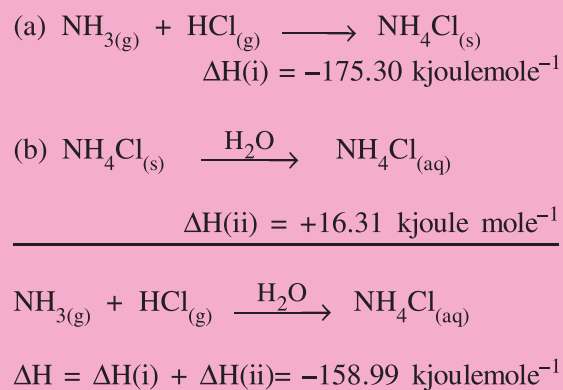
In reaction (a) direct combustion of carbon takes place in one step. While reaction (b) takes place in two steps, when first step (i) and second step (ii) are added, the value of ΔH will be equal to the value of ΔH in reaction (a)

Illustration (b) : Aqueous solution of ammonium chloride from gaseous ammonia can be obtained by two different methods. The different reactions and the different enthalpy changes during these two methods are as follows.

First Method :



Second Method :



3.6 Important Characteristics of Spontaneous Process

The hot tea taken in a saucer or hot water taken in a vessel; gets cold on its own but for how long ? It is found from the general experience that when its temperature becomes equal to that of the surrounding, it stops decreasing. This way hot water goes on losing the heat until thermal equilibrium between water and surrounding does not establish. In the same way the gas filled in a bulb tries to diffuse to the bulb being evacuated till the pressure in both the bulbs become equal. This is also a type of pressure equilibrium condition.

All the chemical reactions continue spontaneously till the equilibrium condition is not established and when equilibrium state is established the concentrations of reactants and products remain constant. If we understand this statement in other way, then it can be said that the spontaneous reactions occur in the direction of establishing equilibrium between reactants and products. When equilibrium is established the reaction is also balanced. Thus, reaction attains equilibrium while going from reactants to products or from products to reactants.

3.7 Second Law of Thermodynamics

The Second law of thermodynamics explains in which direction, either the forward or the reverse, the reaction will spontaneously occur. This law can be as mentioned below :

(i) In all spontaneous processes, the entropy of the universe increases.

(ii) The free energy of the system in all the spontaneous processes decreases.

The examples of spontaneous reactions are as follows.

(i) If two substances having different temperatures are kept in contact with each other, the heat will always spontaneously flow from higher temperature to lower temperature.

(ii) Water always flows from higher level to lower level.

Entropy and free energy are necessary to understand spontaneity. Both of these are state functions.

3.7.1 Entropy and Second Law of Thermodynamics : First, we will understand the term 'entropy' as a physical form and then as a mathematical form. What is entropy? In order to get the answer, it is necessary to ask a second question: What is temperature? We know that temperature of a substance does not express the quantity of heat but the level of the thermal energy in the substance and is associated with the Zeroth law of thermodynamics.

Entropy is the measurement of randomness of the substance. Also, a question will arise, what is meant by randomness? An illustration is necessary to understand before we get the answer.

Suppose, four squares of the size 1 centimetre \times 1 centimetre are drawn on a paper and one honeybee flies over it. Maximum four numbers 1, 2, 3 and 4 will be required to show the position of a honeybee. Now, this honeybee flies over nine squares on the second paper. Maximum nine numbers 1 to 9 will be required to show the position of the honeybee. Thus, more co-ordinates are required to show the position of a honeybee.

1	2
3	4

1	2	3
4	5	6
7	8	9

If we express this phenomenon in scientific language, then it can be said that if the honeybee flies and sits on the second paper then, its entropy will increase. The measurement of entropy of any system is the measure of randomness of the system.

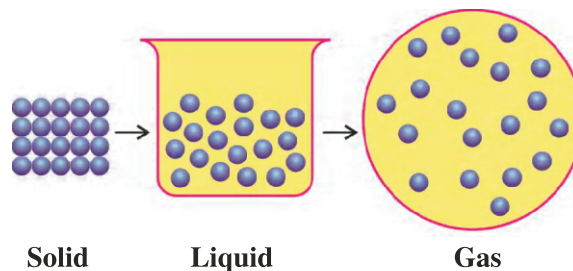


Fig 3.3

As shown in Fig 3.3 the entropy of a crystalline solid substance is the least because the arrangement of molecules is systematic in crystalline solid substance while it is maximum of molecules in the gaseous state, because the randomness of molecules in the gas is maximum. The randomness in liquid falls between these two. Thus, randomness is maximum in gaseous state, entropy in liquid state is less than that in gas but more than that in solid. In a solid, crystal arrangement is comparatively systematic and so entropy is minimum.

In this way, the volume of the gas increases when gas filled in one bulb is connected with other evacuated bulb, which means for the molecules of gas more space is available. Hence, it can be said that randomness increases by diffusion of gas in two bulbs and the entropy of the gas increases. This type of described form of entropy is not useful in understanding the spontaneity of the processes. For this, mathematical form of entropy is needed.

Entropy is expressed by symbol 'S'. Entropy is the state function. In addition, it is an extensive property. It depends on the mass of the substance. In other words, it can be said that the entropy of 1 mole substance has constant value at constant temperature and pressure.

As seen above, the state of system changes its entropy changes. The change in entropy is expressed ΔS ($S_{\text{final state}} - S_{\text{initial state}}$) and its mathematical equation is expressed as follows.

$$S_{\text{final state}} - S_{\text{initial state}} = \Delta S = \frac{q_{\text{rev}}}{T}$$

where q_{rev} is the heat obtained or heat lost by the system reversibly at temperature T . If q_{rev} is expressed in joule unit and temperature T in kelvin unit, then the unit of change in entropy becomes joule per kelvin. It can also be expressed as entropy unit (e.u.) If the value of

entropy is taken for one mole of a substance, then the unit of entropy will be joule per kelvin per mole. The calculations for values of absolute entropies of substances can be calculated. The values of absolute entropies of some elements and compounds are given in Table 3.4.

To determine whether a reaction will occur spontaneously or not, the calculation of change in entropy of the system and the surrounding, assuming that the reaction will occur of ΔS system and ΔS surrounding is carried out.

If the sum of these two values is positive (+ve), then the forward reaction will occur spontaneously and if the sum of these two values is negative (-ve), then the reverse reaction will occur spontaneously and if the sum of these two values is zero, then reaction will be in equilibrium.

$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$, The reaction will occur on its own (Spontaneous reaction)

$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} < 0$, The reaction will not occur on its own (Non-Spontaneous reaction)

$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$, The reaction will remain in equilibrium (Equilibrium reaction)

The changes in entropy of the system when solid is changed to liquid state (fusion) at constant temperature or when liquid is changed to gaseous state (vaporisation) at constant temperature are called molar fusion entropy of the substance and molar vaporisation entropy of the substance. These can be determined from the values of molecular enthalpy of fusion and molecular enthalpy of vaporisation. We know that

$$\Delta H = q_{\text{rev}} \text{ and } \Delta S = \frac{q_{\text{rev}}}{T}$$

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

$$\Delta S_{(\text{Fusion})} = \frac{\Delta H_{\text{fusion}}}{T} \text{ and}$$

$$\Delta S_{(\text{Vaporisation})} = \frac{\Delta H_{\text{vaporisation}}}{T}$$

Similarly, sublimating substances (Direct change in gaseous form from solid form).

$$\Delta S_{(\text{Sublimation})} = \frac{\Delta H_{\text{sublimation}}}{T}$$

Example 10 : 3 moles of water is boiled at 373 K and is changed to vapour state having the same temperature, what will be the change in entropy of the system ? (The molecular enthalpy of vaporisation of water is 40.668 kJoule mole⁻¹)

Solution : The heat absorbed for vaporisation of 3 moles of water,

$$\Delta H_{\text{vap}} = 3 \times 40.668 = 1220.04 \text{ kilojoule}$$

$$\begin{aligned} \Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T} \\ &= \frac{1220.04}{373} = 3.271 \text{ kilojoule kelvin}^{-1} \end{aligned}$$

Example 11 : The enthalpy of vaporisation of benzene is 30.799 kJoule mole⁻¹ and its boiling point is 353 K. Find the change in entropy for the conversion of liquid benzene to its vapour at that temperature.

Solution : Here, the system absorbs the heat

$$\Delta H_{\text{vap}} = 30.799 \text{ kilojoule mole}^{-1}$$

$$\begin{aligned} \Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T} = \frac{30.799}{353} \\ &= 0.0872 \text{ kilojoule kelvinmole}^{-1} \end{aligned}$$

Example 12 : "Will ice having temperature 273 K placed in a surrounding having temperature 298 K will give water having temperature 273 K ?" Prove this statement. The molecular enthalpy of fusion of ice is 6.025 kJoule mole⁻¹.

Solution : 1 mole of ice will have to absorb 6.025 kJoule mole⁻¹ enthalpy from the atmosphere to change into water at 273 K temperature. Hence, the change in entropy of the system and the entropy of the surrounding can be calculated as below :

$$\begin{aligned} \Delta S_{\text{System}} &= \frac{q_{\text{rev}}}{T} = \frac{\Delta H}{T} = \frac{6.025}{273} \\ &= 0.0221 \text{ kilojoule mole}^{-1}. \end{aligned}$$

Surrounding will lose 6.025 kJoule enthalpy but decrease of 6.025 kJoule enthalpy from very large surrounding will not make any real change in the temperature of the surrounding and so it can be neglected.

$$\begin{aligned} \Delta S_{\text{Surrounding}} &= \frac{-\Delta H}{T} = \frac{-6.025}{298} \\ &= -0.0202 \text{ kilojoule K}^{-1}\text{mole}^{-1} \end{aligned}$$

(As it absorbs heat from the surrounding. So it is -6.025)

$$\begin{aligned}\Delta S_{\text{Total}} &= \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}} \\ &= 0.0221 + (-0.0202) \\ &= 0.0019 \text{ kilojoule K}^{-1}\text{mole}^{-1}\end{aligned}$$

Here, $\Delta S_{\text{Total}} > 0$, so the phenomenon will occur on its own.

As the value of ΔS_{total} is positive (+ve), it can be said that if an ice cube is placed in a surrounding having temperature 298 K it will melt on its own and will give water having temperature 273 K. As opposite to this, water kept at temperature 298 K, will not be changed to ice on its own (automatically). Understand the reason for this with the help of calculations.

3.7.2 Change in Entropy : For any process (reaction), like change in enthalpy ($\Delta H = H_p - H_r$), can be calculated and similarly the change in entropy (ΔS) can also be calculated.

$$\Delta S_{\text{reaction}} = \Delta S_{\text{System}} = \text{Entropy change (Reaction or system)}$$

The difference of entropy in initial and final states is change in entropy ΔS . For chemical reaction, this type of change can be expressed as follows :

$$\Delta S = \text{Total entropy of product (S}_p\text{)} - \text{Total entropy of reactant(S}_r\text{)}$$

Increase in Entropy with Increase in Temperature : With the increase in temperature the translational motion as well as rotational motion and vibrational motion increase and so there is increase in randomness at molecular level. Entropy is also a state function like internal energy (U) and enthalpy (H). Hence, entropy change will depend on initial and final states of the system and not on the path for obtaining it. Suppose, the entropy of initial state is S_i and entropy of final state is S_f . If entropy or randomness increases then $\Delta S = (S_f - S_i) > 0$.

3.7.3 Expansion of an Ideal Gas in Vacuum and Change in Entropy : When a vessel filled with one mole of an ideal gas is connected to an evacuated vessel, there is no work done by the system during expansion of the gas on its own, because in $W = P\Delta V$ the value of P is zero because of vacuum. In addition, the gas does not lose or give the heat in this process. Hence, $q = 0$ and as a result $\Delta U = 0$. This process is not

reversible. Hence, $q_{\text{irr}} = 0$. Thus in the expansion of an ideal gas in vacuum, $P = 0$, $\Delta U = 0$ and $q_{\text{irr}} = 0$. As the volume of the gas increases during the reversible process, the change in entropy will be there. We know that, for 1 mole of gas,

$$q_{\text{rev}} = RT \ln \frac{V_2}{V_1}$$

$$\therefore \frac{q_{\text{rev}}}{T} = R \ln \frac{V_2}{V_1}$$

$$\text{As, } \frac{q_{\text{rev}}}{T} = \Delta S$$

$$\therefore \Delta S = R \ln \frac{V_2}{V_1} = 2.303 R \log \frac{V_2}{V_1}$$

where V_1 = initial volume of gas and
 V_2 = final volume of gas

According to Boyle's law,

$$P_1 V_1 = P_2 V_2$$

$$\therefore \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

where P_1 = initial pressure of gas

P_2 = final pressure of gas

$$\therefore \Delta S = R \ln \frac{P_1}{P_2}$$

$$= 2.303 R \log \frac{P_1}{P_2}$$

3.7.4 Free Energy and Second law of Thermodynamics : To know whether a chemical reaction will occur on its own or not can be decided on the basis of the determination of entropy of both the system and surrounding. Free energy is such a state function that in determining, whether reaction will occur on its own or not, only the change in free energy of the system is to be found out. The relation of this state function free energy (G) with enthalpy (H) of the system and the entropy (S) of the system can be shown by following equation.

$$G = H - TS$$

But, if the state of the system changes at constant temperature, there are changes in the values of all the three state functions which can be shown as below :

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

where ΔH and ΔS are the values of change in enthalpy and change in entropy. With

the help of this the value of ΔG can be obtained. The values of these three state functions change with change in temperature.

For a reaction occurring on its own (Spontaneous) the value of ΔG obtained is negative (-ve) because there is decrease in free energy of all the reactions in the system. For reactions not occurring on their own (non-spontaneous), the value of ΔG will be positive (+ve) and ΔG becomes zero (0) in reaction in equilibrium.

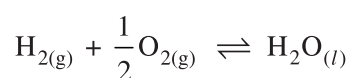
Here, the symbol G is for Gibbs free energy and it is a state function which is an extensive property. The absolute value of free energy of any substance cannot be determined because it depends on the absolute value of enthalpy of the substance. Hence, importance is given to all the three functions.

3.7.5 Standard Free Energy of Formation of Compounds : The values of all the elements in their standard states are accepted as zero. On the basis of this, **"The value of change in free energy in direct reaction when 1 mole compound is produced from its elements in standard state will be equal to the value of change in standard free energy of formation of the compound."**

For example, water is formed by direct reaction of 1 mole of H_2 and half mole of O_2 at 298 K temperature and 1 bar pressure, water is obtained as liquid, then change in free energy of the reaction for,

$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons H_2O_{(l)}$ the value of free energy is -237.13 kilojoule mole⁻¹

The heat of formation for



$$[\Delta_f G^0_{(H_2O)_{(l)}}] = -237.13 \text{ kJoule mole}^{-1}$$

at 298 K is because the values of free energies of $H_{2(g)}$ and $O_{2(g)}$ are accepted as zero.

The Values of standard free energy of formation of compounds at 298 K are given in Table 3.3.

Table 3.3. Values of standard free energy of formation of some compounds (298 K)

Compound	$\Delta_f G^0$ kJ mole ⁻¹	Compound	$\Delta_f G^0$ kJ mole ⁻¹
$H_2O_{(l)}$	-237.19	$CH_3OH_{(l)}$	-166.23
$H_2O_{(g)}$	-228.61	$C_2H_5OH_{(l)}$	-174.77
$CH_4_{(g)}$	-50.79	$HCl_{(g)}$	-95.27
$C_2H_2_{(g)}$	+209.2	$NH_3_{(g)}$	-16.65
$CO_{(g)}$	-137.28	$NO_{(g)}$	+86.69
$CO_2_{(g)}$	-394.38	$NO_2_{(g)}$	+51.84
$C_6H_6_{(l)}$	+124.52		

The change in standard free energy of the reaction can be calculated from the information about free energy of formation of compound.

$$\begin{aligned} \Delta_f G^0_{(\text{Reaction})} &= \sum \Delta_f G^0_{(\text{Product})} - \sum \Delta_f G^0_{(\text{Reactants})} \\ &= (\text{Total standard free energy of formation of products}) - (\text{Total standard free energy of formation of reactants}) \end{aligned}$$

There is a change in volume of an ideal gas when pressure is changed at constant temperature. The change in free energy associated with this can be calculated by the use of following equation :

$$\Delta G = nRT \ln \frac{P_2}{P_1}$$

$$\therefore \Delta G = 2.303 nRT \log \frac{P_2}{P_1}$$

where n is the number of moles, P_1 and P_2 are pressures at initial and final states. For an ideal gas $P_1 V_1 = P_2 V_2$. So the above relation can be written in the following form.

$$\Delta G = nRT \ln \frac{V_1}{V_2}$$

$$\therefore \Delta G = 2.303 nRT \log \frac{V_1}{V_2}$$

where n is the number of moles of the gas and V_1 and V_2 are the volumes of the gas at initial and final state.

Example 13 : The standard free energy of formation of $C_6H_{6(l)}$, $CO_{2(g)}$, and $H_2O_{(l)}$ are 124.52 kJoule mole⁻¹, -394.38 kJoule mole⁻¹ and -237.13 kJoule mole⁻¹ respectively. Find the change in free energy of the reaction.

Equation : $C_6H_{6(l)} + 7.5O_2 = 6CO_{2(g)} + 3H_2O_{(l)}$ at 298 K temperature.

Solution :

$$\begin{aligned}\Delta_f G^0 &= [\sum \Delta_f G^0_{\text{products}} - \sum \Delta_f G^0_{\text{reactants}}] \\ \therefore \Delta_f G^0 &= [6(\Delta_f G^0_{CO_2}) + 3(\Delta_f G^0_{H_2O})] - \\ &\quad [(\Delta_f G^0_{C_6H_6} + 7.5(\Delta_f G^0_{O_2}))] \\ \therefore \Delta_f G^0 &= [6 \times (-394.38) + 3 \times (-237.13)] \\ &\quad - [124.52 + 7.5(0)] \\ &= [-2366.28 + (-711.39)] - (124.52) \\ &= -3077.67 - 124.52 \\ \Delta_f G^0 &= -3202.19 \text{ kJoule mole}^{-1}\end{aligned}$$

3.7.6 Free Energy and Equilibrium

Constant : For, the chemical reactions occurring at constant temperature and constant pressure, free energy is related with equilibrium constant of the reaction (K) by following relation.

$$\Delta_r G^0 = -RT \ln K = -2.303 RT \log K$$

If the system consists of gaseous state, thus $K = K_p$ and if the homogeneous liquid of reactants and products is formed then $K = K_c$.

For, reactions having value of ΔG^0 negative (-ve) the value of equilibrium constant for such reactions is greater than 1 and the reactions in which the value of ΔG^0 is positive (+ve), then the value of equilibrium constant is less than 1.

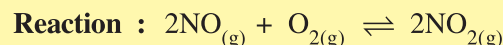
Hence, If $K > 1$; $\Delta G^0 = \text{negative (-ve)}$ and reaction will occur on its own (Spontaneous).

If $K < 1$; $\Delta G^0 = \text{positive (+ve)}$ and reaction will not occur on its own (non-spontaneous)

If $K = 1$; $\Delta G^0 = \text{zero (0)}$ and reaction will be in equilibrium.

Example 14 : The values of standard heat of formation of $NO_{(g)}$ and $NO_{2(g)}$ are 90.37 kJoule mole⁻¹ and 33.85 kJoule mole⁻¹ respectively at

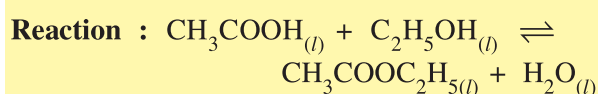
298 K. The entropies of $NO_{(g)}$, $O_{2(g)}$ and $NO_{2(g)}$ at 298 K temperature and 1 bar pressure are 210.45, 205 and 240.6 Joule K⁻¹ mole⁻¹ respectively. Then, calculate the values of ΔH^0 , ΔS^0 and ΔG^0 and equilibrium constant for the following reaction at 298 K temperature.



Solution :

$$\begin{aligned}\Delta H^0 &= [2 \times \Delta H^0_{NO_2}] - [(2 \times \Delta H^0_{NO}) + \\ &\quad (1 \times \Delta H^0_{O_2})] \\ &= [2 \times 33.85] - [(2 \times 90.37) + 1(0.0)] \\ &= 67.7 - 180.74 \\ &= -113.04 \text{ kJoule} \\ &= -113040 \text{ joule} \\ \Delta S^0 &= [2 \times \Delta S^0_{NO_2}] - [(2 \times \Delta S^0_{NO}) + \\ &\quad (1 \times \Delta S^0_{O_2})] \\ &= [2 \times 240.6] - [(2 \times 210.45) + 1(205)] \\ &= 481.2 - 625.9 = -144.7 \text{ joule K}^{-1} \\ \Delta G^0 &= \Delta H^0 - T\Delta S^0 \\ &= [-113040] - [298 \times (-144.7)] \\ &= -113040 + 43120.6 \\ &= -69919.4 \text{ joule} \\ \Delta G^0 &= -2.303 RT \log K_p \\ -69919.4 &= -2.303 \times 8.314 \times 298 \log K_p \\ \log K_p &= \frac{-69919.4}{-2.303 \times 8.314 \times 298} \\ &= \frac{+69919.4}{+5705.85} \\ \text{Taking antilogarithm } \log K_p &= 12.2540 \\ K_p &= 1.795 \times 10^{12} \text{ bar}^{-1}\end{aligned}$$

Example 15 : The value of equilibrium constant of following esterification reaction is 4. Calculate the value of ΔG^0 for this reaction.



$$\begin{aligned}
 \text{Solution : } \Delta G^0 &= - 2.303 RT \log K_c \\
 &= - 2.303 \times 8.314 \times 298 \log 4 \\
 &= - 5705.84 \times 0.6021 \quad (\log 4 = 0.6021) \\
 &= - 3435.49 \text{ joule}
 \end{aligned}$$

3.7.7 Gibbs' Free Energy and Useful Work :

(i) It will be understood from the examples described above that the value of ΔG^0 is the dimension of tendency of the chemical reaction to occur on its own. In addition, free energy also possesses relation with useful work. The change in free energy associated with any process is the value of maximum possible work obtainable from that process, i.e. free energy is associated with maximum useful work viz.

$\Delta G = - W_{\max}$ (negative (-ve) value for reactions occurring on its own.)

Thus, any process can be taken in use for doing the work by that process. The process for which value of ΔG is more negative (-ve), then maximum work can be done by such process.

(ii) When electrochemical cell is in operation the electrical work done by the cell W_{elect} has the following relation with free energy change of the spontaneous chemical reaction.

$$\Delta G = - W_{(\text{elect})}$$

But the electrical work done by the cell is having following relation with cell potential (E_{cell}) and the quantity of electricity obtained from the cell (nf)

$$W_{\text{elect}} = nFE_{\text{cell}}$$

where F = Faraday constant

$$= 96500 \text{ coulomb}$$

n = Number of electrons passing from the external path of the cell

$$\Delta G = -W_{\text{elect}}$$

The following relation can be deduced from the above two equations.

$$\Delta G = - nFE_{\text{cell}}$$

If the cell is in standard state and the change in free energy is associated with reaction and standard electrochemical cell potential, then the relation between them can be shown by following equation.

$$\Delta G^0 = - nFE_{\text{cell}}^0$$

where E_{cell}^0 is the difference of standard reduction potentials of both the half cells of the complete cell.

Example 16 : Find the value of ΔG^0 for the reaction $\text{Zn}_{(\text{s})} + \text{Cu}^{2+}_{(\text{aq})} = \text{Zn}^{2+}_{(\text{aq})} + \text{Cu}_{(\text{s})}$ taking place in a standard cell. The value of standard cell potential (E_{cell}^0) is 1.1 volt at 298 K temperature, F = 96500 coulomb. (4.184 joule = 1 calorie)

$$\text{Solution : } \Delta G^0 = - nFE_{\text{cell}}^0$$

Taking n=2 for the given reaction

$$= - 2 \times 96500 \times 1.1 \text{ volt coulomb}$$

(volt coulomb = joule)

$$= - 212300 \text{ joule}$$

$$4.184 \text{ joule} = 1 \text{ calorie}$$

$$\Delta G^0 = \frac{-212300}{4.184}$$

$$= - 50740.9 \text{ calorie}$$

3.7.8 Limitations of Second Law of Thermodynamics : Whether the reaction has the capacity to take place on its own or not and if it can take place on its own, then, the calculations of equilibrium constant can be done on the basis of the second law of thermodynamics. But this law is not able to give information about the rate of chemical reactions. Thus, the thermodynamics is independent of chemical kinetics.

3.8 Third Law of Thermodynamics

Generally, the value of entropy of a substance increases with increase in temperature, because, the randomness increases with increase in temperature. The value of entropy increases because there is increase in their oscillation

motion, linear motion and rotation motion as against to this, with decrease in temperature, the oscillation motion, linear motion and rotation motion of the molecules of substance decrease and so randomness decrease and decrease in randomness decrease the value of entropy.

German scientist Nernst expressed, in 1906, that the value of entropy of a completely pure crystalline substance decreases with decrease in temperature. On the basis of this, the third law of thermodynamics can be expressed as below :

"The value of entropy of a completely pure crystalline substance is zero at absolute zero temperature" i.e. the arrangement of component particles of an absolutely pure crystalline substance is completely systematic at absolute zero temperature. Hence, entropy is least in solid, more in liquid and highest is gas.

The kinetic energy of the molecules of a substance at absolute zero temperature is almost negligible but its potential energy is not zero. As a result, the value of internal energy is not zero. In addition, the internal energy is the characteristic of a substance. Therefore the value of internal energy cannot be calculated at absolute zero but the absolute value of entropy of substance can be calculated.

The entropy of one mole of a substance is called molar entropy and it is expressed as S_m . The entropy of one mole of a substance at constant temperature and standard state is called standard molar entropy S_m^0 . The molar standard entropy of the substance is also called absolute entropy. The unit of molar entropy is joule kelvin⁻¹ mole⁻¹. The values of absolute entropies of some elements and compounds at 298 K are given in a Table 3.4.

Table 3.4 Values of absolute entropies of some elements and compounds at 298 K

Solid S_m^0		Liquid S_m^0		Gaseous S_m^0	
Element/ Compound	joule K ⁻¹ mole ⁻¹	Element/ Compound	joule K ⁻¹ mole ⁻¹	Element/ Compound	joule K ⁻¹ mole ⁻¹
C (Graphite)	5.740	Hg _(l)	76.62	Hg _(g)	130.68
C (Diamond)	2.377	H ₂ O _(g)	188.83	N _{2(g)}	191.61
S (Rhombic)	31.80	H ₂ O _(l)	69.91	O _{2(g)}	205.14
Al _(s)	28.33	C ₂ H ₅ OH _(g)	282.7	CO _{2(g)}	213.74
NaCl _(s)	72.13	C ₂ H ₅ OH _(l)	160.7	NO _(g)	210.76
NaCl _(aq)	115.5	C ₆ H _{6(l)}	173.3	NO _{2(g)}	240.06
CaCO ₃ (Calcite)	92.9	CH ₃ COOH _(l)	159.8	NH _{3(g)}	192.45
CaCO ₃ (Arogonite)	88.7	CH ₃ OH _(l)	126.8	CH _{4(g)}	186.26
CaO _(s)	39.75				

It can be decided from the values of the absolute entropies of the substances that the value of entropies of solid substance are less, the values

of absolute entropies of the liquids are more than those of solids but less than those of gaseous substances.

SUMMARY

In this unit, the breaking of bonds in reactants and formation of bonds in products are experiencing in chemical reactions. Endothermic and exothermic reactions are explained. Some basic concepts like system, the very small part of the universe which is separated from the rest of the universe by a definite boundary and the observations of doing experiments are called system. The remaining part without the system is called surrounding. On the basis of exchange of matter and energy, the system is divided into three types. viz. open system in which energy and mass both are exchanged. In the closed system matter is not exchanged but only energy is exchanged. In the isolated system neither mass nor energy is exchanged. Processes like isobaric process, isothermic process and adiabatic process are discussed. Extensive properties which depend on the magnitude of the mass and intensive properties which do not depend on the mass. The concept of state function is given. Internal energy (U), enthalpy (H), and internal energy change (ΔU) and change in enthalpy (ΔH) are studied. The relation between them $\Delta H = \Delta U + P\Delta V$ and $\Delta H = \Delta U + \Delta n_g RT$ are studied.

The process of obtaining thermal equilibrium when two diathermic substances are connected is known as zeroth law of thermodynamics. The first law of thermodynamics in reality is the law of conservation of energy which can be expressed in different forms i.e. the total energy of the universe remains constant. The formation or destruction of energy is not possible but it is possible to transfer energy from one form to the other. The symbolic form of First law of thermodynamics is $\Delta U = q + W$ and with the help of mathematical form First law the work done on the system and work done by the system is explained and the change in internal energy occur. Enthalpy and First law of thermodynamics $\Delta H = q_p$, enthalpy change at constant pressure and at constant volume related to enthalpy change and internal energy change can be obtained by illustrations and solutions of examples.

Enthalpy is the function only to measure the heat change in the system at constant pressure. This function is not useful to measure the heat changes at constant volume. Hence, to express the relation between changes at constant pressure or constant volume, and temperature, the function heat capacity is required. Heat capacity is not the state function. Established the concepts of specific heat capacity, molar heat capacity and the relation between C_p and C_v as $C_p - C_v = R$. For an ideal gas $\frac{C_p}{C_v} = \gamma$ the values of γ is 1.4. In the enthalpy of reaction the values of enthalpy of formation of solid, and gaseous molecules in standard state is taken equal to zero, studied the definitions of enthalpy of neutralisation, enthalpy of formation and enthalpy of combustion and obtained solutions of examples based on them. The Hess's law of constant heat summation was studied with the examples of combustion of carbon and formation of ammonium chloride (NH_4Cl) and its importance have been studied.

The limitation of first law of thermodynamics is brought out by examples having physical and chemical changes; the spontaneity and its characteristics are studied to predict whether a reaction will occur on its own or not? Second law of the thermodynamics is expressed for this. According to second law of thermodynamics, the entropy of the universe increases and for any reaction occurring on its own, its free energy decreases. Entropy (S) and free energy (G) entropy change ΔS , which is determined for the surrounding to predict whether reaction will occur on its own or not? If the value of ΔS is positive (+)

the reaction will occur on its own and if the value of ΔS is negative ($-$), the reaction will occur on its own, if ΔS is positive ($+$) and if $\Delta S = 0$, the reaction will be in equilibrium.

$$\Delta S = \frac{\Delta q_{\text{rev}}}{T} = \frac{\Delta H}{T} \quad \text{From this, } \Delta S_{\text{Vaporisation}} = \frac{\Delta H_{\text{vaporisation}}}{T}, \quad \Delta S_{\text{Fusion}} = \frac{\Delta H_{\text{fusion}}}{T} \quad \text{and}$$

$$\Delta S_{\text{Sublimation}} = \frac{\Delta H_{\text{sublimation}}}{T} . \quad \text{In the same way } \Delta S = (S_2 - S_1) > 0_1 \text{ the reaction will occur on its own. On expansion of the ideal gas in vacuum } \Delta U = 0 \text{ and } \Delta H = 0 \text{ and the entropy change } \Delta S = 2.303 R \log \frac{V_2}{V_1} .$$

Whether a reaction will occur on its own or not can be determined on the basis of calculation of total entropies of system and surrounding but the free energy (G) of the system is determined from the free energy changes of the system. Its symbol is G and known as Gibbs' free energy. If the value of free energy change ΔG is negative ($-$) the reaction will occur on its own and if the value of ΔG is positive ($+$) the reaction will not occur on its own. If $\Delta G = 0$, the reaction will be in equilibrium. The relation between free energy (G), enthalpy (H) and entropy (S) is $G = H - TS$. If the state of the system changes at constant temperature, there is change in the values of all the three functions. Hence, $\Delta G = \Delta H - T\Delta S$, where ΔH is enthalpy change and ΔS is entropy change. At definite temperature if the pressure of an ideal gas is changed, there will be change in volume and hence, the change in free energy occurring is $\Delta G = nRT \ln \frac{P_2}{P_1}$

$$\therefore \Delta G = 2.303 nRT \log \frac{P_2}{P_1} \quad \text{and} \quad \therefore \Delta G = 2.303 nRT \log \frac{V_1}{V_2} \text{ can be obtained. The}$$

relation between free energy change and equilibrium constant is $\Delta_f G^0 = -2.303 RT \log K$. If the value of K is more than 1 ($K > 1$), $\Delta_f G^0 =$ negative ($-$) and if the value of K is less than 1 ($K < 1$), $\Delta_f G^0 =$ positive ($+$). The relation between free energy change and the useful work can be shown as $\Delta G = -W_{\text{max}}$ and in electrochemical cell, $\Delta G = -nFE_{\text{cell}}$. The value free energy change can be obtained. This can be understood by illustrations and definitions. The importance and limitation of second law of thermodynamics as well as the third law of thermodynamics given by Nernst can be studied. The third law of thermodynamics is "The value of entropy of a completely pure crystalline substance is zero at absolute zero." Hence, in perfectly pure crystalline substance the arrangement of its component particles is completely in order. Randomness is minimum in solid and in liquid it is more than that of solid and less than that of gas. Gases have maximum entropy. The standard molar entropy is expressed as S_m^0 and its unit is Joule Kelvin $^{-1}$ mole $^{-1}$.

EXERCISE

1. Select the proper choice from the given multiple choices :

- (1) Which of the following is the symbolic form of the first law of thermodynamics ?
- | | |
|-------------------------|-------------------------------|
| (A) $\Delta U = q - W$ | (B) $W = \Delta U - q$ |
| (C) $\Delta U = q + PV$ | (D) $\Delta q + W = \Delta U$ |

- (2) The system in which the property of the system depends on the quantity of substance, such a property is called ?
- (A) Specific property (B) Physical property
(C) Thermal property (D) Extensive property
- (3) For the thermal reaction occurring in nature.
- (A) Temperature is always zero (B) Temperature is always high
(C) Temperature is always low (D) Temperature can be of any order
- (4) In which condition the relation $\Delta H = \Delta U + P\Delta V$ can be said to be true for a closed system ?
- (A) Constant temperature
(B) Constant pressure
(C) Both constant temperature and pressure together
(D) Constant temperature and volume
- (5) For which reaction ΔS can be maximum?
- (A) $\text{Mg}_{(s)} + \frac{1}{2} \text{O}_{2(g)} \rightarrow \text{MgO}_{(s)}$ (B) $\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$
(C) $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$ (D) $\text{N}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{(g)}$
- (6) In which of the following entropy decreases ?
- (A) Preparing aqueous solution of common salt
(B) Change of water into ice
(C) Dry ice placed in an open vessel
(D) Melting of ice
- (7) What change is observed in the isothermal condition of an ideal gas ?
- (A) Decrease in enthalpy (B) Increase in internal energy
(C) Decrease in internal energy (D) Enthalpy will be constant
- (8) Which relation shows the value of ΔS for a reversible reaction ?
- (A) $T - q_{\text{rev}}$ (B) $\frac{q_{\text{rev}}}{T}$ (C) $q_{\text{rev}} + T$ (D) $q_{\text{rev}} - T$
- (9) For a spontaneous reaction
- (A) $\Delta H = +ve, \Delta S = -ve$ (B) $\Delta H = -ve, \Delta S = +ve$
(C) $\Delta G = +ve, \Delta S = -ve$ (D) $\Delta G = +ve, \Delta H = +ve$
- (10) Which of the following relations is correct for free energy change and cell potential ?
- (A) $\Delta G = nFE_{\text{cell}}$ (B) $\Delta G = -\frac{n}{F}E_{\text{cell}}$
(C) $\Delta G = -nFE_{\text{cell}}$ (D) $\Delta G = \frac{nF}{E_{\text{cell}}}$

- (11) The reaction $A + B \rightleftharpoons C + D$ is spontaneous in forward direction, then which signs represent ΔG and ΔS respectively ?
- (A) Positive and negative (B) Positive and positive
(C) Negative and positive (D) Negative and negative
- (12) For an ideal gas, during an adiabatic reaction always,
- (A) Decrease in temperature (B) $q = 0$
(C) $W = 0$ (D) $\Delta H = 0$
- (13) Which of the following statements is correct ?
- (A) ΔG may be less or more or equal to ΔH
(B) ΔG always changes with ΔH
(C) ΔG is always more than ΔH
(D) ΔG is always less than ΔH
- (14) What will be the value of ΔG^0 if $K_c = 1$ for a reaction ?
- (A) Infinite (B) 0 (C) Negative (D) Positive
- (15) Which law of thermodynamics gives information about definite entropy of a substance ?
- (A) First law (B) Second law (C) Third law (D) Zeroth law
- (16) What is the ideal condition for a reaction occurring on its own ?
- (A) $T\Delta S = \Delta H$, $\Delta H = +ve$ $\Delta S = +ve$
(B) $T\Delta S = \Delta H$, $\Delta H = -ve$ $\Delta S = -ve$
(C) $T\Delta S > \Delta H$, $\Delta H = +ve$ $\Delta S = +ve$
(D) $T\Delta S > \Delta H$, $\Delta H = +ve$ $\Delta S = -ve$
- (17) The reaction of quick lime with water is reversible at the room temperature and at low temperature, therefore,
- (A) ΔH and ΔS both +ve (B) $\Delta H = +ve$ and $\Delta S = -ve$
(C) $\Delta H = -ve$ and $\Delta S = +ve$ (D) ΔH and ΔS both -ve
- (18) Which is the correct relation between ΔG^0 and K_p ?
- (A) $K_p = \left(\frac{e}{RT}\right)^{\Delta G^0}$ (B) $K_p = \frac{\Delta G^0}{RT}$
(C) $K_p = e^{-\Delta G^0/RT}$ (D) $K_p = -RT \log \Delta G^0$
- (19) What can be the value of absolute entropy of free element ?
- (A) Always negative (B) Always positive
(C) Always zero (D) Zero at 273 K
- (20) Which system is indicated by the reaction of cooking rice in a pressure cooker ?
- (A) Open system (B) Closed system
(C) Isolated system (D) All the systems

2. Write the answers of the following questions in brief :

- (1) What is meant by a system ?
- (2) What an isolated system is called ? Give example.
- (3) What is meant by closed system ? Give example.
- (4) What exothermic and endothermic reactions are called ?
- (5) What extensive property is called ?
- (6) What an intensive property is called ?
- (7) What a state function is called ?
- (8) Give definitions of internal energy and enthalpy.
- (9) Which types of work are observed in chemistry ?
- (10) Give definition of heat capacity.
- (11) Give definition of enthalpy of reaction and heat of formation.
- (12) What a thermal equilibrium is called ?
- (13) When is the total heat absorbed by the system during the process used up in work ?
- (14) Mention the equation of entropy change for the expansion of an ideal gas in vacuum.
- (15) Write the formula for the entropy of substances experiencing sublimation.
- (16) The ice cube kept at room temperature melts on its own. Which law of thermodynamics is obeyed by the reaction ?
- (17) What is meant by temperature of a substance ?
- (18) The entropy of water vapour is more than that of water. Why ?
- (19) What will be the values of ΔG at 270 K and 275 K ?
- (20) Give definition of standard free energy of formation.
- (21) Write the equation showing relation between free energy change and cell potential.
- (22) Why does the value of entropy of a substance increase with increase in temperature ?
- (23) Write limitations of the second law of thermodynamics.
- (24) Write the third law of thermodynamics.
- (25) Mention the equation showing the relation between free energy and change in pressure of an ideal gas.
- (26) What is meant by entropy ?

- (27) By which system the maximum work can be done ?
- (28) What will be the value of equilibrium constant if $\Delta H < T\Delta S$ at 298 K temperature.
- (29) What will be the value of ΔS for ice kept at 275 K and 265 K temperature ?
- (30) "The value of absolute free energy of any substance cannot be determined." Why ?

3. Write answers of the following questions :

- (1) What is meant by system ? Explain giving its types.
- (2) What is meant by process ? Explain its types.
- (3) Explain extensive and intensive properties.
- (4) Explain in detail the state functions.
- (5) Explain internal energy.
- (6) Write the First law of thermodynamics and give its symbolic equation.
- (7) A system did the work of 785 joule after loss of 525 joule heat. Find the change in its internal energy.
- (8) A system absorbed 650 joule heat and did the work. Its internal energy change is 440 joules, then find out how much work has been done.
- (9) Explain the mathematical form of the first law of thermodynamics.
- (10) Explain enthalpy and First law of thermodynamics.
- (11) Deduce the relation between C_p and C_v .
- (12) Write a short note on heat capacity.
- (13) Write the Second law of thermodynamics and in which forms it can be expressed ?
- (14) Explain the free energy and the Second law of thermodynamics.
- (15) Explain Gibbs free energy and useful work.
- (16) Explain the standard free energy of formation of a compound.
- (17) Explain the expansion of an ideal gas in vacuum and entropy change.
- (18) Explain the Third law of thermodynamics.
- (19) Give limitations of the First law of thermodynamics.
- (20) Discuss characteristics of the reactions occurring on their own.
- (21) What is meant by entropy ? Explain using the concept of entropy, how the direction of a reaction to occur on its own is determined.

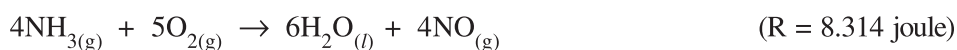
4. Answer the following questions in detail :

- (1) Explain internal energy and enthalpy and deduce the relation between them.
- (2) Write the First law of thermodynamics and explain it in detail in the symbolic equation and in the mathematical form.
- (3) Explain enthalpy of reaction, enthalpy of neutralisation and enthalpy of formation.

- (4) Write the Hess's law of constant heat summation and explain giving example. Mention its uses also.
- (5) Write the Second law of thermodynamics and explain entropy.
- (6) What is meant by free energy ? What is the relation between change in free energy during a chemical reaction and the change in entropy ? On the basis of this, explain under which conditions the reaction will occur on its own.

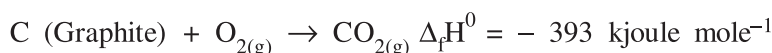
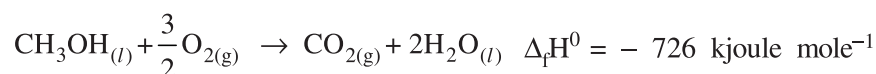
(7) Solve the following examples :

- (1) The change in internal energy of a given reaction at 300 K is -908 kJoule mole^{-1} , then calculate its enthalpy change.



- (2) The enthalpies of formation of $\text{CO}_{(g)}$, $\text{CO}_{2(g)}$, $\text{N}_2\text{O}_{(g)}$ and $\text{N}_2\text{O}_{4(g)}$ are -110 , -393.81 , 82 and 9.7 kJoule mole^{-1} , respectively. Calculate $\Delta_f H$ for the following reaction : $\text{N}_2\text{O}_{4(g)} + 3\text{CO}_{(g)} \rightarrow \text{N}_2\text{O}_{(g)} + 3\text{CO}_{2(g)}$

- (3) On the basis of the following equations, calculate the standard enthalpy of formation of $\text{CH}_3\text{OH}_{(l)}$.

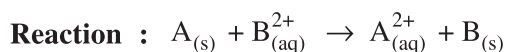


- (4) If $\Delta H = 400$ kJoule mole^{-1} and $\Delta S = 0.2$ kJoule $\text{K}^{-1} \text{ mole}^{-1}$ for a reaction $2x + y \rightarrow z$, at what minimum temperature the reaction will be spontaneous ?
- (5) For the following reaction, $2\text{P}_{(g)} + \text{Q}_{(g)} \rightarrow 2\text{R}_{(g)}$ $\Delta U^0 = -10.5$ kJoule and $\Delta S^0 = -44.2$ jouleKelvin $^{-1}$ Find ΔG^0 for the reaction. Will the reaction occur on its own ? Why ?
- (6) From the given data mention which of the following reaction will occur on their own at 298 K.

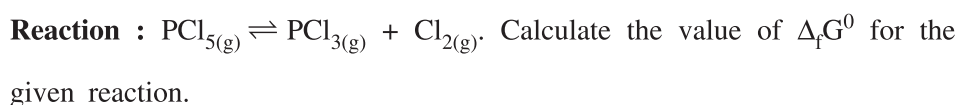


- (7) The changes in enthalpy and entropy for a reaction $\text{P} + \text{Q} \rightleftharpoons \text{R} + \text{S}$ at 320 Kelvin temperature are 170 kJoule and 26 joule Kelvin $^{-1}$. Will this reaction be spontaneous ? Why ? Find out.
- (8) Find out the equilibrium constant of the following given reaction at 298 K temperature $\text{NO}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{NO}_{2(g)}$. The values of $\Delta_f G^0$ for NO and NO_2 are 104.2 and 51.3 kJoule mole^{-1} respectively of 298 K temperature.

- (9) Find the change in standard free energy of formation and equilibrium constant of the reaction $\text{Fe}_{(s)} + \text{Cu}_{(aq)}^{2+} \rightarrow \text{Fe}_{(aq)}^{2+} + \text{Cu}_{(s)}$. The standard electrochemical cell potential is 0.78 volt and $F = 96500$ coulombs.
- (10) The value of change in free energy for the following cell reaction at 298 K temperature is -76322 calories. Calculate the potential of the electrochemical cell. $F = 96500$ coulomb, 1 Calorie = 4.184 joule.



- (11) The equilibrium constant of the following given reaction is $K_p = 2.4 \times 10^{-5}$ at 298 K temperature.



Dr. Venkat Raman Ramakrishnan



Dr. Venkat Raman Ramakrishnan is the seventh Indian (born in India) winner of the nobel prize. He got credit for India because of his birth place in India, in the whole of the world. He was born in 1952, at Chidambaram city which is in Tehil Taluka of Cuddalore district. He, at his age of three years came to Baroda of Gujarat State with his father and mother. He obtained here his primary school education to upto graduate level. He obtained B.Sc. (Physics) degree in 1971 from Maharaja Sayajirao University. As this is also not enough, he remained as student of graduate study in biology for two years in University of California.

Ramakrishnan who did Ph.D. in Physics became postdoctorate (Special research worker after Ph.D.) by doing work on Ribosome. During 1983 to 1995 he continued his research work on Ribosome by joining Brookhaven National Laboratory. He published many research papers about this. He joined University of Utah in 1995 as Professor of Biochemistry. There he started the study on protein-RNA complex and its components. He joined Medical Research Council Laboratory of Molecular Biology, Cambridge, England in 1999 as senior scientist. There he was working as leader of the Structural Study Group. For the years dedicated to work based on Ribosome and his hard work, Dr. Venkat Raman Ramakrishnan and his team was awarded the nobel prize in Chemistry, in 2009 for the research work on 'study of structure of Ribosomes and its working.' The co-scientists this achievement were Thomas A Steitz who is professor of molecular biophysics and biochemistry and Lady Professor Ada-E-Yonath of Isarel, who is an expert in structural biology.